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## FERTILIZER SOLUBILITY

# Effect of Polyphosphate Content on Properties and Use of Liquid Fertilizers

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The solubility and other properties of liquid fertilizers made from electric-furnace phosphoric acids containing 55, 76, and 79%  $P_2O_5$  (24, 33, and 34% P) are compared; the proportion of  $P_2O_5$  in the polyphosphate form in fertilizer solutions made from these acids was about 0, 45, and 70%, respectively. The solubility at 32° F. of the ammoniated acids increased as the polyphosphate content was increased. When 70% of the  $P_2O_5$  was in the polyphosphate form, variations in the N: $P_2O_5$  weight ratio in the range of 0.28 to 0.32 (N:P ratio 0.64 to 0.73) had very little effect on plant nutrient solubility, which was about 48% N +  $P_2O_5$  (27% N + P). Solubility data are given for liquid fertilizers made from the ammoniated acids, urea-ammonium nitrate solution, and potassium chloride. The effectiveness of the polyphosphates in dissolving micronutrients and in sequestering the impurities in liquid fertilizers made from wet-process acid is discussed. Factors affecting the rate of hydrolysis of the polyphosphates to orthophosphate were pH and temperature.

UP TO 5 years ago, furnace-grade orthophosphoric acid was the source of essentially all the phosphate in liquid fertilizers. TVA (6) and others (2, 8) have published solubility data on that system. About 5 years ago, TVA introduced superphosphoric acid (9) which contains phosphate in the form of polyphosphates as well as orthophosphate. As the  $P_2O_5$  content of the acid increases, the proportion of  $P_2O_5$  in polyphosphate form increases and the proportions present as different species of polyphosphate change. Ammoniation of the acid is possible with little change in polyphosphate content. Acid of 76%  $P_2O_5$  (33% P) concentration (shipping grade) contains about 50% of its  $P_2O_5$  in polyphosphate form. Ammoniation yields a liquid fertilizer containing about 45% of its  $P_2O_5$  in polyphosphate form; results of solubility studies on this system have been presented (7). When this work was done, TVA was producing a

solution having an N: $P_2O_5$ :K<sub>2</sub>O grade of 10-34-0 (N:P:K grade, 10-15-0) from acid containing 76%  $P_2O_5$  (33% P).

Acid containing 78 to 80%  $P_2O_5$  (34 to 35% P) has since been produced, and the ammoniated product has been increased in grade to 11-37-0 (11-16-0). The increase in grade was made after studies had shown that the use of 78 to 80%  $P_2O_5$  (34 to 35% P) acid (some 70% of its  $P_2O_5$  as polyphosphates) resulted in a product of higher solubility than that made from acid containing 76%  $P_2O_5$  (33% P). Results of these studies are presented here. Effects of polyphosphate content of ammoniated superphosphoric acid on solubility are discussed, and a solubility diagram is presented for N:P:K liquid fertilizers made by adding supplemental nitrogen and potassium to 11-37-0 (11-16-0). Also given are results of studies on use of polyphosphates to solubilize micronutrients and

to sequester impurities in liquid fertilizers made from wet-process phosphoric acid.

### Procedure

Superphosphoric acids were obtained from the TVA plant or were prepared by dissolving phosphorus pentoxide in reagent-grade orthophosphoric acid. Source of the acid made little difference in solubility measurements, except that the small amount of impurities in the plant acid promoted supercooling and thus lengthened the time required for measurements.

The phosphoric acids were ammoniated to different degrees either in the plant or in the laboratory to produce solutions that are conveniently called "base solutions," since other fertilizer materials usually are added to produce the final liquid fertilizer. To minimize hydrolysis, the pH was kept above 5.5 and the temperature below 180° F.

during ammoniation of the acid, and the base solutions were stored at 32° F. Chemical analyses of some of the base solutions are shown in Table I, along with properties of the acids from which they were made. An assumption that the acids contained the same proportions of orthophosphates reported by Huhti and Gartaganis (7) leads to the conclusion that some of the polyphosphates were hydrolyzed to orthophosphate during ammoniation. With this exception, distribution of the various forms of phosphate in the ammoniated superphosphoric acids was roughly similar to that in the original acids.

Most of the solubility studies were made at 32° F. by a crystal-seeding method (6). Aqueous solutions of given nutrient ratio were chilled to promote crystallization, and the crystallizing phase was determined petrographically. Seed crystals of this phase then were added to solutions of different concentrations, and the concentration at which there was neither growth nor dissolution of the crystals was taken as the nutrient solubility. With reagent grade acid (and constant agitation) a determination took 2 to 3 weeks—with plant acid, 2 to 3 months.

At temperatures above and below 32° F., solubilities were determined by cooling (with agitation) until crystals formed and then warming slowly (2° F. per hour) until the crystals dissolved. Quiescent storage was used for sequestration tests.

### Effect of Polyphosphate Level on Properties of Liquid Fertilizers

**Solubility.** The effects of the proportion of polyphosphates and of the degree of ammoniation on solubility at 32° F. are shown in Figure 1. The upper curve is representative of the polyphosphate level in 11-37-0 (11-16-0) base solution, the middle curve 10-34-0 (10-15-0) base solution, and the bottom curve 8-24-0 (8-10-0) base solution made from orthophosphoric acid. Data for the lower two curves were obtained previously (5, 7).

