

High-Analysis Liquid Fertilizer from Superphosphoric Acid

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High-analysis liquid fertilizers were obtained when superphosphoric acid, a mixture of polyphosphoric and orthophosphoric acids, was neutralized with ammonia. An 11-33-0 grade with a salting-out temperature below 32° F. was made with acid that contained 76% phosphorus pentoxide (105% phosphoric acid equivalent) whereas 8-24-0 was the highest grade with a salting-out temperature below 32° F. that could be made with the common 54% phosphorus pentoxide acid (75% phosphoric acid). More concentrated three-component (nitrogen-phosphorus pentoxide-potassium oxide) solutions also were obtained and larger amounts of some of the important trace elements could be dissolved in such solutions than in solutions made with orthophosphoric acid.

COMMERCIAL LIQUID FERTILIZERS usually are made by neutralizing phosphoric acid (about 75%) with ammonia to form a solution of ammonium orthophosphates. A neutral liquid with a nitrogen-phosphorus pentoxide weight ratio of 1 to 3 is produced in this manner. The 8-24-0 grade is the highest that will not salt out when stored at 32° F. Materials such as urea, urea-ammonium nitrate solutions, and potassium chloride may be added to produce liquid fertilizers with grades as high as 9-9-9, 7-14-7, and 6-18-6 that do not salt out at 32° F. In some cases it is preferable to neutralize the acid with ammonia-urea solutions because such solutions are a cheaper source of urea than the solid material.

Generally, the liquid fertilizer industry is handicapped in formulating from economic raw materials grades as high as those commonly available as solid fertilizers. The relatively low analysis of the phosphoric acid commonly available and of the products create problems in procurement and storage during periods of peak demand. Work by the Tennessee Valley Authority has shown that more concentrated liquid fertilizers can be made with phosphoric acids of such high concentration that they contain significant proportions of pyrophosphoric acid and higher polyphosphoric acids.

Huhti and Gartaganis (2) showed that when the phosphorus pentoxide content of phosphoric acid exceeds about 68% (94% phosphoric acid equivalent), pyrophosphoric acid appears in addition to orthophosphoric acid and that the proportion of orthophosphoric acid decreases with an increase in the phosphorus pentoxide content. At concentrations above about 74% phosphorus pentoxide, higher polyphosphoric acids appear. In the region above 72.4%

phosphorus pentoxide (superphosphoric acid) the polyphosphoric acid content increases greatly with a small increase in the pentoxide. Phosphoric acids of 68 to approximately 75% phosphorus pentoxide, including the 100% equivalent orthophosphoric acid (72.4% phosphorus pentoxide), are solids at room temperature and are inconvenient to handle. Acid which contains 76% phosphorus pentoxide (105% phosphoric acid equivalent), the production and properties of which have been described (5), is a liquid at room temperature; 49% of the pentoxide is present as orthophosphoric acid, 42% as pyrophosphoric acid, and 9% as higher polyphosphoric acids.

This paper describes the results of small-scale and pilot plant tests of the use of superphosphoric acid in the production of liquid fertilizers. Methods of operation were developed that are adaptable to existing plants and are now being used commercially.

Small-Scale Tests

Exploratory tests in beakers in an ice bath showed that superphosphoric acid of 76% phosphorus pentoxide content could be mixed with anhydrous or aqueous ammonia and water to produce neutral solutions of fertilizers of grades as high as 11-33-0 that met an arbitrary requirement of storage of 1 week at 32° F. without the formation of crystals. The pH values of the liquids were in the range of 6.2 to 6.6 and the specific gravity was 1.35 at 75° F. The salting-out temperature of a slowly cooled solution that contained 10.7% nitrogen and 32.2% phosphorus pentoxide was 0° F. and such a solution was stored for 1 week at this temperature without salting out. Good results were obtained (Table I) when, with constant agitation,

acid was placed in the beaker and then ammonia and water were added or a previously prepared neutral solution was added first to provide for effective mixing of the reactants and then the acid, ammonia, and water were added simultaneously. The tests were made in an ice bath because it was thought that hydrolysis of the polyphosphoric acids might occur at higher temperatures.

