

from the bottom of the tank. Data in the tabulation above show a decreasing difference between the phosphate contents of the lower layer and the stirred suspension as the sedimentation volume is increased.

### Discussion and Conclusions

Production of a satisfactory liquid fertilizer of the suspension type from wet-process phosphoric acid appears to depend on several factors, of which the major ones are those associated with handling and application of the product. If the situation is such that the product can be applied to the soil with little delay after production, it should be feasible to substitute wet-process acid for the furnace type without any change in procedure. Immediate settling is much less severe, if the acid and ammonia are added to the reactor simultaneously, as is done in many commercial plants. However, even stepwise addition should give a product of sufficient fluidity for immediate application.

If the product is to be stored for several days, settling and crystal growth become problems. Batch ammoniation is likely to give a product difficult to remove from storage tanks. Continuous ammoniation gives much better fluidity, but settling and crystal growth give rise to other problems in use.

The problem resulting from settling is difficult to evaluate. Assuming continuous ammoniation and storage not longer than 30 days, the present tests indicate that most products would be fluid enough for pumping and spraying although somewhat settled. The main problem from settling may be segregation

of plant nutrients, either from variation in composition as product is drawn from storage tanks or from difficulty in sampling for official inspection. This can be avoided by stirring before withdrawal or sampling. However, it would be desirable to avoid the need for stirring or minimize the degree of stirring needed.

Settling can be kept to a low level either by using clay as a suspending agent or neutralizing at a pH of 7.0 rather than the usual value of 6.6 to 6.7. Of the two, the latter appears preferable in the continuous ammoniation process because it does not require an additional raw material or special mixing equipment. For batch ammoniation, where neutralization pH cannot be held constant, clay addition is the only alternative.

Whether or not struvite crystal growth is a problem depends on the type of application equipment. Squeeze pump applicators, which do not have small openings in the flow path of the suspension, should handle the largest crystals formed in the present tests without difficulty. However, most of the applicators in general use are equipped with spray nozzles of one type or another, and the openings are therefore relatively small. For the range of orifice sizes normally used, the larger ones should be able to handle the crystals, but the smaller ones would not.

Crystal growth can be repressed adequately by using a product pH of roughly 5.8 to 6.2, depending on characteristics of the acid. Low pH aggravates settling, however, so high neutralization pH should be used also. Possible disadvantages of the low product pH are that corrosion may be increased and that the N:P<sub>2</sub>O<sub>5</sub> weight ratio will be a little lower

than 1:3. The latter is a problem only if a 1:3 ratio is desired in the product. However, this ratio can be obtained by adding a small amount of supplemental nitrogen. Available data on corrosion (7) indicate little effect of pH in the range in question. These data were for solutions made from reagent materials; however, similar results were obtained in unpublished work with solutions made from wet-process acid.

Tests indicated that quick cooling is also an effective method. However, the rate of cooling required is higher than could be accomplished in most existing plants.

It should be noted that acids from some sources gave satisfactorily low settling and crystal growth without any adjustment of manufacturing procedure. Products from other acids varied widely in the degree of objectionable characteristics. This indicates that, in practice, a testing procedure might be desirable for routine checking of incoming acid to determine the best procedure for using it. Alternatively, the combination high neutralization-low product pH might be adopted in a plant as standard procedure to ensure against trouble from a change in the character of the acid.

### Literature Cited

- (1) Hatfield, J. D., Slack, A. V., Crow, G. L., Shaffer, H. B., Jr., *J. AGR. FOOD CHEM.* 6, 524-31 (1958).
- (2) Houston, E. C., Yates, L. D., Haunschild, R. L., *Ibid.*, 3, 43-8 (1955).
- (3) Wilbanks, J. A., Nason, M. C., Scott, W. C., *Ibid.*, 9, 174 (1961).

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## FERTILIZER TECHNOLOGY

### Wet-Process Phosphoric Acid in Mixed Fertilizers

PHOSPHORIC ACID is a well known commodity in the fertilizer industry. For many years it has been used in the manufacture of high analysis triple superphosphate, and to a much lesser extent as a phosphate material for direct application in the irrigated areas of the West. In recent years, while its use in these two areas has increased greatly, the acid has also become a basic raw material in the manufacture of both solid and liquid mixed fertilizers. These changes are

causing a sizable expansion in facilities for producing phosphoric acid (7).

Two types of phosphoric acid are marketed—a purified acid made by the electric furnace method and a less pure, dark acid made by the wet-process method. The information presented here relates primarily to wet-process phosphoric acid made from Florida pebble phosphate by the Dorrco process (14).

While wet-process phosphoric acid has

been used in the fertilizer industry for a number of years, its advent as an important raw material for mixed fertilizers dates back only a few years. Its use in solid mixed fertilizers began about 1955 (6); its use in liquid mixed goods, first reported in 1957 (10), is only now coming into prominence. The growth in the use of wet-process phosphoric acid in mixed fertilizers and for direct application has been phenomenal—from less than 50,000 tons of P<sub>2</sub>O<sub>5</sub> in 1957-58 to an

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Wet-process phosphoric acid, first used in granular mixed fertilizers in 1955 and in liquid fertilizers in 1957, has become a basic raw material in the mixed fertilizer industry. Its corrosive nature, high viscosity, and content of impurities (iron, aluminum, and solids) cause many difficulties for the fertilizer manufacturer. Problems have been minimized by selection and installation of suitable equipment for handling the acid, modification of existing process equipment, and development of new techniques of formulation and operation. Economic factors favor the continued rapid increase in the use of wet-process phosphoric acid, as a replacement for sulfuric acid and triple superphosphate in granular fertilizers and for furnace-process phosphoric acid in liquid fertilizers.