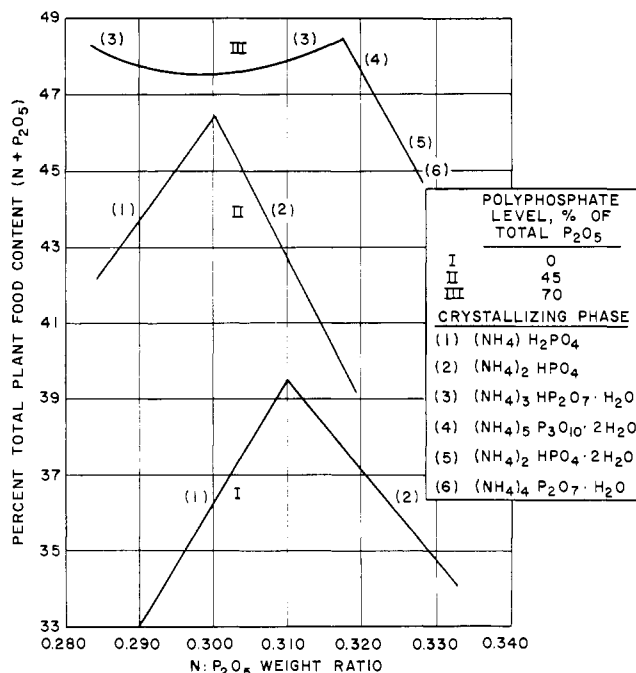
Maximum solubility increased from about 39% of total plant food (N + P<sub>2</sub>O<sub>5</sub>) in the orthophosphate system (0% polyphosphate), to about 46% at the 45% polyphosphate level, and to about 48% at the 70% polyphosphate level. The points of maximum solubility at the 0 and 45% polyphosphate levels were at N:P<sub>2</sub>O<sub>5</sub> weight ratios of 0.31 and 0.30 (N:P, 0.71 and 0.69). The curve for the 70% polyphosphate level sloped upward as the N:P<sub>2</sub>O<sub>5</sub> weight ratio was decreased to 0.283 (N:P, 0.648), but the study was not extended to lower ratios to determine a point of maximum solubility because of the likelihood of excessive hydrolysis and corrosiveness of the solution.

**Table I. Chemical Analyses of Base Solutions Produced by Ammoniation of Phosphoric Acids**

Nominal grade	8-24-0 (8-10-0)	10-34-0 (10-15-0)	11-37-0 (11-16-0)	11-44-0 (11-19-0)	8-28-0 <sup>a</sup> (8-12-0)
Acid concentration, %					
P <sub>2</sub> O <sub>5</sub>	55	76	79	83	...
P	24	33	34	36	...
Solution pH	6.5	6.0	6.0	5.6	6.4
Chemical analysis of base solution, wt. %					
N	8.0	10.0	10.9	11.0	8.4
P <sub>2</sub> O <sub>5</sub>	24.1	34.5	37.0	43.8	28.1
P	10.5	15.1	16.1	19.1	12.3
Distribution of P <sub>2</sub> O <sub>5</sub> , % of total	100(100) <sup>b</sup>	55(49)	28(20)	10(5)	55
Ortho	...	39(42)	44(46)	18(18)	9
Pyro	...	5(8)	19(20)	19(16)	12
Tripoly	...	(1)	6(9)	16(16)	7
Tetrapoly	...	...	2(3)	11(12)	5
Pentapoly	...	1	1(2)	26(33)	12
Other	...	...	...	...	...

<sup>a</sup> Base solution produced by blending nominal 11-44-0 (11-19-0) with 8-24-0 (8-10-0). The 11-44-0 (11-19-0) was not stable at 32° F.

<sup>b</sup> P<sub>2</sub>O<sub>5</sub> distribution in acid shown in parentheses (7).



**Figure 1. Effect of polyphosphate level and N:P<sub>2</sub>O<sub>5</sub> weight ratio on solubility of ammoniated phosphoric acids at 32° F.**

The curve shows little change in solubility between N:P<sub>2</sub>O<sub>5</sub> weight ratios of 0.283 and 0.320 (N:P, 0.648 and 0.733), but a maximum is indicated at 0.317 (N:P, 0.726). According to petrographic analyses, the points of maximum solubility for the lower (0 and 45%) polyphosphate levels apparently occurred at a eutectic between monoammonium phosphate on the left and diammonium phosphate on the right. At the higher polyphosphate level (70%), the maximum occurring at the N:P<sub>2</sub>O<sub>5</sub> weight ratio of 0.317 (N:P, 0.726) was apparently at a eutectic between hydrates of triammonium pyrophosphate on the left and pentammonium tripolyphosphate on the right.

These solubility studies led to an increase in the grade of TVA's ammoniated superphosphoric acid base solution from 10-34-0 (10-15-0) to 11-37-0 (11-16-0); a decision was made also to keep the polyphosphate level at about 70%. The N:P<sub>2</sub>O<sub>5</sub> weight ratio of 11-37-0 (11-16-0) is about 0.30 (N:P, 0.69), which is at the point of maximum solubility for the 10-34-0 (10-15-0) system (45% of the P<sub>2</sub>O<sub>5</sub> in polyphosphate form). This ratio would be desirable for the 11-37-0 (11-16-0) if hydrolysis occurred to the extent that solubility followed the peaked curve for the 45% polyphosphate level. The flat solubility curve at the 70% polyphosphate level indicates that close con-

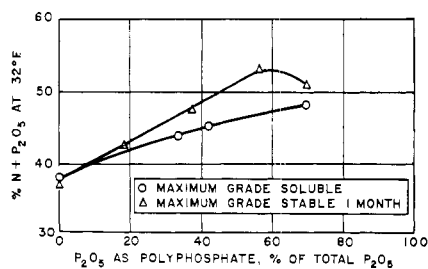


Figure 2. Effect of polyphosphate content on plant food solubility and stability at N:P<sub>2</sub>O<sub>5</sub> weight ratio of 0.30

control of ammoniation would not be required if there were no hydrolysis during storage.