About 50% of the phosphate in the liquids was found by chemical analysis and by paper chromatography (2) to be in the orthophosphate form. The remainder of the phosphate was present as pyrophosphate and higher polyphosphates. The published information (2) indicated that acid of 76% phosphorus pentoxide content contains 49% of its pentoxide as orthophosphoric acid, thus apparently no hydrolysis of the polyphosphoric acid occurred.

Crystals formed either when aqueous ammonia was placed in the beaker first or when agitation was not adequate to prevent local overammoniation. Crystallization also occurred in the high-analysis products when water was added to the acid prior to neutralization, as often is done in the production of liquid fertilizers of lower analysis from orthophosphoric acid, because the polyphosphoric acids hydrolyzed to orthophosphoric acid. Upon dilution, the polyphosphoric acids in superphosphoric acid hydrolyzed rapidly, whereas the ammonium polyphosphates were found to be relatively stable in neutral solutions. Analysis of 11-33-0 liquid after storage at room temperature for 3 months revealed no hydrolysis.

Tests also were made with acid of 77% phosphorus pentoxide content, of which 41% is orthophosphoric acid, 46% is pyrophosphoric acid, and 13% is higher polyphosphoric acids. This acid contained crystals at room temperature;

hence it was heated to 125° F. to permit it to be metered. By procedures similar to those described above, and using less water, solutions of 12-36-0 grade were produced which did not salt out on storage at 32° F. (Table I). When the amount of water was reduced further in an attempt to produce a solution of 13-39-0 grade, crystallization of diammonium phosphate occurred either during ammoniation or very shortly thereafter. Finally, the production of the 13-39-0 grade by the use of a small amount of urea was accomplished.

Brosheer and Anderson (1) reported on the solubility relationships in the system ammonia-orthophosphoric acid-water which showed that 11-33-0 and 12-36-0 liquids in which the phosphate was present only in the ortho state salted out at 150° and 185° F., respectively. Evidently, the presence of polyphosphoric acids in the superphosphoric acid made possible the production of liquids with grades of 11-33-0 and 12-36-0 with much lower salting-out temperatures. As a result of the higher analysis and increased specific gravity of these solutions, they contained 47 and 65%, respectively, more plant nutrient per gallon than the ordinary 8-24-0 grade.

Pilot Plant Tests

The pilot plant study consisted of two phases. One involved neutralization of superphosphoric acid to produce the highest analysis fertilizer solutions of 1 to 3 nitrogen-phosphorus pentoxide weight ratio that would not salt out when stored at room temperature for one month or at 32° F. for 1 week. The other phase involved the production of liquids of various grades by the addition of potassium chloride and supplemental nitrogen as required. In some cases the supplemental materials were added during ammoniation of the acid; in other cases they were added to the base solution after ammoniation was completed.

Neutralization of Superphosphoric Acid

The pilot plant in which neutralization of superphosphoric acid was studied consisted of a stainless steel cone-bottom tank (reactor) 12 inches in diameter, 22 inches high, equipped with an agitator and with internal cooling coils arranged to serve as baffles. The reactor had an effective volume of 6 gallons. Figure 1 is a simplified flowsheet of the pilot plant. Superphosphoric acid, produced in the Tennessee Valley Authority acid plant, aqueous ammonia, and water, as required, were fed by gravity into the top of the reactor. When anhydrous ammonia was used, it was fed from a cylinder through a sparger that

Table I. Small-Scale Production of High-Analysis Liquid Fertilizers

Acid			
Chemical analysis, wt. %			
P ₂ O ₅	76.0		77.0
Equivalent H ₃ PO ₄	105.0		106.3
Form of phosphate, ^a % of total			
Orthophosphate	49		41
Pyrophosphate	42		46
Higher polyphosphate	9		13
Liquid produced on neutralization			
Expected grade	11-33-0	11-33-0	12-36-0
Method of addition of acid, ammonia, and water	Simultaneous	Acid first and then ammonia and water	Simultaneous
pH	6.6	6.2	6.6
Specific gravity at 75° F.	1.36	1.35	1.40
Chemical analysis, wt. %			
N	11.1	10.5	12.1
Total P ₂ O ₅	33.5	33.9	36.9
P ₂ O ₅ in orthophosphate form, wt. % of total P ₂ O ₅	51	51	41
Condition after storage			
1 month at ordinary temp.	Clear	Clear	Clear
1 week at 32° F.	Clear	Clear	Clear
^a From published data (2).			

discharged near the bottom of the reactor. Calibrated orifices were used to control the acid, ammonia, and water feed rates. The temperature of the liquid in the reactor during ammoniation was controlled by passing water through the cooling coils. Additional mixing was provided by circulating liquid, with a centrifugal pump, from the bottom to the top of the reactor.