**Table I. Typical Composition of Wet-Process Phosphoric Acid**

Constituent	Weight %
H <sub>2</sub> O	16.53
H <sub>3</sub> PO <sub>4</sub> <sup>a</sup>	75.16
H <sub>2</sub> SO <sub>4</sub>	4.68
Fe <sub>2</sub> O <sub>3</sub>	1.25
Al <sub>2</sub> O <sub>3</sub>	1.53
F	1.06
Solids	0.80

<sup>a</sup> Total P<sub>2</sub>O<sub>5</sub> content expressed as H<sub>3</sub>PO<sub>4</sub>.

estimated 130,000 tons in 1959-60. Consumption of the acid for these purposes is expected to increase more than twofold in the next 5 years.

### Chemical and Physical Properties

Of prime interest to the users of wet-process phosphoric acid are its chemical and physical properties. These characteristics, although similar in many respects to those of purified phosphoric acid, are sufficiently different to merit careful study. Also, since wet-process phosphoric acid is produced from a phosphate raw material that is nonuniform in composition, and by methods of manufacture that differ in some details, the properties of the acid from different suppliers may vary to some extent. Practically the only specification set for wet-process acid is its P<sub>2</sub>O<sub>5</sub> content; other chemical constituents are present in varying amounts.

In the Dorrco process phosphoric acid is manufactured by reacting sulfuric acid with finely ground phosphate rock. The gypsum formed in the reaction is filtered off, and the acid, about 32% P<sub>2</sub>O<sub>5</sub> in strength, is concentrated to 52 to 54% P<sub>2</sub>O<sub>5</sub> in vacuum evaporators. The manufacturing process has been amply described by Waggaman (14) and Eisenhart (2).

Most of the elements found in Florida pebble phosphate are also found in the acid. A typical analysis for wet-process phosphoric acid, in which the major

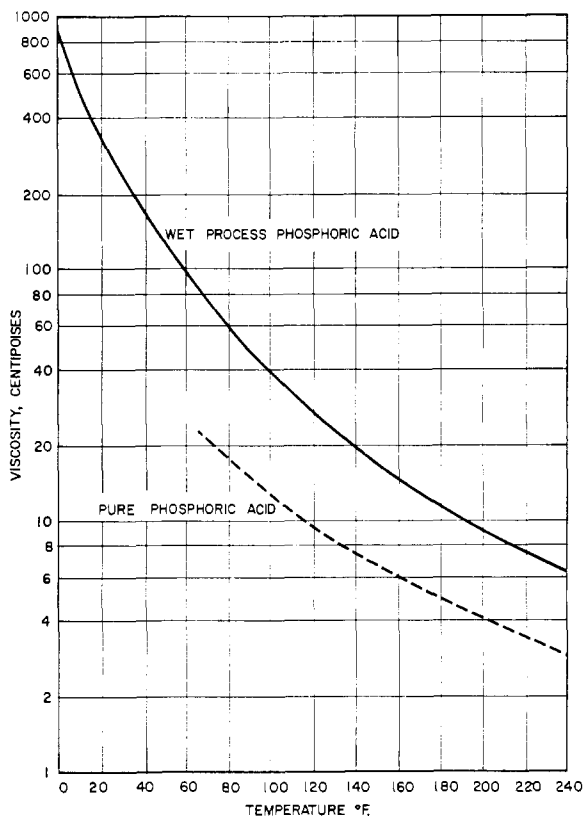


Figure 1. Viscosity of phosphoric acid  
54.4% P<sub>2</sub>O<sub>5</sub>

**Table II. Analysis of Solids from Wet-Process Phosphoric Acid**

Solids from	Analysis, Per Cent by Weight						
	P <sub>2</sub> O <sub>5</sub>	Ca	SO <sub>4</sub>	Al	Fe	F	SiO <sub>2</sub>
32% P <sub>2</sub> O <sub>5</sub> acid to evaporators	1.9	14.8	38.9	0.3	0.2	19.9	10.3
54% P <sub>2</sub> O <sub>5</sub> acid from evaporators	6.8	12.9	29.0	5.1	0.3	22.0	5.3
54% P <sub>2</sub> O <sub>5</sub> acid after storage	38.9	3.3	4.7	1.5	9.6	12.9	6.1

constituents are listed, is given in Table I. The acid contains from 3 to 5% of sulfuric acid and about 1% each of iron, aluminum, and fluorine. Approximately 15 other elements are present in wet-process phosphoric acid, in amounts ranging from less than 1% to a trace (7).

Principal elements in this group are boron, calcium, chlorine, manganese, magnesium, silicon, sodium, and zinc.

The analysis shown in Table I represents acid that was treated with a settling agent, retained in a storage tank to achieve partial settling of the solids,

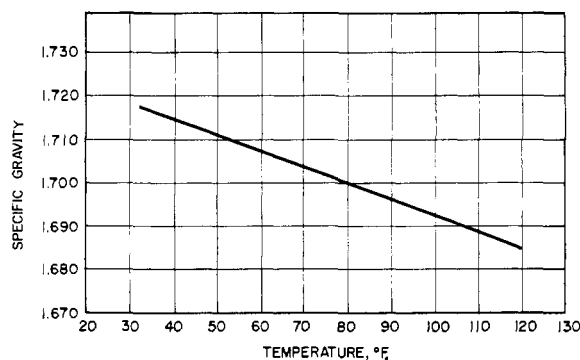


Figure 2. Specific gravity of wet-process phosphoric acid

54.4%  $P_2O_5$

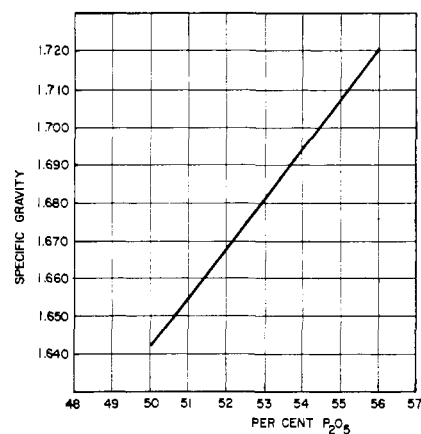


Figure 3. Specific gravity of wet-process phosphoric acid at 70° F.

and drawn from the upper part of the tank. Solids content was measured by filtering the acid through a Gooch crucible having a pore size of about 4 microns, washing the solids with acetone, and drying and weighing the solids.