**SUPERCOOLING.** As superphosphoric acid and products of its ammoniation will supercool, the effect of polyphosphate level on stability of ammoniated plant phosphoric acid at 32° F. was investigated in relation to true solubility. Stability tests involved determination of the maximum total plant nutrient content that could be held in metastable aqueous solution during quiescent storage for a month. Figure 2 shows that both solubility and stability at 32° F. increase as the polyphosphate level of ammoniated phosphoric acid (N:P<sub>2</sub>O<sub>5</sub> weight ratio, 0.30; N:P, 0.69) is increased from 0 to about 60%. Since the stability curve has a steeper slope than the solubility curve, it appears that the polyphosphate content has a greater effect on supercooling than on true solubility. Above about the 60% polyphosphate level, the crystallizing phase changes from ortho- to polyphosphates, and the effect on supercooling decreases. At polyphosphate levels of 40 and 60%, stability at 0° F. was the same as at 32° F. No value could be obtained for solutions containing no polyphosphates or for the 20% polyphosphate level; salt appeared in a short time at the higher concentrations, and ice formed at the lower concentrations.

**MULTICOMPONENT LIQUID MIXES.** Ammoniated superphosphoric acid [11-37-0 (11-16-0), 70% polyphosphate level], urea-ammonium nitrate solution (weight ratio, 0.8), and potassium chloride were used in a solubility study of the N:P<sub>2</sub>O<sub>5</sub>:K<sub>2</sub>O system. The results are compared in Table II with solubilities at the 0 and 45% levels obtained earlier. The 8-24-0 (8-10-0) base solution at the 0% polyphosphate level (6) had an N:P<sub>2</sub>O<sub>5</sub> weight ratio of 0.33 (N:P, 0.76), the ratio used in commercial practice; this is higher than the ratio of maximum solubility for the 45% polyphosphate level.

Increasing the polyphosphate level increased plant nutrient (N + P<sub>2</sub>O<sub>5</sub> + K<sub>2</sub>O) solubility significantly for non-

Table II. Effect of Proportion of P<sub>2</sub>O<sub>5</sub> as Polyphosphate on Solubility of Liquid Fertilizers

N:P <sub>2</sub> O <sub>5</sub> :K <sub>2</sub> O Weight Ratio	N:P:K Weight Ratio	P <sub>2</sub> O <sub>5</sub> , % of Total Plant Food	Solubility at 32° F., % Plant Food (N + P <sub>2</sub> O <sub>5</sub> + K <sub>2</sub> O) at Indicated Polyphosphate Level		
			0 <sup>a</sup>	45 <sup>b</sup>	70 <sup>c</sup>
4:1:0	1:0.1:0	20	...	30.3(1) <sup>d</sup>	32.5(2)
3:1:0	1:0.1:0	25	...	31.1(1)	33.1(2)
2:1:0	1:0.2:0	33	23.7(1)	32.3(1)	34.8(2)
1:1:0	1:0.4:0	50	26.9(1)	35.5(3)	39.7(2)
1:2:0	1:0.9:0	67	26.9(1)	40.1(3)	46.1(2)
1:3:0	1:1.3:0	75	33.9(1)	43.3(3)	49.4(2)
1:1:1	1:0.4:0.8	33	21.3(4)	21.9(4)	...
3:3:1	1:0.4:0.3	43	23.0(1)	27.9(4)	27.3(4)
1:2:1	1:0.9:0.8	50	30.1(4)	31.1(4)	...
3:6:1	1:0.9:0.3	60	32.0(5)	36.5(4)	36.9(4)
1:3:1	1:1.3:0.8	60	31.9(1)	36.9(5)	37.3(5)
3:9:1	1:1.3:0.3	69	35.0(1)	45.7(6)	49.5(6)
2:1:2	1:0.2:0.8	20	16.5(4)	17.9(4)	...
6:3:2	1:0.2:0.3	27	...	22.7(4)	22.5(4)
1:1:3	1:0.4:2.5	20	19.9(5)	21.5(5)	...
1:2:3	1:0.9:2.5	33	22.3(5)	23.3(5)	...
1:3:3	1:1.3:2.5	43	24.3(5)	24.9(5)	...

<sup>a</sup> Base solution, 8-24-0 (8-10-0) (7).

<sup>b</sup> Base solution, 10-34-0 (10-15-0) (4).

<sup>c</sup> Base solution, 11-37-0 (11-16-0).

<sup>d</sup> Numbers in parentheses indicate crystalline phase: (1) (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, (2) (NH<sub>4</sub>)<sub>5</sub>-P<sub>3</sub>O<sub>10</sub>·2H<sub>2</sub>O, (3) NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, (4) KNO<sub>3</sub>, (5) KCl, (6) NH<sub>4</sub>Cl.

<sup>e</sup> Estimated value calculated from polythermal data.

potash ratios—up to 13 percentage points (1:2:0 ratio, 1:0.9:0 N:P:K ratio) when the polyphosphate level was increased from 0 to 45%. The increase in going from the 45 to 70% polyphosphate level ranged from 2 to 6 percentage points as the proportion of total plant food present as P<sub>2</sub>O<sub>5</sub> was increased from 20 to 75%. When the amount of potash corresponded to a K<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> weight ratio of 0.5 (K:P, 0.95) or greater, the polyphosphate level had little effect on solubility. With a few exceptions, the crystallizing phases at 32° F. were the same at the 0 and 45% polyphosphate levels. The phosphate precipitated as the monoammonium and diammonium ortho salts at the lower levels and as pentammonium triphosphate dihydrate at the 70% level.

Figure 3 is a three-component solubility diagram for the 11-37-0 (11-16-0) system, based on data from this study and data on the indicated ratios that were assumed to have the same solubility as in the 10-34-0 (10-15-0) system (7). In the earlier work, the solubility at these ratios did not increase very much when the proportion of P<sub>2</sub>O<sub>5</sub> as polyphosphate was increased from 0 to 45%, and it was considered unlikely that a further increase in the polyphosphate content would appreciably change the solubility. This assumption was confirmed for several nutrient ratios by the polythermal method described earlier. Data for the nitrogen-potash base line were taken from a study by Kapusta (3).