Three methods of operation similar to those used in industry with orthophosphoric acid were tested. Satisfactory products were obtained by each method when either aqueous or anhydrous ammonia was used.

Batch Method

Simultaneous Addition of Acid and Ammonia. Most of the pilot plant work was carried out by a batchwise method in which the acid, ammonia, and water were added simultaneously to a heel of a previously prepared neutral solution in the reactor. The tests generally ran for 30 to 60 minutes. The rate of production ranged from 5 to 10 gallons per hour. The pH of the liquids, which was measured continuously, generally was kept in the range of 6.3 to 6.5. Base solutions of approximately 11-33-0 grade that stored satisfactorily at temperatures below 32° F. had nitrogen-phosphorus pentoxide weight ratios less than 1 to 3 and pH values less than 6.6. In 27 solutions which were stored 7 days at 32° F. without salting out, the nitrogen-phosphorus pentoxide weight ratio averaged 0.32 and the pH 6.4. Two solutions of 10.7-33.2-0 and 10.8-33.4-0 grade were stored for 7 days at 0° F. without salting out. Tank car shipments of such solutions to the Pacific Northwest encountered temperatures below 0° F.

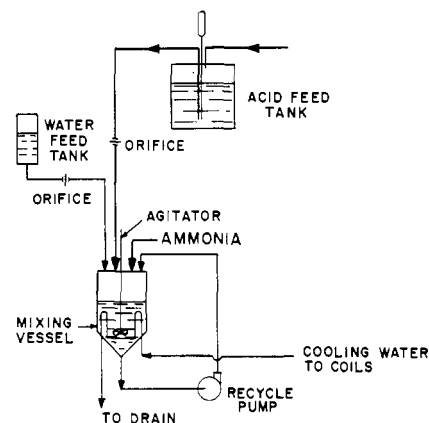


Figure 1. Flow sheet of pilot plant for production of high-analysis liquid fertilizers from superphosphoric acid

without salting out. In 13 solutions in which salting out occurred either at 32° F. or higher, the nitrogen-phosphorus pentoxide weight ratio averaged 0.34 and the pH 6.7. When the pH of the 11-33-0 solution was allowed to exceed about 6.7, loss of ammonia was appreciable and diammonium phosphate crystallized.

EFFECT OF TEMPERATURE. Five tests (Table II) were made in which acid that contained about 76% phosphorus pentoxide was neutralized to produce 11-33-0 grade liquid fertilizer at temperatures ranging from 120° F. to the boiling point (about 220° F.). The temperature was controlled by varying the amount of cooling water. Products that stored satisfactorily at 32° F. were obtained in each test. When the neutralization was carried out near the boiling temperature, considerable make-up water was required to replace that lost by vaporization. Material balances indicated that over 99% of the input ammonia was recovered in the form of

liquid fertilizer. No odor of ammonia was detected above the mixing vessel during the tests.

EFFECT OF ACID CONCENTRATION. Acids of 75.6, 77, and 78.2% phosphorus pentoxide contents were used in a study of the effect of acid concentration on the grade of liquid fertilizer produced (Table III). A small variation of the phosphorus pentoxide content of the acid in this range had a great effect on the percentage of pentoxide present as polyphosphoric acids. Neutralization of acid which contained 75.6% phosphorus pentoxide, of which 48% was in the form of polyphosphoric acids, yielded 11-33-0 grade liquid satisfactorily. However, when the proportion of water was decreased in an attempt to produce a liquid of 12-36-0 grade, diammonium phosphate crystallized either during the run or shortly thereafter. Neutralization of acid which contained

77% phosphorus pentoxide of which 59% was in the form of polyphosphoric acids, resulted in a product of about 12-36-0 grade that stored satisfactorily.