Impurities in wet-process phosphoric acid become troublesome only when they crystallize from the acid as solids. This may happen when the acid is concentrated from 32%  $P_2O_5$  to 54%  $P_2O_5$ , or during prolonged storage, or when the acid is neutralized. Typical analyses of the solids found in wet-process acid are given in Table II. In the 32%  $P_2O_5$  acid fed to the evaporators solids are composed primarily of gypsum and fluosilicates. Solids separated from newly prepared 54%  $P_2O_5$  acid are similar in composition, except for an increase in the amount of aluminum phosphate. The solids which appear on further handling and storage of the acid are different; they contain little gypsum and appear to be complex compounds containing iron and aluminum phosphates, fluosilicates, and possibly fluorides.

Practically all of the iron and aluminum precipitate as phosphates when the acid is neutralized. According to Wag-gaman (14) the iron and aluminum phosphates are mostly citrate-soluble.

One of the important properties to consider in the handling of wet-process phosphoric acid, especially at temperatures below 32° F., is viscosity. In comparison with pure phosphoric acid, the viscosity of wet-process phosphoric acid is considerably higher. This is shown in Figure 1, where viscosity values at various temperatures for the two acids are plotted. Viscosity values for wet-process phosphoric acid (sample described in Table I) were measured with a Cannon-Fenske viscosity pipet at temperatures above 32° F. and with a Brookfield viscometer at 32° F. and lower temperatures. Acid with a higher content of solids or dissolved impurities would have higher viscosity values.

Specific gravity information (Figures 2

and 3) was also obtained on the typical sample of Table I. Specific gravity of wet-process phosphoric acid is much greater than that of the pure acid (1.708 as compared to 1.583 at 60° F.). While the specific gravity of each shipment of wet-process phosphoric acid may differ, its variation with temperature or concentration will be similar to that shown.

As wet-process phosphoric acid exhibits a high degree of supercooling, its temperature can be lowered considerably below its true freezing point without the formation of crystals. Amounts of impurities present also affect the freezing point. Because of these factors, the actual freezing point of a sample is unpredictable. When the weight ratio of  $P_2O_5$  to water is more than 3.2, acid containing 54%  $P_2O_5$  occasionally freezes at temperatures above 0° F. The crystals which form, identified as  $H_3PO_4 \cdot \frac{1}{2}H_2O$ , do not redissolve until the acid is either warmed considerably above its apparent freezing point or diluted with water.

Wet-process acid is corrosive to mild steel. In laboratory tests at ambient temperatures, rates of corrosion of over 300-mil penetration per year have been observed.

#### Equipment for Handling and Storage

Wet-process phosphoric acid is shipped in rubber-lined carbon steel tank cars of 50- to 70-ton capacity. To unload the acid, air pressure is applied to the tank car to force the acid through transfer lines to process or storage. Because of the high viscosity of wet-process acid at low temperatures, it is advisable to insert a centrifugal pump in the transfer line and provide transfer lines of adequate size. Centrifugal pumps lined with rubber or made of a resistant alloy such as Durimet 20 are suitable for handling wet-process acid at ordinary temperatures. Pipelines of rubber-lined carbon steel, poly(vinyl chloride), or lead, and valves of the Saunders dia-

phragm type, made of rubber-lined carbon steel or of poly(vinyl chloride), have proved satisfactory.

The use of carbon steel tanks, lined with  $\frac{3}{16}$ -inch-thick natural rubber, for storage of wet-process acid has been the accepted practice for many years. It still appears to be the most trouble-free method for storing the acid.

Some fertilizer companies are using a vertical, cylindrical, carbon steel tank containing a vinyl plastic bag insert for the storage of wet-process phosphoric acid. The bag is not attached to the walls of the tank, but is supported by wires fastened to the top of the tank. Cost of the bag liner is one third to one half the cost of  $\frac{3}{16}$ -inch rubber lining. One problem with the plastic bag is its susceptibility to damage in installation or when it becomes necessary to remove accumulated solids from the bottom of the tank.

A recent and interesting development in the storage of wet-process acid has been the installation of asphalt-lined pits by a few companies. After the pit is excavated it is first lined with  $\frac{1}{2}$ -inch mesh wire screen and then covered with alternate layers of asphalt and burlap cloth. The completed lining is about  $\frac{3}{4}$  inch thick. At this date the asphalt-lined storage pit appears to be practical in locations where the structure of the soil is sound enough to support the weight of the acid, where the water table is below the bottom of the pit, and where possible damage from frost is not a concern. Cost per ton of acid capacity for the asphalt-lined pit is about one fifth of that for a rubber-lined steel tank.