Contours of constant plant nutrient content are shown as solid lines in the diagram. The label 25 on the contour

line, for example, indicates that all solutions along the line have a total nutrient solubility of 25% at 32° F. Broken lines mark the areas wherein the specific salts named are the crystallizing phase. Since the data are insufficient for accurately defining the position of the boundary lines, the indicated positions should be considered rough approximations.

**EFFECT OF TEMPERATURE ON SOLUBILITY.** Geographical and seasonal variations in weather conditions make desirable a knowledge of solubility of liquid fertilizers at temperatures other than 32° F., or knowledge of the salting-out temperature of a particular grade. In the present and the previous work (6, 7), the temperature-solubility relationship proved linear.

$$y = a + b(t - 32^\circ \text{ F.}) \quad (1)$$

where  $y$  = total plant food content for a saturated solution of given ratio and temperature, %;

$a$  = total plant food content for a saturated solution of given ratio at 32° F.;

$b$  = temperature-solubility coefficient for the particular salt in equilibrium with saturated solution;

$t$  = equilibrium temperature.

Estimates of solubilities at various temperatures or of salting-out temperatures of various grades thus are possible through use of Figure 3 in conjunction with the proper temperature-solubility coefficients (Table III).

Except for pentammonium triphosphate dihydrate, which precipitates

**Table III. Temperature-Solubility Coefficients for Liquid Fertilizers Made from 11-37-0 (11-16-0) Base Solution**

Crystallizing Phase	Change in Total Plant Nutrient Solubility, Percentage Points/ <sup>o</sup> F. (b in Equation 1)	a
(NH <sub>4</sub> ) <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ·2H <sub>2</sub> O	0.047	a
NH <sub>4</sub> NO <sub>3</sub>	0.143	a
NH <sub>4</sub> Cl	0.052	a
KCl	0.084	±0.011
KNO <sub>3</sub>	0.215	±0.017

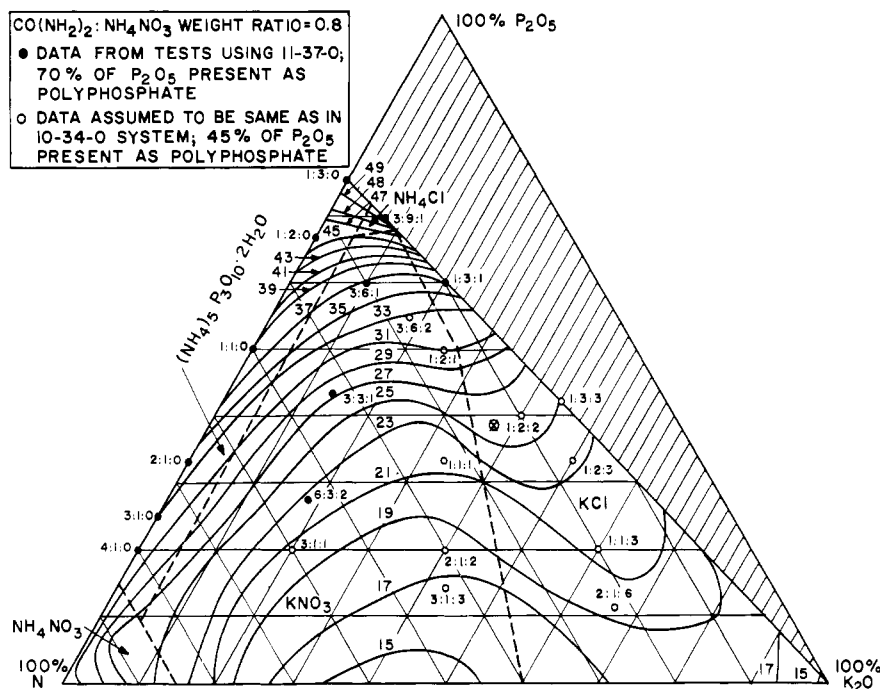
<sup>a</sup> Too few points in these precipitating areas to derive standard deviations.

at 32° F. instead of monoammonium or diammonium phosphate, the coefficients in Table III are the same as those for the 45% polyphosphate level. There was little change in the value of the coefficients in going from 0 to 45% polyphosphate levels, so little change was expected in going from 45 to the 70% level.

**USE OF DIAGRAM.** The maximum grade for a ratio not plotted is found by plotting the new ratio on the triangular diagram and then interpolating between the curved lines of constant nutrient content. A determination of the position on the diagram corresponding to the ratio 2:3:3 (N:P:K, 1:0.7:1.2) will illustrate. This ratio represents nitrogen, phosphorus pentoxide, and potassium oxide in the proportions 25.0, 37.5, and 37.5%. First, interpolate between the 30 and 40% guidelines for phosphorus pentoxide to get a 37.5% line. Then interpolate to get a 37.5% line for potassium oxide. The juncture of these lines (X on the chart) is the point desired. This point reads 25% on the nitrogen guidelines. The total plant nutrient content at point X is about 25.5%, for which the maximum grade of a 2:3:3 (N:P:K, 1:0.7:1.2) ratio is 6-9-9 (6-4-7).

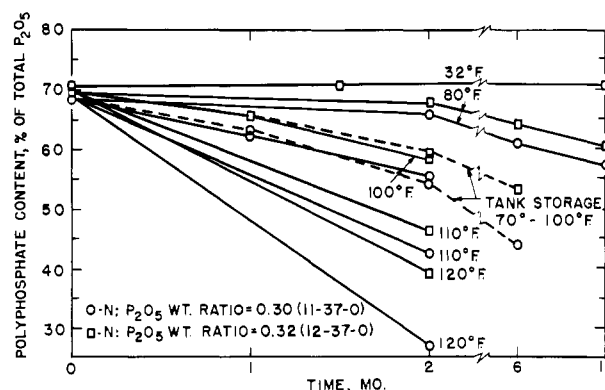
Equation 1 is used in finding the maximum grade for temperatures other than 32° F. For the 2:3:3 (N:P:K, 1:0.7:1.2) ratio, the crystallizing phase (Figure 3) is potassium chloride; for this salt, *b* is 0.084 and *a* is 25.5. If the temperature in question is 70° F., the total plant nutrient content, *y*, is 28.7% and the grade is 7.2-10.8-10.8 (7.2-4.7-9.0).

