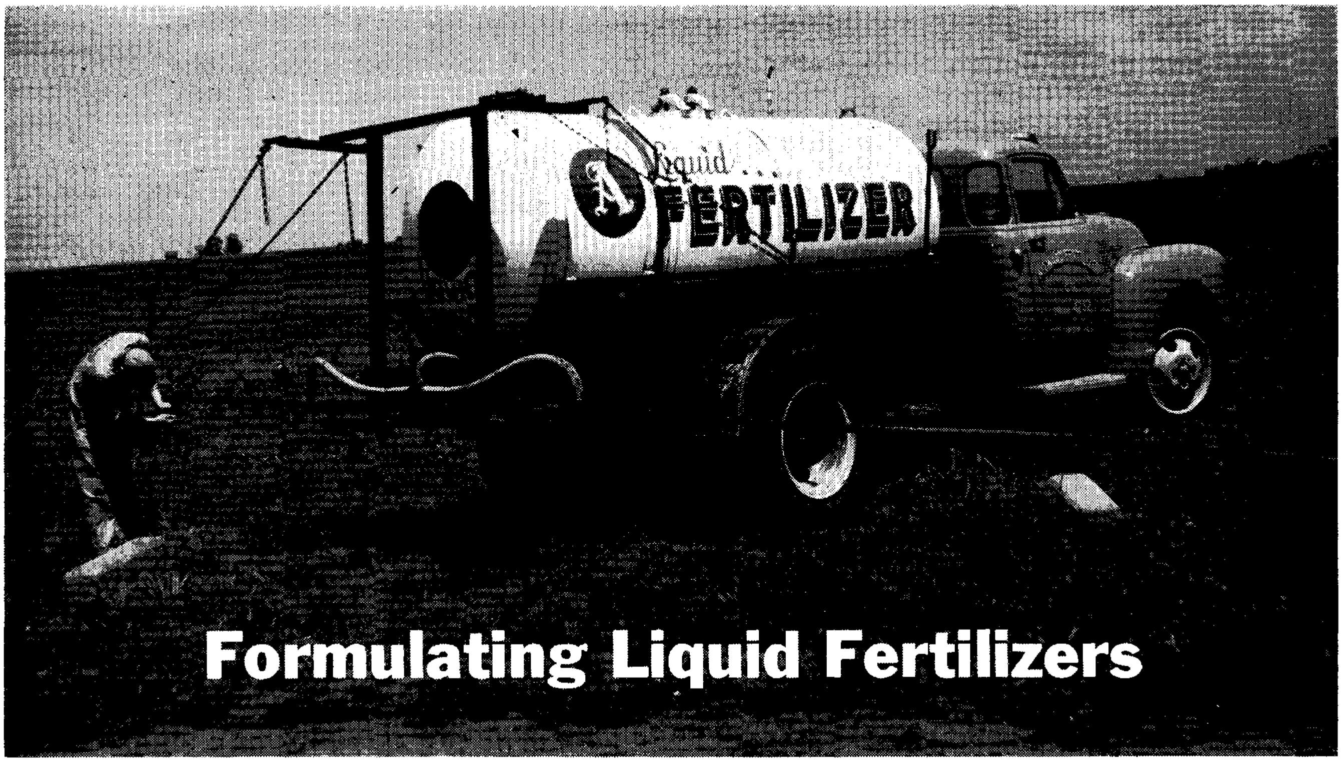

Formulating Liquid Fertilizers

Liquid fertilizer pilot plant furnishes information on solubility of raw materials and equipment and operating costs for formulators. Liquid mixes of all three plant foods offer farmer as high a nutrient content as dry fertilizers

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THE RAPID GROWTH of liquid fertilizers has resulted largely from the success achieved in the development of suitable formulations. In order to realize the advantages associated with the application of fertilizers in the liquid form, it is necessary to produce a product which can be easily handled. The corrosion problems originally associated with the liquid fertilizers produced in California, (by dissolving urea, ammonium nitrate and potassium chloride in phosphoric acid) have been essentially eliminated by the formulation of neutral solutions. By the proper selection of raw materials, formulations can be produced which approach and, in many cases, equal the total nutrient content and the ratios of nutrients found in dry fertilizers.