When acid of 78% phosphorus pentoxide content was used in an attempt to produce a liquid of 13-39-0 grade, diammonium phosphate crystallized out. However, when this acid was ammoniated to a slightly lower pH (6.2 *vs.* 6.4), a liquid of 12-40-0 grade was produced. After storage for 3 months at room temperature, the samples of this liquid salted out. Analyses of the samples at this time revealed that 15% of the polyphosphates had hydrolyzed to orthophosphates.

Liquid of 12-40-0 grade was mixed with a small amount of urea to produce the desired 13-39-0 grade (pH of 6.3) which stored satisfactorily at room temperature for one month and at 32° F. for 1 week.

Successive Addition of Acid and Ammonia. The production of 11-33-0 liquid was studied at 180° F. by the addition to the reactor, in successive steps, of acid of 76% phosphorus pentoxide content, aqueous ammonia, and water or by the addition of such acid followed by the simultaneous use of anhydrous ammonia and water. In each case considerable thickening of the material in the reactor occurred at pH 2. At this stage it was difficult to agitate and recycle the liquid, and heat transfer to the cooling water was so poor that the temperature could not be controlled without decreasing the flow of ammonia. However, as the neutralization progressed, the liquid became more fluid. When the final pH of 6.3 to 6.5 was reached, the liquid was fluid and easy to pump. The amount of orthophosphate present in the liquids produced by this method was higher (about 75% of the total phosphate) than in the liquids produced by either the batch simultaneous addition method or the continuous method (about 50 to 60%). The increased hydrolysis probably occurred at the elevated temperature in the early stages of the reaction when the acidity was high.

While the increase in viscosity in the first stages of neutralization probably would not make the production of high-analysis liquids by this procedure impracticable on a large scale, the operation might be more difficult than that in which the raw materials were added simultaneously.

Continuous Method

A few tests were made in which acid, ammonia, and water were added simultaneously to the mixing vessel in suitable proportions to produce liquid of 11-33-0 grade. The neutralization temperature was maintained at about 180° F. This method differed from the batch method, in which the raw materials were added simultaneously, in that the product overflowed continuously from the reactor and that there was a need for accurate control of flow rates at all times. In the batch process it was possible to adjust the composition of the product at the end of each batch. Only a few plants operate a continuous process in which the raw materials are fed simultaneously and the product flows continuously from the reactor, because of the greater care required in operation and because of the higher investment cost involved in the equipment for such an operation.

Use of Ammonia-Urea Solutions for Neutralization

Superphosphoric acid was ammoniated with ammonia-urea solution that contained 30.6% ammonia, 43.1% urea,

Table II. Pilot Plant Production of 11-33-0 Liquid Fertilizer

	Neutralizing Temp., °F.				
	120	150	180	210	220
Acid					
Chemical analysis, wt. %					
P ₂ O ₅	75.6	75.6	75.6	76.5	76.5
Equivalent H ₃ PO ₄	104.3	104.3	104.3	105.7	105.7
Orthophosphate, ^a % of total P ₂ O ₅	52	52	52	45	45
Feed rate, lb./hr.	40.0	37.3	37.6	31.2	31.2
Ammonia ^b feed rate, lb./hr.	50.2	45.6	45.3	42.0	42.0
Water feed rate, lb./hr.	0	2.4	3.2	6.5	6.5
Test length, hr.	1.0	1.2	1.3	0.7	0.5
Liquid produced on neutralization					
pH	6.3	6.4	6.3	6.5	6.4
Specific gravity at 75° F.	1.36	1.36	1.36	1.35	1.36
Chemical analysis, wt. %					
N	11.1	11.0	10.9	11.0	10.9
P ₂ O ₅	32.8	33.9	34.7	33.0	33.7
Orthophosphate, ^c % of total P ₂ O ₅	60	61.9	62	53	54

^a From published data (2).

^b Aqueous ammonia containing 19 to 21% nitrogen.

^c By chemical analysis.