The procedure for determining the equilibrium temperature for a specific grade of liquid fertilizer also is relatively simple. Assume a 12-24-4 (12-10-3) grade. The ratio is 3:6:1 (N:P:K, 1:0.9:0.3). The crystallizing phase (Figure 3) is potassium nitrate, for which *b* is 0.215 (Table III). The value for *a* is 37, and the value for *y* is 40. With these values in the equation, solution for *t* shows an equilibrium temperature of 46° F.



**Figure 3. Three-component solubility diagram**

11-37-0: urea-ammonium nitrate-potassium chloride-water at 32° F. 70% of P<sub>2</sub>O<sub>5</sub> present as polyphosphate



**Figure 4. Effect of time and temperature on hydrolysis of ammoniated superphosphoric acid solutions**

In using the temperature coefficients and solubility diagrams, consideration must be given to phase changes that may occur with some ratios at temperatures other than 32° F. Phase changes will introduce error; fortunately, they usually occur near boundary lines between phases, and allowance can be made for possible error in these regions. An additional safety factor is found in the tendency of many of the fertilizer solutions to supercool somewhat before crystallization occurs.

**Hydrolysis.** The effects of time, temperature, and N:P<sub>2</sub>O<sub>5</sub> ratio on hydrolysis of ammoniated superphosphoric acid solutions are shown in Figure 4. No measurable amount of hydrolysis of 11-37-0 (11-16-0) occurred on 1 year of storage at 32° F. In 2 months of storage at 80° F., the decrease in polyphosphate level was 2 to 3 percentage points, which

is equivalent to less than 1 percentage point of total plant food solubility at 32° F. The decrease in polyphosphate level was greater as the temperature was increased and less as the N:P<sub>2</sub>O<sub>5</sub> ratio was increased. For example, at 120° F. the decrease in polyphosphate level was 42 and 30 percentage points, respectively, for N:P<sub>2</sub>O<sub>5</sub> ratios of 0.30 and 0.32 (N:P, 0.69 and 0.73). These decreases are equivalent to 5 to 8 percentage points of solubility at 32° F.

Figure 4 also shows data on the amount of hydrolysis that might be expected during storage of 11-37-0 (11-16-0) in outdoor tanks. Closed containers of base solution were submerged in a large outdoor tank of liquid, exposed to direct sunlight, to simulate large-scale storage. The tests were conducted in the period April to October. During the last 3 months, a

minimum-maximum thermometer submerged in the tank showed that the temperature ranged from 70° to 100° F. During the first 2 months, the hydrolysis rate of solutions stored in the outside tank was about the same as the rate in the laboratory at 100° F. The polyphosphate level of the solution having an N:P<sub>2</sub>O<sub>5</sub> ratio of 0.30 (N:P, 0.69) decreased about 25 percentage points during the full 6 months of storage in the outside tank. The final polyphosphate level was about 44%, which would amount to a decrease in solubility of about 2 percentage points.

Other tests showed that the 11-37-0 (11-16-0) solution hydrolyzed faster than 10-34-0 (10-15-0) solution, with its smaller proportion of P<sub>2</sub>O<sub>5</sub> as polyphosphates. The tabulation below shows, for example, that the polyphosphate level of the 11-37-0 (11-16-0) decreased 42 percentage points in 2 months at 120° F.; that of the 10-34-0 (10-15-0), only 26 percentage points.

Nominal Grade of Solution	Before storage	Polyphosphate P <sub>2</sub> O <sub>5</sub> Content, % of Total P <sub>2</sub> O <sub>5</sub>			
		After Storage for 2 Months at Indicated Temperature			
		80° F.	100° F.	110° F.	120° F.
11-37-0 (11-16-0)	69	66(3) <sup>a</sup>	56(13)	43(26)	27(42)
10-34-0 (10-15-0)	55	53(2)	49(6)	33(22)	29(26)

<sup>a</sup> Numbers in parentheses indicate decrease in polyphosphate P<sub>2</sub>O<sub>5</sub> content, % of total P<sub>2</sub>O<sub>5</sub>.

Not only did the 11-37-0 (11-16-0) solution contain a greater proportion of polyphosphates, but it also contained more of its P<sub>2</sub>O<sub>5</sub> in forms more highly condensed than the pyro form. Thus, the P-O-P bond in the more highly condensed phosphates seems to hydrolyze more readily than those in the pyrophosphate form.

**Sequestration.** In earlier work (10) on use of 10-34-0 (10-15-0) to sequester impurities in wet-process acid, thus holding them in solution when the acid is ammoniated to produce liquid fertilizers, the superphosphoric acid was of shipping grade (76% P<sub>2</sub>O<sub>5</sub>, 33% P), and the 10-34-0 (10-15-0) base solution made with it contained only about 47% of its total P<sub>2</sub>O<sub>5</sub> in polyphosphate form (mostly pyrophosphate); 20 to 40% of the P<sub>2</sub>O<sub>5</sub> as sequestrant was required. The sequestering power of this solution is compared with that of 11-37-0 (11-16-0) in Table IV.

Selected grades of two- and three-component solutions were prepared with wet-process acid (54% P<sub>2</sub>O<sub>5</sub>, 24% P) containing 0.9% by weight of solid impurities. The order of mixing was water, wet-process acid, ammonium hydroxide, sequestrant, urea-ammonium nitrate solution (urea:AN weight ratio, 0.8), and potassium chloride. The proportion of the total P<sub>2</sub>O<sub>5</sub> supplied as sequestrant was varied in increments of 5 percentage points.