The total nutrient concentration that can be achieved for a liquid fertilizer is not entirely dependent on the solubility of the raw materials, since reactions may occur between these raw materials in solution to produce salts of lower solubility. Because mutual solubility of all of the nutrient sources cannot be predicted, solubility characteristics of the individual formulations must be tested in the laboratory.

Work presented in this paper outlines the methods of formulation which will provide maximum nutrient content for various base ratio solutions and illustrates the advantages which can be achieved through proper selection of raw materials.

Pilot-plant studies were conducted to demonstrate the feasibility of direct introduction of liquid anhydrous ammonia into phosphoric acid as one of several methods for producing neutral solutions.

Solubility, Availability, and Cost Limit Choice of Raw Materials

Although a great variety of raw materials may be used in the formulation of liquid fertilizers, consideration of such factors as solubility in water, availability, cost, and nutrient concentration suggest the preference of specific raw materials. These raw materials and their minimum guaranteed analysis are given in Table I.

Potassium chloride and urea can be obtained in grades containing insoluble materials (example, potassium chloride, 60% potash) but these are generally not used in the liquid fertilizer manufacture since additional processing is required to remove the insoluble materials. Ammonium nitrate solution is used in preference to solid ammonium nitrate since the latter usually contains water-insoluble conditioners.

Monoammonium and diammonium phosphate can be used to supply the P_2O_5 content of any formulation in place of phosphoric acid and are therefore listed as P_2O_5 source materials. Potassium sulfate and potassium nitrate are not common K_2O source materials, but find special uses in areas, such as tobacco lands, where high chloride content cannot be tolerated.

There are several nutrient source materials which are not used in liquid fertilizer manufacture primarily because of their solubility and high cost per unit of nutrient content. These materials and the reasons which preclude their use are given in Table II.

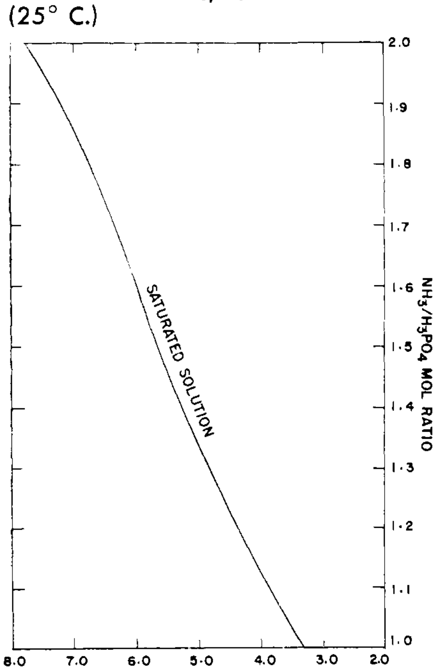
In the formulation of liquid fertilizers the most important properties to consider are solubility and corrosiveness. The various nutrients must be completely soluble not only at room temperature but also at temperatures close to freezing. How low a temperature a liquid fertilizer should withstand without starting to crystallize depends on location and time of year. A temperature of 32° F. has been selected as the reasonable temperature at which no crystals should precipitate from solution. All formulations mentioned in this article, unless otherwise stated, will have crystallization temperatures below this value.

Preventing Corrosion

The pH value of liquid fertilizers should lie in the range of 6.5 to 7.0. In order to reduce the corrosion on mild steel storage and application equipment, the solutions should not be too acidic. A pH of above 6.5 is therefore desirable. It is also desirable not to have an odor of ammonia over these solutions and to maintain high solubility of the ammonium phosphates. As the pH value of these solutions is increased, an ammonia odor develops over them and the solubility of the phosphates decreases. Thus, the maximum desirable pH is about 7.0.

The pH value of a balanced liquid fertilizer is established by adjusting the ratio of ammonia to phosphoric acid in the formulation. Other nutrient materials, which are added to furnish additional nutrient value, have little or no effect on final pH. Figure 1 shows the effect on pH of varying the mole ratio of ammonia to phosphoric acid. This plot is drawn for saturated solutions of ammonium phosphates at 25° C. Since liquid fertilizer solutions are not saturated with ammonium phosphates at 25° C., but at some temperature below 0° C. (32° F.), the observed pH values will be slightly higher than is read from Figure 1. In practice, four pounds of anhydrous ammonia, or its equivalent

Figure 1. pH values of saturated solutions of ammonium phosphate as a function of NH_3/H_3PO_4 mol ratio (25° C.)