Various types of flowmeters are being used to measure the flow of wet-process phosphoric acid. The electromagnetic flowmeter is particularly suitable for this purpose, for it has no pockets, crevices, or stagnant areas where solids in the acid may collect to cause the meter to become inaccurate or inoperative. Its measurement of the volume rate of flow is not affected by viscosity, which for wet-

**Table III. Raw Material Costs for Granular Mixed Fertilizers**

Material	Plant Food Content	Unit Cost <sup>a</sup>	Grade 5-20-20				Grade 12-12-12			
			With Phosphoric Acid		Without Phosphoric Acid		With Phosphoric Acid		Without Phosphoric Acid	
			Lb.	Cost	Lb.	Cost	Lb.	Cost	Lb.	Cost
Ammonium sulfate	21.0% N	\$1.70	...	...	...	...	191	\$ 3.41	286	\$ 5.11
Nitrogen solution <sup>b</sup>	44.0% N	1.44	...	...	45	\$ 1.43	471	14.92	425	13.46
Anhydrous ammonia	82.3% N	1.20	125	\$ 6.17	101	4.99	...	...	...	...
Normal superphosphate	20.0% P <sub>2</sub> O <sub>5</sub>	1.10	862	9.48	440	4.84	802	8.82	475	5.23
Triple superphosphate	46.0% P <sub>2</sub> O <sub>5</sub>	1.26	127	3.68	695	20.14	...	...	326	9.45
Phosphoric acid	54.0% P <sub>2</sub> O <sub>5</sub>	1.48	328	13.11	...	...	157	6.27	...	...
Sulfuric acid, 66° Bé.	...	1.15 <sup>c</sup>	...	...	120	1.38	80	0.92	160	1.84
Potash	61.0% K <sub>2</sub> O	0.63	656	12.60	656	12.60	393	7.55	393	7.55
			2098	\$45.04	2057	\$45.38	2094	\$41.89	2065	\$42.64

<sup>a</sup> Costs at Indianapolis.

<sup>b</sup> Solution 440 (22-66-6).

<sup>c</sup> Per hundred pounds.

process phosphoric acid varies widely with temperature, and its accuracy is independent of the density and turbulence of the acid. For phosphoric acid the meter should have a Teflon liner and be equipped with electrodes made of Hastelloy C or platinum. It has been found absolutely necessary to have the acid stream and the meter body well grounded, for any stray electrical currents will cause the meter to read erroneously.

Rotameters of 316 stainless steel are sometimes used to measure the flow of wet-process phosphoric acid. Provisions must be made to wash out the lines and rotameter once a day to prevent an accumulation of solids which would affect the accuracy of the rotameter. The meter is also sensitive to changes in the density and viscosity of the acid. If facilities are available for holding the temperature of the acid reasonably constant so that changes in the viscosity and density of the acid are minimized, the measurement of flow with the use of a rotameter is satisfactory.

Volumetric meters of the positive displacement type, made of 316 stainless steel, are often used for wet-process phosphoric acid, usually at plants where liquid fertilizers are manufactured. Because the clearance between moving parts is necessarily small in these meters, they are generally not recommended for a liquid that contains solids, for the meter may become clogged or undergo excessive wear. Yet many manufacturers are using the meter successfully, where the acid contains less than 1% of fine, suspended solids and the meter is periodically flushed with clean water.

### Granular Mixed Fertilizers

Wet-process phosphoric acid is used widely in the manufacture of solid mixed fertilizers and to a lesser extent in the manufacture of liquid mixed fertilizers. Use of the acid as a raw material for direct application in irrigated areas, though limited, is increasing. The eco-

nomics underlying its use in fertilizer manufacture, as well as a number of technical aspects in these developments, are of interest.

When granular mixed fertilizers are made with wet-process phosphoric acid, in nearly all cases the total cost of raw materials is lowered, even though the acid is a more costly source of phosphate than either normal superphosphate or triple superphosphate. Several factors are responsible for this situation.

The use of phosphoric acid reduces or eliminates the amounts of triple superphosphate and sulfuric acid needed in the formula.

The ammoniation capacity of phosphoric acid is much higher than that of other phosphates, and as a result more low-cost ammonia and ammonia-containing solutions can be substituted for the higher cost, solid forms of nitrogen.

Because both phosphoric acid and ammonia are highly concentrated forms of plant food and because the amount of sulfuric acid is reduced or eliminated, more room is available in the formula for low-cost normal superphosphate.

In practice, the economics of using wet-process phosphoric acid in the production of granular mixed fertilizers depends largely upon the relative cost of phosphoric acid, triple superphosphate, normal superphosphate, and sulfuric acid. Table III shows formulas and raw material costs for grades 5-20-20 and 12-12-12, made with and without phosphoric acid. Costs are based on the delivered price of raw materials at Indianapolis, Ind. For grade 5-20-20, the saving amounts to \$0.34 per ton of product; for 12-12-12, \$0.75 per ton of product.

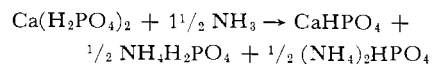
Savings with the use of phosphoric acid will be greater or smaller than those shown in the two examples, depending on the grade made and raw material costs at a particular plant. No general rule can be stated; but each manufacturer must evaluate at his locality the economics of using wet-process phosphoric acid.

**Table IV. Rates and Heats of Ammoniation**

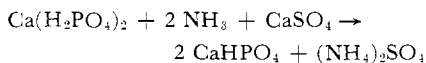
Material Reacted with Ammonia	Rate of Ammoniation, Lb. NH <sub>3</sub> /Unit P <sub>2</sub> O <sub>5</sub>	Heat of Ammoniation, B.t.u./Lb. NH <sub>3</sub>
Normal superphosphate	5.8	1430
Triple superphosphate	3.8	1540
Phosphoric acid	7.2 <sup>a</sup>	1780
Sulfuric acid, 66° Bé.	0.324	2940

<sup>a</sup> Rate of ammoniation can be increased in presence of normal superphosphate. As a general rule each unit of P<sub>2</sub>O<sub>5</sub> from phosphoric acid that can be paired with 2 units of P<sub>2</sub>O<sub>5</sub> from normal superphosphate will react with an additional 2.4 pounds of ammonia.