The 11-37-0 (11-16-0) seemed slightly more effective than the 10-34-0 (10-15-0) per unit of total P<sub>2</sub>O<sub>5</sub> but

**Table IV. Comparison of 10-34-0 (10-15-0) and 11-37-0 (11-16-0) Ammoniated Superphosphoric Acid as Sequestrants for Impurities in Liquid Fertilizers Made from Wet-Process Acid**

Product Grade <sup>a</sup>	Sequestrant Nominal grade	Sequestrant Requirement <sup>b</sup>			Av. pH
		% of total P <sub>2</sub> O <sub>5</sub> in polyphosphate form	% of total P <sub>2</sub> O <sub>5</sub> added as base solution	% of total P <sub>2</sub> O <sub>5</sub> added as polyphosphate in base solution	
8-24-0 <sup>c</sup> (8-10-0)	11-37-0	70.5	15	10.6	6.25
8-24-0 <sup>c</sup> (8-10-0)	10-34-0	48.1	20	9.6	6.15
8-16-8 (8-7-7)	11-37-0	70.5	25	17.0	6.40
8-16-8 (8-7-7)	10-34-0	48.1	30	14.4	6.50
7-7-7 (7-3-6)	11-37-0	70.5	30	21.2	6.45
7-7-7 (7-3-6)	10-34-0	48.1	35	16.8	6.40

<sup>a</sup> Formulated from wet-process acid [54% P<sub>2</sub>O<sub>5</sub> (24% P), 0.9% solids], ammonium hydroxide, sequestrant, urea-ammonium nitrate solution (32% N), and potassium chloride.

<sup>b</sup> Essentially free of solids after storage for 30 days at 80° F.

<sup>c</sup> Required no supplemental nitrogen.

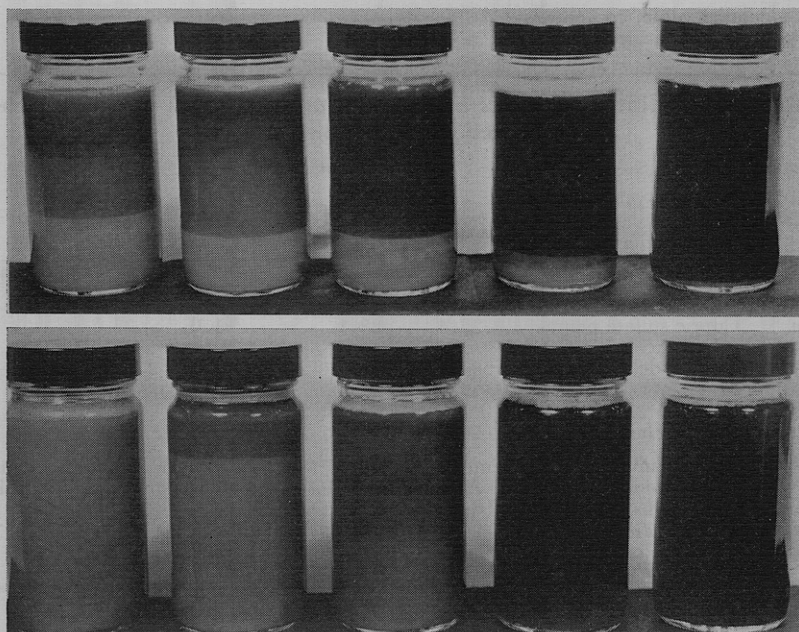
slightly less effective per unit of polyphosphate P<sub>2</sub>O<sub>5</sub>. This suggested that pyrophosphate may be more effective as

polyphosphate but different ratios of pyrophosphate to more condensed phosphates (Figure 5). The high-pyrophosphate sequestrant was typical of the 10-34-0 (10-15-0) base solution once produced by TVA. The low-pyrophosphate sequestrant was prepared by blending a base solution prepared from 83% P<sub>2</sub>O<sub>5</sub> (36% P) acid, which contains 77% of its P<sub>2</sub>O<sub>5</sub> in forms more condensed than pyrophosphate, with 8-24-0 (8-10-0) grade orthophosphate solution (Table I).

Solutions made with 20% of the P<sub>2</sub>O<sub>5</sub> from high-pyrophosphate sequestrant were as satisfactory as those made with 40% of the P<sub>2</sub>O<sub>5</sub> from low-pyrophosphate

a sequestrant than the more condensed phosphates.

Further indication of a superiority of pyrophosphate was found in tests with sequestering solutions containing the same proportion (45% of total P<sub>2</sub>O<sub>5</sub>) of



**Figure 5. Effect of phosphate species in ammoniated superphosphoric acid on sequestering efficiency in production of 8-24-0 made from wet-process acid**

Proportion of total P<sub>2</sub>O<sub>5</sub> supplied as sequestrant

Upper. Left to right, 20, 25, 30, 35, 40 (low pyro, 9% of P<sub>2</sub>O<sub>5</sub> as pyro and 36% as higher polyphosphates)

Lower. Left to right, 0, 5, 10, 15, 20 (high pyro, 39% of P<sub>2</sub>O<sub>5</sub> as pyro and 6% as higher polyphosphates)

**Table V. Comparison of Solutions of High- and Low-Pyrophosphate Content as Sequestrants for Impurities in Ammoniated Wet-Process Acid**

% of P <sub>2</sub> O <sub>5</sub> in Product <sup>a</sup> Added as		pH of Product	Condition of Product <sup>b</sup> after Indicated Storage		
Sequestrant	Polyphosphate		As made	7 days at 32° F.	30 days at 80° F.
Tests with High-Pyrophosphate Sequestrant <sup>c</sup>					
0	0	6.2	Poor	Poor	Poor
5	2.25	6.0	Poor	Poor	Poor
10	4.50	6.2	Poor	Poor	Poor
15	6.75	6.3	Quest.	Quest.	Good
20	9.00	6.2	Good	Good	Good
Tests with Low-Pyrophosphate Sequestrant <sup>d</sup>					
20	9.00	6.3	Poor	Poor	Poor
25	11.25	6.2	Poor	Poor	Poor
30	13.50	6.3	Poor	Poor	Quest.
35	15.75	6.3	Quest.	Poor	Good
40	18.00	6.3	Good	Good	Good

<sup>a</sup> Nominal 8-24-0 (8-10-0).