Table III. Pilot Plant Production of High-Analysis Liquid Fertilizers—Effect of P₂O₅ Content of Superphosphoric Acid

Acid			
Chemical analysis, wt. %			
P ₂ O ₅	75.6	77.0	78.2
Equivalent H ₃ PO ₄	104.3	106.3	107.9
Form of phosphate, ^a % of total			
Orthophosphate	52	41	26
Pyrophosphate	40	46	49
Higher polyphosphate	8	13	25
Feed rate, lb./hr.	31.6	31.7	23.8
Ammonia			
Form	Gaseous	Gaseous	Gaseous
Feed rate, lb./hr.	9.7	9.7	6.9
Water feed rate, lb./hr.	29.4	25.2	15.6
Test length, hr.	2.2	0.9	0.8
Liquid produced on neutralization ^b			
pH	6.5	6.4	6.2
Specific gravity at 75° F.	1.36	1.40	1.43
Chemical analysis, wt. %			
N	10.9	11.8	12.4
Total P ₂ O ₅	33.9	37.7	40.3
Form of phosphate, % of total			
Orthophosphate	54	41	35
Pyrophosphate	39	48	42
Higher polyphosphate	7	11	23

^a From published data (2).

^b Produced by batch-simultaneous addition method.

and 26.3% water to produce 12-20-0 grade liquid with a pH of 6.9 and 13-23-0 grade liquid with a pH of 6.6. These liquids had about 40% of the phosphorus pentoxide as polyphosphates and were stored for a week at 32° F. without salting out. Solutions produced in this manner use a cheaper form of nitrogen than solid urea and provide the base solution from which to produce the other grades.

Heat Removal

The heat removed in the production of several grades of liquid fertilizers was measured in the pilot plant to provide an indication of the cooling that would be needed when superphosphoric acid is used to produce high-analysis liquids as compared with that needed in the production of 8-24-0 grade liquid from ordinary phosphoric acid. Some of the measurements were made at a low temperature (100° F.) and adjusted on the basis of thermochemical data (3) to 180° F., a typical operating temperature. The values for liquid anhydrous ammonia were calculated from the thermochemical data and from measurements in the pilot plant when aqueous and gaseous ammonia were used.

ucts with superphosphoric acid. Good results were obtained up to 220° F.

About three fourths as much heat must be removed when superphosphoric acid is neutralized with the ammonia-urea solution described above to produce the 12-20-0 liquid as when aqueous ammonia (20% N) is used to produce the 11-33-0 liquid.

Three-Component Liquid Fertilizers

When potassium chloride or supplemental nitrogen was added to the 11-33-0 base solution, the resulting liquids were, in general, of higher grade for a given salting-out temperature than liquid prepared by adding the same material to an 8-24-0 liquid produced from ordinary phosphoric acid. Table IV shows some of the grades from the two sources that did not salt out upon storage at 32° F. except as indicated. The products made from superphosphoric acid contained 11 to 25% more plant nutrient than products of comparable ratios made from orthophosphoric acid. Lower grades generally were obtained when ammonium nitrate or urea-ammonium nitrate solution was used instead of urea.

Table V shows the salting-out temper-

With superphosphoric acid it is possible to economize on the supplemental nitrogen requirements for some grades. For example, 10-10-10 produced from orthophosphoric acid with supplemental nitrogen supplied as solid urea normally salts out at about 60° F. This grade with essentially the same salting-out temperature was made with superphosphoric acid and urea-ammonium nitrate solution, which is a cheaper form of supplemental nitrogen. If the price of nitrogen in urea-ammonium nitrate solution is assumed to be \$1.60 per unit and in solid urea is \$2.30 per unit, the savings with this grade would be about \$15 per ton of plant nutrient when the nitrogen solution is used. However, where ammonia-urea solution is available, the cost of the supplemental nitrogen (urea) would be about the same as that for urea-ammonium nitrate solution but the products would have lower salting-out temperatures.

Table VI shows the materials required for production of the 11-33-0 base solution and other grades of liquid fertilizers from superphosphoric acid.