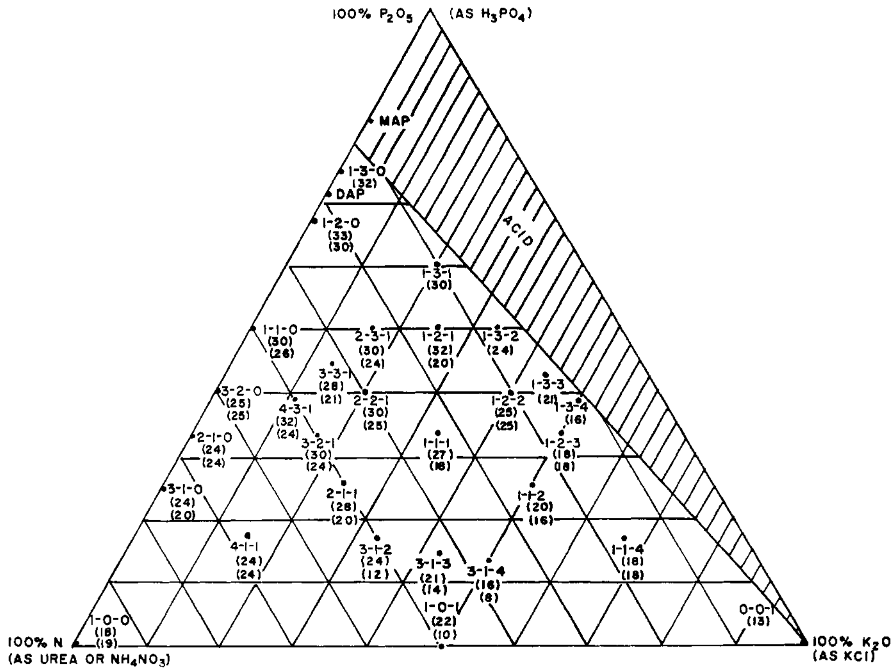


Figure 2. Effect of various nutrient sources on maximum nutrient content that can be obtained for solutions of different base ratios. Numbers in parentheses represent the maximum total nutrient contents for neutral solutions with crystallization temperatures below 32° F; first number represents total maximum nutrient content for solutions containing urea as supplementary nitrogen and second number that for solutions containing ammonium nitrate

Table I. Raw Materials for Liquid Fertilizer Manufacture

Raw Materials	*Minimum Guaranteed Analysis* ($N-P_2O_5-K_2O$)
NITROGEN SOURCE MATERIALS:	
Anhydrous ammonia	82–0–0
Aqueous ammonia	24–0–0[a]
Ammonia-ammonium nitrate solutions	41.0–0–0[a]
Ammonia-urea solutions	33.5–0–0[a]
Urea	46–0–0
Ammonium nitrate	35–0–0
Ammonium nitrate solution	21–0–0
Urea-ammonium nitrate solution	32–0–0
P_2O_5 SOURCE MATERIALS:	
Phosphoric Acid (75%)	0.54.3–0
Monoammonium phosphate	12.1–61.6–0
Diammonium phosphate	21–53.8–0
K_2O SOURCE MATERIALS:	
Potassium chloride	0–0–62.5
Potassium sulfate	0–0–54
Potassium nitrate	13.7–0–46.0

[a] One example of a group having various concentrations.

Table II. Raw Materials not Acceptable for Liquid Fertilizer Manufacture

Raw Materials	*Solubility*		*High Cost Per Unit of Nutrient*	*Low Analysis*	*High Sodium Content*
	Incomplete in liquid fertilizer formulations	*Low*			
Superphosphate	X				
Wet process phosphoric acid	X				
Calcium phosphates	X				
Sodium phosphates			X		X
Potassium phosphates			X		
Ammonium sulfate		X		X	
Potassium sulfate		X	X		
Calcium nitrate	X				
Potassium nitrate			X		
Sodium nitrate			X	X	X