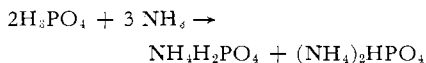
Aside from the economics, two of the more important factors to consider in the manufacture of granular mixed fertilizers with wet-process acid are rates of ammoniation and heats of ammoniation. Phosphoric acid's high capacity for ammonia is best illustrated by referring to a set of simplified chemical equations which represent the over-all chemical reactions that take place during ammoniation of the various phosphates in normal plant practice. Triple superphosphate, which is mainly monocalcium phosphate, reacts with 1½ moles of ammonia per mole of P<sub>2</sub>O<sub>5</sub>, to give dicalcium phosphate and mono- and diammonium phosphates.



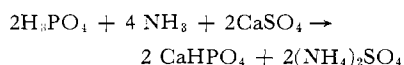
Normal superphosphate, which contains large amounts of gypsum in addition to monocalcium phosphate, can be reacted with 2 moles of ammonia per mole of P<sub>2</sub>O<sub>5</sub>; the gypsum reacts rapidly with diammonium phosphate formed as an intermediate material and the end products in this case are dicalcium phosphate and ammonium sulfate.



Phosphoric acid, on the other hand, can be combined with 3 moles of ammonia per mole of  $\text{P}_2\text{O}_5$  without excessive loss of ammonia; mono- and diammonium phosphates are formed.



Approximately half of the gypsum present in normal superphosphate is consumed when the superphosphate is ammoniated; the rest is available for utilization during ammoniation of other phosphates. When excess gypsum is present during ammoniation of phosphoric acid, up to 4 moles of ammonia per mole of  $\text{P}_2\text{O}_5$  can be reacted to form dicalcium phosphate and ammonium sulfate.



In actual practice, normal and triple superphosphates are ammoniated at rates slightly higher than those indicated by the above equations. Practical ammoniation rates for the phosphates and sulfuric acid are given in Table IV. One unit of  $\text{P}_2\text{O}_5$  in the form of normal superphosphate will react with 5.8 pounds of ammonia; the corresponding values for triple superphosphate and phosphoric acid are 3.8 and 7.2 (4). The ammoniation rate for phosphoric acid can be increased when normal superphosphate is present. Each unit of  $\text{P}_2\text{O}_5$  from phosphoric acid that can be paired with two units of  $\text{P}_2\text{O}_5$  from normal superphosphate will react with an additional 2.4 pounds of ammonia, or a total of 9.6 pounds. Thus, in the formulation of fertilizers which contain sufficient gypsum from normal superphosphate, the allowable ammoniation rate of phosphoric acid is more than double that of the triple superphosphate it replaces.

Rates of ammoniation higher than these are to be avoided, for they lead to loss of ammonia, or to the formation of basic phosphates which are not readily available to plant life.

Not all of the  $\text{P}_2\text{O}_5$  in wet-process acid can react with ammonia, for part of it is already combined with iron, aluminum, and other metallic impurities. However, because of the sulfuric acid content of wet-process acid, its over-all ammoniation capacity per unit of  $\text{P}_2\text{O}_5$  is only slightly less than that of pure phosphoric acid. For all practical purposes, the ammoniation rates for pure phosphoric acid apply also to wet-process acid.

A second important factor to consider in formulation of granular mixed fertilizers with phosphoric acid is its heat of ammoniation. These heats for the various phosphates and sulfuric acid are

shown in Table IV (3). Much less heat is derived from phosphoric acid than from sulfuric acid (1780 B.t.u. per pound of ammonia as compared to 2940). In the 5-20-20 formulas shown in Table III, the one made with phosphoric acid has a heat of ammoniation of 205,000 B.t.u., whereas that made with sulfuric acid has 230,000 B.t.u. When low nitrogen grades are manufactured with phosphoric acid, care should be taken to minimize heat losses from the ammoniator, or to provide supplemental heat by introducing steam in the mixture or by returning hot recycle material.

In the high nitrogen grades, the lower heat of reaction of phosphoric acid is an advantage. More ammonia can be absorbed in the mixture before over-agglomeration, caused by excessive temperatures, becomes a problem.

The two principal processes for manufacturing granular mixed goods differ only in the type of mixer employed. One process uses a pugmill for mixing; the other a TVA-type continuous ammoniator. There is no basic difference in formulation principles, chemical reactions, temperature control, or auxiliary equipment for premixing, metering, drying, cooling, and screening (5).

A pugmill is a trough U-shaped in cross section, which contains one or two rotating shafts positioned lengthwise within the trough. Attached to the shafts are many paddles. Pugmills commonly used vary from 2 to 5 feet in width, 3 to 4 feet in depth, and 10 to 15 feet in length. Solid raw materials are introduced at one end and discharged at the opposite end. Liquid raw materials (anhydrous ammonia, nitrogen solutions, sulfuric acid or phosphoric acid, and water) are introduced through short pipe spargers which deliver the liquids underneath the bed of solid materials. The spargers are located as close to the paddles as possible.

Granules from a pugmill are generally harder, stronger, but more irregular in shape than those discharged from a TVA-type ammoniator. Heat and moisture levels required for granulation are usually lower in a pugmill. However, because it is difficult to distribute liquids uniformly under the bed of solid materials in a pugmill, the neutralization of high amounts of acid with ammonia often results in excessively high temperatures in localized areas, loss of ammonia, or formation of ammonium chloride fume.