Addition of Trace Elements

Borax and sulfates of iron, zinc, manganese, and copper were added individually, at room temperature, to high-analysis liquid fertilizers of 11-33-0, 10-10-10, 9-18-9, and 7-21-7 grades prepared from superphosphoric acid. With the exception of manganese sulfate, which had a low solubility, the solubilities of the other materials were sufficient to supply from 50% to several hundred per cent of the amounts of trace elements normally applied to correct deficiencies of these elements in the soil. Except for borax, these compounds were insoluble in liquids of the grades commonly produced in the following ratios from orthophosphoric acid (8-24-0, 9-9-9, 8-16-8, and 6-18-6). As a result of

Grade	Ammonia	Phosphoric Acid Concn., % P ₂ O ₅	Heat Removed at 180° F., B.t.u./Lb.		
			P ₂ O ₅	Solution	Plant Nutrient
8-24-0	Aqueous (20% N)	54	290	70	219
8-24-0	Aqueous (20% N)	76	320	77	240
11-33-0	Aqueous (20% N)	76	400	132	300
11-33-0	Liquid anhydrous	76	480	158	358
11-33-0	Gaseous anhydrous	76	716	236	536
12-36-0	Aqueous (23% N)	77	453	163	340
12-40-0	Liquid anhydrous	78	506	203	390
12-20-0	Ammonia-urea solution ^a	76	300	60	188

^a Solution contained 30.6% ammonia, 43.1% urea, and 26.3% water.

The heat removed in the production of ordinary 8-24-0 grade liquid from orthophosphoric acid of 54% phosphorus pentoxide content was about the same as when that grade was made from superphosphoric acid of 76% phosphorus pentoxide content. It increased with an increase in the grade of the solution, was greater when liquid anhydrous ammonia was used than when aqueous ammonia was used, and was still greater when gaseous ammonia was used. The production of 11-33-0 grade liquid from aqueous ammonia required the removal of about a third more heat per pound of plant nutrient than was required for the 8-24-0 grade.

In the production of some grades in the pilot plant, cooling was obtained by the addition of supplemental nitrogen and of potassium chloride to the reactor during ammoniation as is sometimes done commercially. Other common practices are to employ external heat exchangers or to spray water on the sides of the reactor. Any of these methods should yield satisfactory prod-

uctures for several grades produced from superphosphoric acid, and saturation temperatures for these products and for

Table IV. Some Liquid Fertilizers Did Not Salt Out on Storage

Ratio	Additional Nitrogen Supplied as	Base Solution	
		8-24-0 ^a	11-33-0
1:1:1	Urea-ammonium nitrate Solution ^b	7-7-7	8-8-8
1:2:1		7-14-7	8-16-8
1:1:1	Ammonium nitrate	5-5-5	6-6-6
1:2:1		5-10-5	7-14-7
1:1:1	Urea	9-9-9	10-10-10 ^c
1:2:1		7-14-7	8-16-8
1:3:1	None	6-18-6	7-21-7
1:3:2		4-12-8	5-15-10 ^d

^a Based on data of Slack *et al.* (4). ^b Solution contained 38.8% ammonium nitrate, 31.0% urea, and 30.2% water. ^c Crystals appeared at 41° F. and dissolved at 47° F. ^d Crystals appeared at 36° F. and dissolved at 40° F.

ucts of the same grades made from orthophosphoric acid. The liquids produced from superphosphoric acid had saturation temperatures from 13° to 55° F. lower than liquids of the same grades made from orthophosphoric acid.

the much greater solubility of the trace elements in the liquid fertilizers which contain polyphosphates, it would be possible to incorporate significant amounts of such elements in liquid fertilizers, as is often done with solid fertilizers.

Table V. Salting-Out and Saturation Temperatures for Some Liquid Fertilizers

Grade	Additional Nitrogen Supplied as	Liquid Produced from Superphosphoric Acid		Liquid Produced from Orthophosphoric Acid, Saturation ^c Temp., °F.
		Solting-out ^a temp., °F.	Saturation ^b temp., °F.	
10-10-10	Urea	41	47	61
9-9-9	Urea	8	12	25
8-16-8	Urea	14	20	43
8-16-8	Urea-ammonium nitrate solution ^d	14	21	39
7-21-7	None	12	19	74
5-15-10	None	36	40	67

^a Determined by cooling 4° F. per hour in critical range until crystals appeared. ^b Determined, after crystals had formed, by warming solution at 4° F. per hour until crystals dissolved. ^c Based on data of Slack *et al.* (4). ^d Solution contained 38.8% ammonium nitrate, 31.0% urea, and 30.2% water.