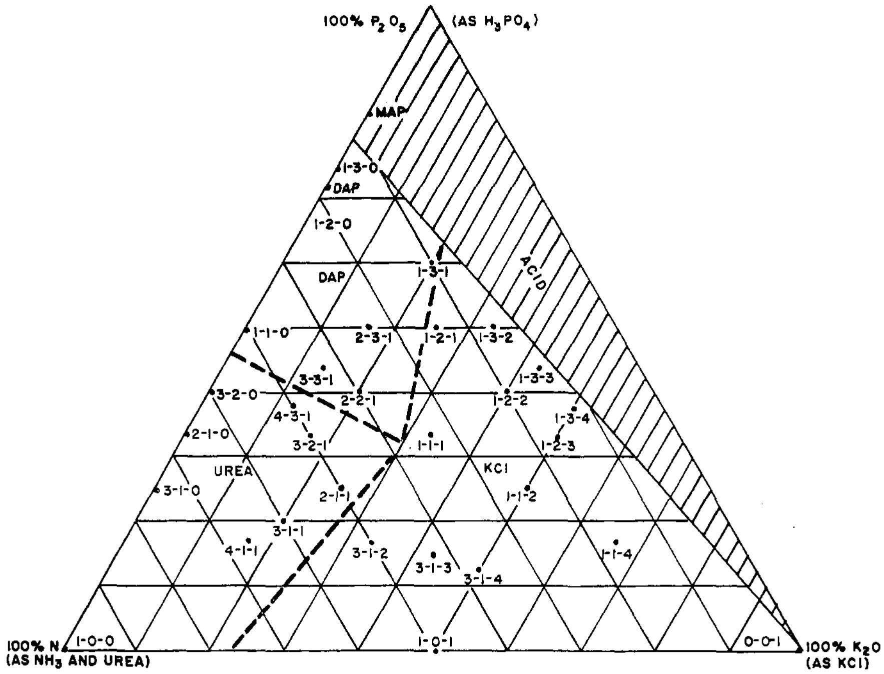


Figure 3. Solid phases responsible for limiting total nutrient contents of corumaltions containing urea as supplementary nitrogen

from aqueous ammonia, is generally used for every 10 pounds of P_2O_5 derived from phosphoric acid to give a N to P_2O_5 fertilizer base ratio of $^1/_3$ with the ammonia to phosphoric acid mole ratio of 1.7. For example, an 8–24–0 solution has a pH of about 6.7. Because of the pH limitations set on these formulations, all solutions with common N to P_2O_5 base ratios lower than $^1/_3$ are too acidic to be considered unless some of the phosphoric acid is neutralized with caustic potash. Since the present cost of caustic potash limits its use as a fertilizer raw material, solutions with N to P_2O_5 base ratios lower than $^1/_3$ will not be considered in this paper. Solutions which have N to P_2O_5 ratios greater than $^1/_3$ are made by adding neutral forms of nitrogen to the ammonium phosphate solution. This type of nitrogen, termed "supplementary nitrogen," can be supplied by urea or ammonium nitrate as solids or in solution, separately or as mixtures. This term distinguishes the ammonia combined with nitrate in neutral ammonium nitrate from free ammonium used for neutralizing phosphoric acid. This distinction is important because supplementary nitrogen may be added independently of the amount of phosphate present while free ammonia must be added *in a fixed ratio to the phosphoric acid.*

Amount of Nitrogen Solution Determined by Free NH_3

Ammonia-ammonium nitrate and ammonia-urea solutions can be used to neutralize the phosphoric acid in place of ammonia. The amount of these solutions to be used is fixed by their free ammonia content, since four pounds of free ammonia must be added for every 10 pounds of P_2O_5 added as phosphoric acid to ensure a neutral solution. Since these ammoniating solutions carry supplementary nitrogen in addition to free ammonia, the minimum N to P_2O_5 ratio that can be formulated will be limited. Table III lists percentages of the total nitrogen in these solutions which must be present as free ammonia in order to formulate the indicated base ratio solutions. The N to P_2O_5 ratio can always be made greater than that which can be obtained with the ammoniating solutions by adding supplementary nitrogen containing no free ammonia.