<sup>b</sup> Good = wet-process acid impurities completely sequestered; Quest. = questionable, small amount of unsequestered impurities; Poor = poorly sequestered.

<sup>c</sup> Prepared by ammoniation of 76% P<sub>2</sub>O<sub>5</sub> (33% P) superphosphoric acid; chemical analysis: 10.0% N, 34.5% P<sub>2</sub>O<sub>5</sub> (14% P); 39% of total P<sub>2</sub>O<sub>5</sub> in pyrophosphate form, 45% of total in polyphosphate form.

<sup>d</sup> Prepared by mixing ammoniated orthophosphoric and ammoniated superphosphoric [82.9% P<sub>2</sub>O<sub>5</sub> (36% P)] acids; chemical analysis: 8.4% N, 28.1% P<sub>2</sub>O<sub>5</sub> (12.3% P); 9% of total P<sub>2</sub>O<sub>5</sub> in pyrophosphate form, 45% of total in polyphosphate form.

**Table VI. Solubility of Micronutrients after 24 Hours at 80° F.**

Materials Added	In 11-37-0 (11-16-0)			Micronutrient element (B, Zn, Mn, Fe, Cu)	Time stable, days	In 8-24-0 (8-10-0)
	Composition, Wt. %					Wt. %
	N	P <sub>2</sub> O <sub>5</sub>	P			Micronutrient Element, (B, Zn, Mn, Fe, Cu)
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	10.2 <sup>a</sup>	34.5 <sup>a</sup>	15.1	0.9	>30	0.9
ZnO	10.7 <sup>a</sup>	36.1 <sup>a</sup>	15.8	2.1	90 <sup>b</sup>	0.05
ZnSO <sub>4</sub>	10.4 <sup>a</sup>	34.9 <sup>a</sup>	15.2	2.3	3 <sup>b</sup>	0.06
Mn <sub>3</sub> O <sub>4</sub>	10.9	36.9	16.1	0.2	>30	...
MnSO <sub>4</sub> ·H <sub>2</sub> O	10.9	36.9	16.1	<0.08	0	<0.08
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	10.5 <sup>a</sup>	35.5 <sup>a</sup>	15.5	1.0 <sup>a</sup>	>30	0.08
CuO	10.8	37.0	16.1	0.7	>30	...
CuSO <sub>4</sub> ·5H <sub>2</sub> O	10.4 <sup>a</sup>	35.2 <sup>a</sup>	15.4	1.5 <sup>a</sup>	>30	0.13

<sup>a</sup> Calculated value, no analysis.

<sup>b</sup> Precipitate identified as form of ZnNH<sub>4</sub>PO<sub>4</sub>.

**Table VII. Addition of Mixture of Micronutrients to 11-37-0 (11-16-0) Ammoniated Superphosphoric Acid<sup>a</sup>**

Description of Micronutrient		Element in source, %	Weight of Source Added, lb./Ton 11-37-0 <sup>b</sup> (11-16-0)	Micronutrient in Product, %				
Element	Source			B	Cu	Zn	Mn	Mo
B	Sodium borate <sup>c</sup>	20.5	109.2	1.0				
Cu	Cupric sulfate pentahydrate	25.4	88.1		1.0			
Zn	Zinc oxide	80.3	27.9			1.0		
Mn	Manganous-manganic oxide	69.8	6.4				0.2	
Mo	Molybdenum trioxide	66.7	6.7					0.2

<sup>a</sup> At 180° F. [plant-production temperature for 11-37-0 (11-16-0)], amounts of materials shown dissolved in 10 minutes. At 80° F., two thirds of these weights of solids dissolved overnight. Solutions remained clear during storage at 80° F. for 5 months.

<sup>b</sup> Final grade of product was 9.8-33.1-0 (9.8-14.4-0).

<sup>c</sup> Commercial mixture of sodium pentaborate and sodium tetraborate.

sequestrant (Table V). Both types of solutions were satisfactory at 32° and at 80° F. for 1 month. Solutions made with 15% of the P<sub>2</sub>O<sub>5</sub> from high-pyrophosphate sequestrant and 30 and 35% from low-pyrophosphate sequestrant cleared up in a month or less at 80° F. but not at 32° F. Paper chromatographic analysis indicated that the clearing resulted from hydrolysis of the more condensed phosphates to pyrophosphates, which confirmed the superiority of pyrophosphates for sequestration.

**Incorporation of Micronutrients.** Problems involved in adding micro-

nutrients to liquid fertilizers and some data on solubility of micronutrient sulfates in liquid fertilizers made from superphosphoric acid have been discussed (4). Additional data are shown in Table VI, including data on solubility of micronutrient oxides in 11-37-0 (11-16-0).

Except for boron, the micronutrients were sparingly soluble in 8-24-0 (8-10-0) grade orthophosphate solution; in general, they were much more soluble in 11-37-0 (11-16-0). A few tests were made of the solubility of micronutrients in 10-34-0 (10-15-0) containing about 50% of the P<sub>2</sub>O<sub>5</sub> in polyphosphate form, but the accuracy of the tests was not sufficient to indicate any difference in solubility from that in 11-37-0 (11-16-0).

As sources of zinc and manganese, zinc oxide (ZnO) and manganese oxide (Mn<sub>3</sub>O<sub>4</sub>) are more suitable for use in 11-37-0 (11-16-0) than the corresponding sulfates commonly used in commercial solid fertilizers. In addition to their higher solubility or better stability, the oxides contain higher proportions of micronutrient elements and thus lead to less dilution. Also, some cost advantage may be found in the oxides.

About 2% zinc could be dissolved as zinc oxide or zinc sulfate (ZnSO<sub>4</sub>·H<sub>2</sub>O). However, the solution made with zinc oxide was much more stable.