Table VI. Materials Used for Production of Liquid Fertilizers from Superphosphoric Acid

Raw Materials	Grade					
	11-33-0	10-10-10	8-8-8	8-16-8	7-21-7	5-15-10
Superphosphoric acid (76% P ₂ O ₅)	868	263	210	421	553	395
Aqueous ammonia (20% N)	1110	337	270	540	707	505
Urea (46% N)	...	290	...	116
Urea-ammonium nitrate solution (28% N)	380
Potassium chloride (60% K ₂ O)	...	333	266	266	233	333
Water	22	777	874	657	507	767
Total	2000	2000	2000	2000	2000	2000

Typical results of the solubility of trace elements in liquid fertilizers of 9-9-9 grade, which was one of those studied, were as follows:

Trace Element ^a	Trace Element, Wt. %, Added to Liquid Produced from	
	Superphosphoric acid base soln.	Orthophosphoric acid base soln.
Iron (Fe ⁺⁺)	0.56	0.01
Copper (Cu ⁺⁺)	0.53	0.04
Zinc	0.64	0.03
Manganese (Mn ⁺⁺)	0.07	0.03
Boron	0.94	1.74

^a Boron added as solid Na₂B₄O₇ · 10H₂O. Other elements added as approximately saturated solutions of sulfates.

The presence of sulfur compounds is desirable also in the fertilizer to be used in regions where soils are deficient in sulfur. In exploratory tests, liquid fertilizers of 1:1:1 ratio prepared from superphosphoric acid were mixed with sulfur compounds in proportions to supply 8 parts of sulfur per 100 parts of phosphorus pentoxide. When sulfur was supplied as ammonium sulfite, the maximum grade in this ratio which stored satisfactorily at 32° F. was 9-9-9 and with ammonium sulfate it was 7-7-7.

Discussion

Superphosphoric acid can be used to produce high-analysis liquid fertilizers in the same equipment and by procedures similar to those currently used in the

production of liquid fertilizers from electric furnace phosphoric acid of ordinary concentration. Table VII summarizes the procedures currently used in industry and indicates the minor modifications needed to permit the use of superphosphoric acid. Superphosphoric acid should not be added directly to water, because hydrolysis of the polyphosphoric acids will occur before the acid can be neutralized. Neither should the acid be added to ammonia, because crystals will form. When superphosphoric acid and aqueous ammonia are added simultaneously in the batch

process, some solution from a previous run should be retained in the reactor, because the amount of water ordinarily required in the formulation is too small to permit initial effective mixing and cooling.

Plants producing liquids from ordinary phosphoric acid by the batch-successive addition method need to avoid the direct addition of superphosphoric acid to water and provide good mixing of the reactants, particularly during the stage when thickening occurs. In these plants the acid may be added first to the reactor, followed by the ammonia and water. No change in procedure is required when liquid fertilizers are made by a continuous process in which the product overflows from the reactor.

A reactor for use with superphosphoric acid may be constructed of the same materials commonly used for ordinary phosphoric acid. In some cases the reactor is made of mild steel and is equipped with a relatively small stainless steel tube which discharges into the reactor and in which the acid and ammonia are mixed. In this case the solution must be kept neutral at all times. If acid is to be charged to the reactor before ammonia is introduced, and possibly if supplemental materials are to be added to the hot solution in the reactor, the vessel should be built of stainless steel. The base solutions and the mixed liquid fertilizers made with superphosphoric acid, however, are essentially neutral and may be stored in mild steel tanks. Superphosphoric acid may be stored in stainless steel tanks or mild steel tanks lined with some of the commonly used rubber or plastic lining materials used with orthophosphoric acid (5).

Superphosphoric acid of 76% phosphorus pentoxide content, although liquid at room temperature, is more

Table VII. Procedures for Producing Fertilizers^a

From 75% H ₃ PO ₄		From Superphosphoric Acid	
Batch-Simultaneous Addition Method		Batch-Successive Addition Method	
1. Add required amount of water.	2. Add acid and ammonia simultaneously at rates to maintain the desired pH.	1. Add required amount of water and, if necessary, sufficient neutral solution to permit agitation.	2. Add acid and ammonia simultaneously at rates to maintain the desired pH.
3. Add supplemental materials as required.			
Continuous Method			
1. Add acid, ammonia, and water continuously in such proportions as to maintain desired pH and concentration in mixture at all times.	2. Withdraw solution continuously.	1. Add required amount of acid.	2. Add required amount of ammonia and water.
3. Add supplemental materials as required either continuously to solution in reactor or batchwise to solution in storage.		3. Add supplemental materials as required.	