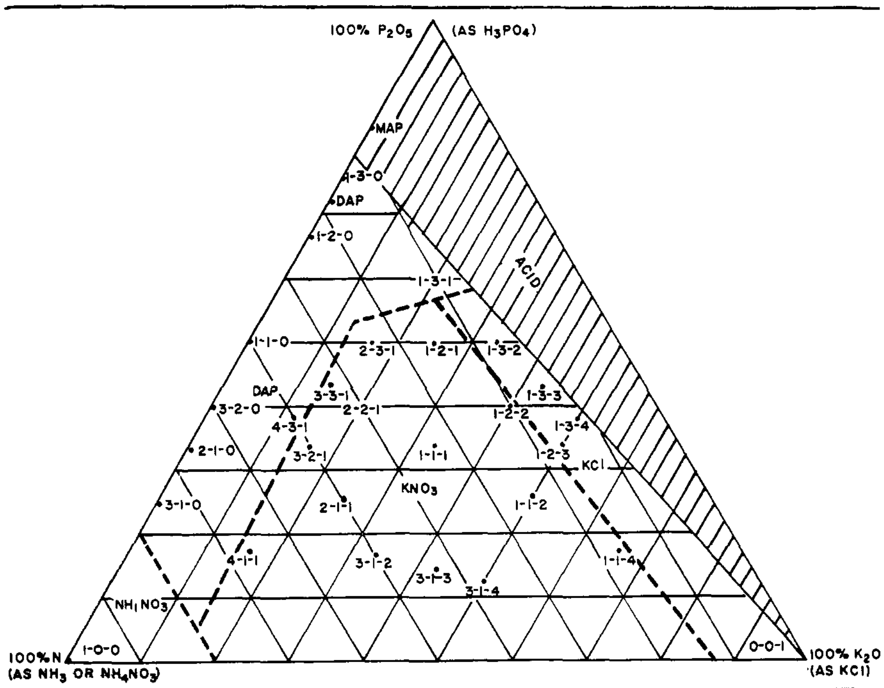
Table III. Percentage of Total Nitrogen Required as Free Ammonia in Ammoniating Solutions to Formulate Different Base Ratio Solutions

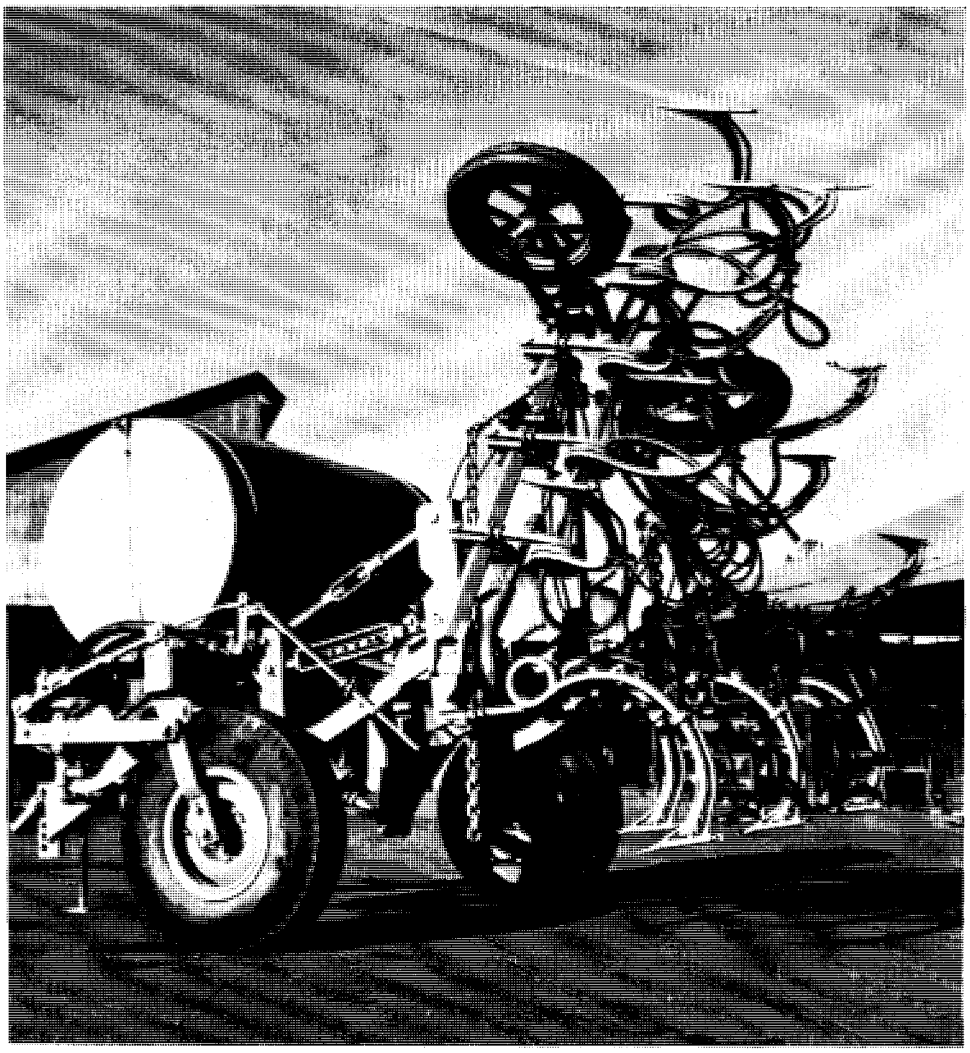
$N\text{-}P_2O_5$ Base Ratio	% of Total Nitrogen as Free Ammonia Nitrogen
1–3	100
1–2	66.7
2–3	50.0
1–1	33.3
2–1	16.7
3–1	11.1