The lower level of heat needed in a pugmill to obtain granulation is an advantage in the manufacture of those grades where heat supplied by the ammoniation of phosphates is minimal. In the manufacture of other grades containing high amounts of phosphoric acid, the difficulties noted above are generally avoided by reacting the acid with

ammonia in a preneutralizer, and introducing the resulting ammonium phosphate slurry into the pugmill.

The TVA-type ammoniator is a drum, usually 6 to 8 feet in diameter and from 6 to 14 feet long, which rotates at 8 to 12 r.p.m. Solid raw materials are fed in continuously at one end of the ammoniator and discharged at the other. Liquid raw materials are generally introduced through pipe spargers which are placed parallel to the axis of the drum and deep under the 2-foot bed of solid raw materials. Liquids emerge from the sparger through a row of uniformly spaced holes on one side of the sparger. A scraper mounted to bear against the inside shell of the drum keeps material from adhering to the shell.

Wet-process phosphoric acid is generally introduced into the ammoniator through a pipe sparger placed under the bed of material. Sometimes it is added through a sparger placed above the bed. The sparger under the bed of material is preferred. The sparger is located parallel to and behind the sparger for ammonia or nitrogen solutions, so that the solid particles in the bed move first past the ammonia sparger and then past the acid sparger. As mixing parallel to the axis of the ammoniator is slow, it is good practice to have the holes in the acid sparger in line with those in the ammonia sparger. The introduction of ammonia and acid close together minimizes the possibility of localized acidic areas where corrosion may occur or fumes of ammonium chloride may originate.

Hastelloy C has proved to be a highly resistant material of construction for the sparger placed under the bed of solid materials in the ammoniator. Spargers placed above the bed where operating conditions are less severe are often made of poly(vinyl chloride).

The TVA-type ammoniator, properly operated, is an excellent device for obtaining uniform distribution of liquid raw materials into solid raw materials. As optimum rates of ammoniation are possible, the full economic potential of the use of wet-process phosphoric acid can be realized in this unit.

The use of phosphoric acid in the manufacture of many high analysis grades being marketed today is a necessity, as other competitive phosphate materials are not concentrated enough. With the steady increase in the production of high analysis fertilizers, use of phosphoric acid in mixed fertilizers will most certainly increase.

### Liquid Mixed Fertilizers

Production of liquid mixed fertilizers is still small in comparison to that of solid fertilizers, but its growth has been steady. In 1961 production in units of plant food is expected to amount to more than 5% of the total fertilizer market.

Perhaps the most promising development in the manufacture of liquid mixed fertilizers, as far as costs are concerned, is the increasing use of wet-process phosphoric acid. For many years the main source of phosphate for liquid fertilizers has been, and still is, electric furnace acid, even though substitution of wet-process acid offers the possibility of lowering the cost of phosphate raw materials by \$0.05 to \$0.20 per unit of  $P_2O_5$ . Improvements in the quality of the acid, and new techniques of manufacturing liquid fertilizers to overcome the limitations of wet-process acid, are making it possible for some manufacturers to realize savings from the use of wet-process acid.

The major drawback to the use of wet-process phosphoric acid in the manufacture of liquid mixed fertilizers is that the impurities in the acid precipitate when the acid is ammoniated to its neutral point. The precipitated solids, which are mainly iron and aluminum phosphates, settle in storage tanks and may cause stoppages both in transfer lines and in spray nozzles on application equipment. Another drawback is that the fine solids which are present in the acid as received cause undue wear on the volumetric meters through which the acid is metered.

Much time and effort have been expended to find ways to avoid or eliminate difficulties with wet-process acid. In both government and private laboratories methods for purifying the acid and techniques for utilizing it successfully in liquid mixed fertilizers are being developed. Adding chemicals such as polyacrylamides or other flocculating agents of high molecular weight at the point of production to hasten settling of the solids and removing the settled solids by decantation before the acid is shipped have improved the quality of the acid. Also, close control of operating conditions in the manufacture of wet-process acid has been found to yield a better acid.

In the manufacture of liquid mixed fertilizers, four techniques of using the wet-process acid effectively are worthy of mention.

1. The liquid mixed fertilizer is applied as soon as it is made, before the solids have had time to settle. Many manufacturers who are using the acid at present are following this procedure, which of course limits the use of the acid to periods of actual fertilizer distribution. Liquid fertilizers that are to be stored for any length of time in the off-season are generally made with electric furnace acid.

2. A second method, developed by TVA, is to control conditions during the ammoniation step in such a way that the iron and aluminum impurities precipitate as colloidal-type particles (73). Acid and ammonia are fed simultaneously in proportions that will maintain the pH of the mixture at 8.0; when all

of the ammonia has been added, additional acid is introduced to bring the pH of the mixture to 6.6. The temperature of the reactants should be held below 175° F. to obtain best results. The colloidal-type particles settle very slowly; can be resuspended with mild agitation, and are too fine to cause stoppages in lines and equipment.

3. A sequestering agent is added to the mixture to keep metallic impurities in solution during the ammoniation step. Nearly all of the chemicals that will sequester the metallic impurities are too costly, but TVA has found the polyphosphates to be economically feasible for this purpose (72). They can be supplied to the mixture as a superphosphoric acid containing about 76%  $P_2O_5$  or as an ammoniated solution of superphosphoric acid containing 10 to 11% N and 33 to 34%  $P_2O_5$ . Depending on the grade of fertilizer and the quality of the wet-process phosphoric acid, from 10 to 50% of the  $P_2O_5$  in the mixture needs to be supplied by the polyphosphates.