^a Frequently it is necessary to control the temperature in the reactor to prevent violent boiling and loss of ammonia. The temperature may be controlled in a number of ways as discussed in the text.

viscous than ordinary phosphoric acid and may develop crystals on long storage in cold weather. It may be desirable, if practicable, to ammoniate the acid as it is received rather than to store it for long periods. When storage is required, care should be exercised to exclude water and moist air. Burying the storage tank or heating its contents may be desirable in cold climates.

The efficiency of centrifugal pumps with superphosphoric acid of 76% phosphorus pentoxide content at ordinary temperatures is low, and positive displacement pumps such as gear, lobe, or screw pumps would be more suitable. Weight tanks, tanks equipped with sight gages, positive displacement meters, magnetic flow meters, etc., may be used to measure the acid. However, with rotameters or orifice meters, which are sensitive to viscosity changes, the acid should be heated and kept at a constant temperature. Any general-purpose pump designed for pumping ordinary liquid fertilizers should be suitable for pumping the high-analysis liquids.

The production of high-analysis liquids

from superphosphoric acid offers advantages to the liquid fertilizer industry. Improved formulations, decreased storage and handling costs, and better distribution procedures for the products are possible with this material. The 11-33-0 grade contains 47% more plant nutrient per gallon than the 8-24-0 grade. The 11-33-0 liquid may be produced as the base solution in centrally located plants and distributed to mixing plants where potassium chloride and supplemental nitrogen may be added, thereby providing for more widespread distribution.

Greenhouse and field tests indicate that the crop response from liquids produced from superphosphoric acid has been equal to that obtained with standard fertilizer materials.

Superphosphoric acid is being used in the production of high-analysis liquids by several companies. The Tennessee Valley Authority has operated a small plant to produce high-analysis liquid fertilizers for demonstration purposes.

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FERTILIZER MATERIALS ANALYSIS

Colorimetric Determination of Aluminum in Acid Solutions of Phosphate Rock

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A procedure is presented to eliminate the interference of iron in the colorimetric determination of aluminum in acid solutions of phosphate rock. It involves extraction of the iron-cupferron complex with chloroform, leaving the aluminum in solution to be determined colorimetrically using Alizarin Red S as the color complex. Aluminum was determined in synthetic samples containing iron oxide-alumina ratios up to more than 7 to 1.

THE GRAVIMETRIC (Glaser) method (1, 5) commonly used for the determination of aluminum in phosphate rock is time-consuming and subject to serious error. Wide variations in the results obtained by this method by different analysts on identical samples of phosphate rock are cited by Barton (3), who states, "The alumina results reported on monthly check samples seldom vary by less than 40% between the maximum and minimum values and occasionally vary by as much as 200%." The chief source of error is the coprecipitation and retention of phosphate in excess of the iron and aluminum phosphates. The hydrolysis of these salts when washed

with water or a solution of an electrolyte like ammonium nitrate makes it difficult, if not impossible, to judge by a test for phosphate when the excess phosphate has been removed (5, p. 505).

In view of these disadvantages a reliable colorimetric method was sought, based on the sodium alizarin sulfonate (Alizarin Red S) procedure proposed by Atack (2). According to Yoe and Hill (10), calcium and phosphate do not interfere in this procedure, but iron and fluorine do. Iron is the more troublesome of the two, because fluorine is easily eliminated by evaporation of the test solution to fumes with sulfuric acid (3). Barton (3) found that aluminum

can be best determined at a wave length of 370 m μ in the presence of iron, if the test sample does not contain more than 0.05 mg. of iron oxide with a like amount of alumina.

The procedure here described is based on colorimetric determination of aluminum in an acid solution of phosphate rock after the iron has been separated by solvent extraction of the cupferron-iron complex with chloroform (7-9). Vanadium is extracted along with the iron (7). Tests with synthetic mixtures showed that chromium at the concentrations occurring in most western rocks does not interfere with the aluminum determination. Alumina in synthetic