The P_2O_5 content of liquid fertilizers may be supplied by dissolving ammonium phosphate salts rather than from phosphoric acid. While this is a simple method of production, the ammonium phosphate salts are more expensive per unit of plant food than ammonia and phosphoric acid. If ammonium phosphate salts are used for their P_2O_5 value, pH of the solution is controlled by the ratio of monoammonium phosphate to diammonium phosphate in the formulation. To obtain the same N to P_2O_5 ratio (as when phosphoric acid, equivalent to 10 pounds of P_2O_5, is neutralized with four pounds of ammonia) 27.5% of the total P_2O_5 must be derived from monoammonium phosphate and 72.5% from diammonium phosphate.

Potassium chloride is almost always used as the potassium source. Potas-

Figure 4. Solid phases responsible for limiting total nutrient contents of formulations containing ammonium nitrate as supplementary nitrogen





Heavy duty applicator rig for liquid fertilizer has outriggers which can be folded like the wings on a carrier-based airplane. Liquid is pump fed. Shown here, ready for towing down highway, the unit is manufactured by Towner Mfg. Co.

sium sulfate may be substituted for the potassium chloride in special formulations, but it generally lowers the obtainable total nutrient content. Potassium nitrate is sometimes used but generally does not prove economical because of the high cost per unit of total nutrient value.

The effect of various nutrient sources on the maximum nutrient content that can be obtained for solutions of different base ratios can be seen in Figure 2. Figures 3 and 4 show the solid phase responsible for limiting the total nutrient analysis of these solutions. The base ratios for several solutions have been located on these trilinear diagrams by plotting the percentage of the total nutrient as N, P_2O_5, and K_2O. In Figure 2, the maximum total nutrient contents for solutions with neutral pH values and crystallization temperatures below 32° F. are represented in parentheses under the base ratios. The first number in parenthesis represents the total maximum nutrient content for solutions containing urea as supplementary nitrogen, and the second number that for solutions containing ammonium nitrate. For example, for solutions with a 1-2-1 base ratio, an 8-16-8 (total of 32) formulation can be made if urea is used as the supplementary source of nitrogen, while a 5-10-5 (total of 20) can be made if the supplementary nitrogen is derived from ammonium nitrate. Formulations for solutions with a 1-3-x base ratio have only one number for the total maximum nutrient content since ammonia can supply the entire nitrogen requirement. From these data, it can be seen that the maximum nutrient concentration that can be achieved for liquid fertilizers with the common raw materials is in the order of 30%.

The effect of increasing the potash content in liquid fertilizer formulations can be noted from Figure 2 by observing the change in the total maximum nutrient content when moving across the diagram on a line connecting a base ratio point on the N-P_2O_5 base line to the K_2O vertex. These changes are summarized for the 1-3-x and 1-1-x base ratio lines in Tables IV and V respectively.