4. The mixing is done in the presence of a suspension of colloidal attapulgite clay. TVA, Minerals & Chemicals Corp., and others have been instrumental in developing this technique (8, 9, 73). An aqueous solution containing 15% clay is first prepared, and is then added to the mixing tank to provide 1 to 2% clay in the final liquid fertilizer product. In the presence of clay the impurities in the acid apparently precipitate as very fine particles; and the product can be stored for considerable lengths of time without appreciable settling of particles. Control of temperature below 175° F. in the mixing step is again important to prevent formation of coarse crystals of iron and aluminum phosphates. Although the use of attapulgite clay as a suspending agent results in a satisfactory product, the cost of the clay and the higher degree of skill needed with the method have prevented most manufacturers from making liquid fertilizers in this manner.

Liquid fertilizer plants are of two types—batch or semicontinuous. In a typical batch plant, a stainless steel tank equipped with an agitator and capable of holding 2 to 5 tons of finished product is mounted on a platform weighing scale. Water, phosphoric acid, ammonia or ammonia-containing solutions, potash, and supplemental nitrogen materials are batch-weighed consecutively in the stainless steel tank, in amounts according to a predetermined formula. In some batch plants separate weighing systems are installed for ammonia or ammonia-containing solutions, potash, and supplemental nitrogen materials. In other plants liquid raw materials are measured with volumetric meters. The finished batch is pumped to a storage tank or a transport truck.

In batch plants, wet-process phosphoric acid is being used successfully, where either the product is distributed immediately after it is made, or the mixture is sequestered with polyphosphates obtained from TVA.

When superphosphoric acid is used to sequester iron and aluminum impurities, piping and metering changes are made to allow the simultaneous addition of superphosphoric acid, wet-process phosphoric acid, and ammonia (or ammonia solutions) to the required volume of water in the mixing tank. The mixture must be maintained at the neutral point throughout the batch cycle or else the polyphosphates will revert to orthophosphates and no sequestration of impurities will occur.

When neutral polyphosphate solution 11-33-0 is used as a sequestering agent, it may be mixed with the required volume of water in the mixing tank, after which wet-process acid and ammonia are added simultaneously, with care being taken to keep the mixture neutral, or it may be added after the wet-process acid has been neutralized with ammonia in the usual batch manner. The latter way is simpler, but more 11-33-0 is needed to achieve adequate sequestration of iron and aluminum impurities.

The preparation of suspensions with or without clay is not practical at batch plants, unless the plant has a means of keeping the mixture below 175° F. during ammoniation.

In the semicontinuous type of plant, phosphoric acid and ammonia, or an ammonia-containing solution, are metered and fed concurrently to a reaction vessel. The reaction vessel is usually a small stainless steel pipe section from which the neutralized ammonium phosphate solution either overflows or passes through into a carbon steel batch tank. Potassium chloride and supplemental nitrogen materials are weighed and added to the batch tank to make the desired grade. Heat of reaction is generally dissipated by recirculating the neutral solution through an external cooler.

Because semicontinuous plants have a means of cooling the mixture, any of the four methods described are applicable. However, the preferred method is that in which a suspension is prepared by controlling the pH at 8.0 and the temperature below 175° F. during ammoniation of the wet-process acid and adjusting the final pH to 6.6. A product which can be stored satisfactorily is obtained at lowest cost. It is important that a high degree of mixing be obtained in the reaction vessel. Care should also be taken not to exceed the solubility limits as outlined by Slack (71) or else the precipitation of iron and aluminum phosphates plus the partial crystallization of other ingredients may raise the solids concentration to a point where the mixture becomes a gel.

The usual procedure for the manufacture of suspension-type fertilizers is as follows:

Volumetric-type meters for measuring the flow of ammonia and wet-process



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Figure 4. Phosphoric acid and anhydrous ammonia being added to irrigation water



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Figure 5. Nurse tanks supplying anhydrous ammonia and phosphoric acid to irrigation water



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Figure 6. Rig for injecting anhydrous ammonia and phosphoric acid in soil

acid are first calibrated to ensure their accuracy. Then a tentative schedule showing the cumulative amounts of ammonia and acid to be added at each minute of the initial batch cycle is prepared. This schedule is designed to have all the ammonia in the batch when about 86% of the total acid has been added. On the basis of pH measurements made during the initial batch cycle, the tentative schedule is modified to achieve a pH of 8.0 when all of the ammonia has been added and a pH of 6.6 when all of the acid has been added. This schedule is used for subsequent batches. Recirculation through the cooler is adjusted to hold the temperature of the mixture below 175° F.

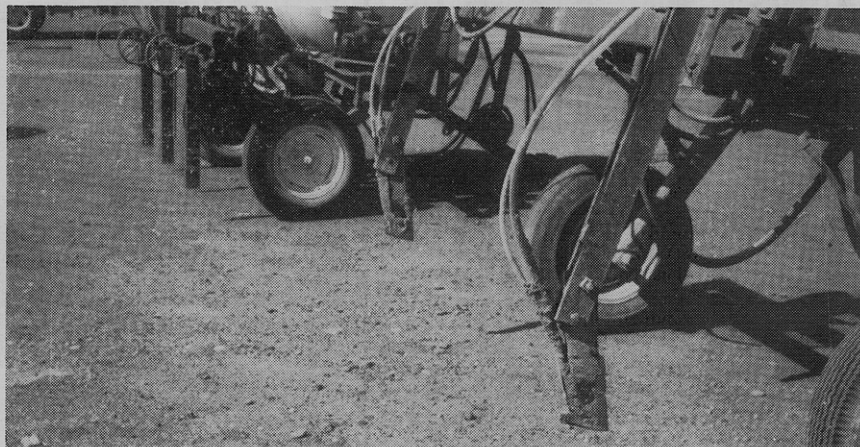
In time some settling of the suspended particles is unavoidable; also, growth of struvite crystals ( $MgNH_4PO_4 \cdot 6H_2O$ ) may occur (13). Means for agitating the product in storage tanks and for recirculating the product in nurse tanks before it is transferred to other containers should be provided. A squeeze-type hose pump on field applicators is preferred, for it can meter the mixture without becoming clogged. When broadcast application is practiced, opening of spray nozzles should be  $\frac{1}{16}$  inch or larger. With reasonable care along these lines, wet-process phosphoric acid is a suitable raw material for liquid mixed fertilizers.