In only a few tests were combinations of micronutrients dissolved in 11-37-0 (11-16-0). One test (Table VII) was made with a mixture of sodium pentaborate and tetraborates, cupric sulfate, zinc oxide, manganese oxide (Mn<sub>3</sub>O<sub>4</sub>), and molybdenum trioxide containing somewhat less of the micronutrients than was soluble individually (0.67% each of B, Cu, and Zn, and 0.13% of Mn and Mo). At 80° F., the mixture dissolved in less than 24 hours. When 1.5 times these amounts were added, the mixture failed to dissolve in 24 hours at 80° F. but dissolved in 10 minutes at 180° F. The solutions remained satisfactory at 80° F. for 5 months. Further efforts are being made to devise practical methods for incorporating micronutrients in shorter lengths of time.

**Acknowledgment**

F. D. Nix made the solubility tests and A. W. Frazier the petrographic analyses.

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## PHOSPHORUS SOURCES

# Phosphorus Availability of Monocalcium and Diammonium Phosphates in Calcareous Soils

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Monocalcium phosphate monohydrate and diammonium phosphate were applied to calcareous soils and evaluated as phosphorus sources for oats by a short-term growth technique in the greenhouse. Soils were chosen on the basis of low available phosphorus and pH above 7. Several soil types which occur extensively in Minnesota were used. Monocalcium phosphate monohydrate and diammonium phosphate (-20-mesh) applied to calcareous soils by mixed placement were not found to be significantly different as phosphorus sources for oats. Phosphorus yield of oats grown on either treated or untreated soil did not show an inverse relationship to calcium carbonate equivalence. When the carbonates present as dolomite were subtracted from total carbonates, greatest phosphorus uptake by oats was from two soils with 0.2 and 4.0% calcium carbonate. There was no quantitative relationship between plant uptake of phosphorus and calcium carbonate equivalence of soils having between 9 and 24% calcium carbonate.

MONOCALCIUM phosphate (MCP) and diammonium phosphate (DAP) have been widely used as phosphorus (P) fertilizers. Ensminger (6) concluded, on the basis of 358 location-year experiments, that MCP and DAP applied with dolomitic lime were equally satisfactory as phosphorus sources for cotton. Beaton and Nielsen (7), comparing MCP and DAP on two calcareous soils, found that MCP increased yield of alfalfa more than DAP, while DAP increased per cent phosphorus more than MCP. There was no significant difference between MCP and DAP as indicated by total phosphorus yield. Bouldin and Sample (3) reported that MCP was superior to DAP as a phosphorus source for oats grown on a calcareous soil. The purpose of this study was to compare MCP and DAP further as phosphorus sources when applied to a larger number of calcareous soils.

### Procedure

Bulk soil samples were taken from the plow layer of seven calcareous Minnesota soils, air-dried, screened, and thoroughly mixed.

Reagent grade  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (MCP) and  $(\text{NH}_4)_2\text{HPO}_4$  (DAP) were used as the sources of P. They were passed through a 20-mesh sieve, washed in acetone, and placed in a calcium chloride desiccator.

Fertilizer salts were added to soils in three ways: mixed, banded, and spot-placed. When mixed placement was

used, 1000 grams of soil and a given amount of fertilizer were placed in an end-over-end divider-type mixer and allowed to mix for at least 20 minutes. The soil-fertilizer mixture was then divided into five portions of 200 grams each and placed in 12-ounce wax-lined Dixie cups. For band placement fertilizer was mixed with 0.1 gram of pure 40-mesh quartz sand. The fertilizer-sand mixture was then placed in a circular band (5.5 cm. in diameter)  $\frac{1}{2}$  inch below the surface of the soil. For spot application the fertilizer was placed in a single spot  $\frac{1}{2}$  inch below the surface of the soil.

The soils were watered to  $\frac{1}{8}$ -atm. moisture content and maintained at this level for 2 weeks. After the incubation period the surface of the soils was leveled and available P determined using the short-term method of Stanford and DeMent (14). Oats used as the test crop were grown in sand culture for 14 days. The cultures were then placed on the surface of the test soils and allowed to grow for 9 days. Then the plants were clipped at the sand surface, dried, weighed, and per cent P was determined colorimetrically using the vanadomolybdophosphoric yellow color method in a nitric acid system (7).

Chemical determinations were made on soils treated in the same way as those used in plant uptake studies. Two replicates were prepared and sealed in polyethylene bags for 2 weeks. Samples were air-dried, ground, and analyzed in duplicate for available P by the Bray No. 1 (soil to solution ratio of 1 to 50), Morgan, sodium bicarbonate, and water-

soluble methods (2, 4, 7, 12). Phosphate content of the solutions was determined colorimetrically by the molybdenum blue method of Dickman and Bray (5). Boric acid was added to the Bray No. 1 extracts to reduce fluoride interference.

Calcium carbonate equivalence and per cent dolomite were determined by the manometric technique outlined by Skinner, Halstead, and Brydon (13).

### Experimental Results

Some chemical characteristics of the soils under study were determined (Table I). These data show that the Clyde soil has a higher level of organic matter than the other soils. Bearden and McIntosh soils contain less calcium carbonate than others in this group.

**Effect of Fertilizer Placement on Phosphorus Uptake by Oats.** The objective of this study was to evaluate the short-term technique using various fertilizer placements. MCP and DAP were applied mixed, banded, or spot-placed at rates of 50 and 100 p.p.2m. P (parts per 2,000,000 P) or as 114.5 and 229 p.p.2m.  $\text{P}_2\text{O}_5$ , respectively, to Bearden, Clyde, and McIntosh soils. The results from all soils were averaged.

The results shown in Figure 1 indicate that under these conditions MCP and DAP were not different as phosphorus sources for oats.

At both rates of application mixed placement increased phosphorus uptake more than band placement, which was