#### Direct Application

A development closely associated with the liquid mixed fertilizer industry is the application of phosphoric acid simultaneously with anhydrous ammonia to the soil. For example, as practiced in the irrigated plains of West Texas, the acid either alone, or sometimes combined with potash to make a 0-30-10, is injected directly into water flowing in an irrigation ditch (Figure 4). From a 1000-gallon nurse tank, placed by the ditch, the acid flows by gravity through a  $\frac{1}{8}$ -inch plastic tube into the irrigation ditch. Its flow is controlled by a needle valve. Anhydrous ammonia contained in an adjacent tank is injected into the water at the same time. After the flows of ammonia and acid have been set, the nurse tanks are left unattended during the major portion of the application period (Figure 5).

When wet-process phosphoric acid is metered into irrigation water, its solids content becomes all-important. Very few solids need to be present to restrict or stop the flow of acid through the needle valve of  $\frac{1}{8}$ -inch tube. Not only should solids content be less than 0.5% at time of application, but the solids which are present should be in the form of very fine particles that are slow to settle.

Some phosphoric acid is also injected directly into the soil. The injection rig is a two-wheeled trailer carrying two tanks, one for anhydrous ammonia, the other for acid (Figure 6). Feed lines



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Figure 7. Plow on injection rig

from the tanks terminate at the base of three plows, which in operation allow the ammonia and acid to be placed 6 to 9 inches below the surface of the ground (Figure 7). The ammonia outlet precedes the acid outlet. A metering pump consisting of a rotating reel which presses against a number of plastic hoses is used to maintain a uniform flow of acid to each plow. In the operation of injection rigs the presence of solids in wet-process acid is less critical, for the acid is moved by a nonclogging, positive displacement pump, and the flow of acid can be constantly supervised by the operator of the rig.

Both electric furnace acid and wet-process acid are used in the above ap-

plications. The bulk of the acid applied is electric furnace acid, but for economic reasons as the quality of wet-process acid is improved, its use in irrigated areas is certain to increase.

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#### Literature Cited

- (1) *Chem. Eng. News* **38**, 19-21 (Aug. 29, 1960).

- (2) Eisenhart, C. L., "Production of Wet-Process Phosphoric Acid," Division of Fertilizer and Soil Chemistry, 138th Meeting, ACS, New York, N. Y., September 1960.
- (3) Hardesty, J. O., Ross, W. H., *Ind. Eng. Chem.* **29**, 1283-90 (1937).
- (4) Hein, L. B., Hicks, G. C., Silverberg, Julius, Seatz, L. F., *J. AGR. FOOD CHEM.* **4**, 318-30 (1956).
- (5) Hignett, T. P., Slack, A. V., *Ibid.*, **5**, 814-31 (1957).
- (6) Iliff, J. E., *Agr. Chem.* **11**, 35-7, 103-4 (1956).
- (7) Jacob, K. D., "Fertilizer Technology and Resources," pp. 142, 182, Academic Press, New York, 1953.
- (8) Newsom, W. S., *Solutions* **2**, 30-5 (1960).
- (9) Sawyer, E. W., *Ibid.*, **2**, 36-7, 39, 41, 43 (1960).
- (10) Slack, A. V., *Com. Fertilizer* **95**, 28 (1957).
- (11) Slack, A. V., Hatfield, J. D., Shaffer, H. B., Driskell, J. C., *J. AGR. FOOD CHEM.* **7**, 404-8 (1959).
- (12) Striplin, M. M., Jr., Stinson, J. M., Wilbanks, J. A., *Ibid.*, **7**, 623-8 (1959).
- (13) Tennessee Valley Authority, "Proceedings of Liquid Fertilizer Conference," Wilson Dam, Ala., June 11, 1959.
- (14) Waggaman, W. H., "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers," 2nd ed., pp. 174-209, Reinhold, New York, 1952.

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## FERTILIZER MICROSTRUCTURE

# Preparation of Thin Sections of Triple Superphosphate for Microscopic Examination

**D**URING a study of the physical properties of triple superphosphate, a method was needed for microscopic comparison of samples with respect to crystal growth, porosity, and general structure of the particle. The usual method of preparing and examining thin sections of a sample seemed attractive because it allows a minute study of the internal structure of the particle. Methods for preparing thin sections of hard, brittle materials, such as geological specimens, for microscopic examination

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are well documented in the technical literature (1-3, 5).

Techniques and types of materials used in the procedure vary with the type of sample being examined. The soft, porous, water-soluble properties of triple superphosphate cause it to require special consideration when making it into thin sections, in order to avoid smearing and other distortion of the grain structure during grinding and polishing of the specimen. Common procedures applicable to geological specimens needed modification when applied to triple superphosphate. For example, the

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method of Reed and Mergner (6) for impregnating limestone samples with Canada balsam dissolved in xylene is not satisfactory for superphosphate because of the difficulty in evaporating the xylene from the pores and interstices of the particle. The present paper describes a technique which was developed for encapsulating and impregnating triple superphosphate with a thermosetting polyester-type resin which could be sawed, ground, and polished without smearing, to give a thin section for microscopic examination in either reflected or transmitted light.