Increasing Potash Content Decreases Total Nutrients

It is clear from Figure 2 and Tables IV and V that increasing the potash content of liquid formulations decreases the total maximum nutrient content that can be obtained in solution. For formulations with high nitrogen and low potash ratios, the total concentration that can be obtained with either urea or ammonium nitrate as the supplementary nitrogen is about the same. However, in solutions of medium potash content, the maximum nutrient concentrations for the formulation containing urea are higher than for those containing ammonium nitrate. This is explained by the fact that potassium chloride which has a greater potash content than potassium nitrate, also has a greater solubility. This is borne out in Figures 3 and 4 which show that more formulations are limited by the potassium nitrate solubility when ammonium nitrate is present in the solutions than by the potassium chloride solubility when the supplementary nitrogen is derived from urea. For formulations with low nitrogen and high potash content this difference in total maximum nutrient content that can be achieved has disappeared because of the low nitrate concentration.

The total maximum nutrient concentration that can be obtained for a given base ratio formulation when a mixed urea-ammonium nitrate solution is used as a supplementary nitrogen source is generally lower than for a solution of the same base ratio containing all the supplementary nitrogen as urea. This rule does not hold for formulations with low nitrogen and high potash contents; in this case the total nutrient concentrations that can be achieved are about the same.

Manufacture a 2-Step Process

The manufacture of liquid fertilizers is essentially a two-step process which consists of (1) the neutralization of phosphoric acid with ammonia followed by (*2*) the addition of other nutrient sources required to give the desired complete liquid formulation. Anhydrous ammonia, aqueous ammonia, ammonia-ammonium nitrate solutions, or ammonia-urea solutions may be used to neutralize the phosphoric acid. The latter two solutions combine neutralization with the addition of the supplementary nitrogen which is present with the ammonia. Steps 1 and 2 may be carried out simultaneously or separately, depending on the process.

A pilot plant was constructed to demonstrate the neutralization of phosphoric acid with liquid anhydrous ammonia. This scheme eliminates the equipment otherwise required if aqueous ammonia is first prepared. Since liquid ammonia is introduced directly in the reaction tank, there is no need for ammonia vaporizing equipment. Some cooling may be necessary in order to facilitate further handling and storage of the finished product. If cooling is not employed, formulations containing in excess of 16% P_2O_5 will liberate a portion of the heat by vaporization of water from the boiling solution.

Phosphoric acid and water are weighed separately into the 40-gallon stainless steel weigh tank and gravity-fed into the 250-gallon stainless steel reactor equipped with a one-half horsepower agitator. The required quantities of these raw materials might also be obtained by metering rather than weighing.

Liquid anhydrous ammonia from a cylinder is introduced into the reactor through spargers mounted through the side of the reactor tank just above the dish-shaped bottom. The pilot unit is equipped with two spargers and a purging line. At the end of the ammoniation cycle the liquid ammonia between the ammonia cylinder and the reactor tank is discharged through the purge line and blown out with air. A hydraulic hose is used as the flexible connection between the reaction tank and the ammonia reservoir. The amount of liquid ammonia fed into the reactor is controlled by orifices in the two spargers and measured by a platform scale. The ammonia tank is placed horizontally so that ammonia liquid can be drawn from the tank.

In the ammonia sparging and purging unit, the needle valves, nipples and caps are all of 316 stainless steel since they come in contact with the unneutralized phosphoric acid. The other fittings are of mild steel.

When the ammoniation process is 75% or more completed, the solid raw materials are added to the open reactor. After complete dissolution has been obtained, the liquid fertilizer is pumped to storage drums. A filter is necessary only when raw materials are used that have some insoluble content. This pilot unit is capable of producing a 1.5-ton batch every 30–45 minutes or a total of 16 to 24 tons per eight-hour day. Aqueous ammonia, ammonia-ammonium nitrate, or ammonia-urea solutions

Table IV. Nutrient Analysis, Total Nutrient Content, and Crystalline Phase for 1-3-x Base Ratio Formulations

Base Ratio	Nutrient Analysis	Total Nutrient Content	Crystalline Phase
1-3-0	8-24-0	32	DAP[a]
1-3-1	6-18-6	30	DAP[a]
1-3-2	4-12-8	24	KCl
1-3-3	3-9-9	21	KCl
1-3-4	2-6-8	16	KCl

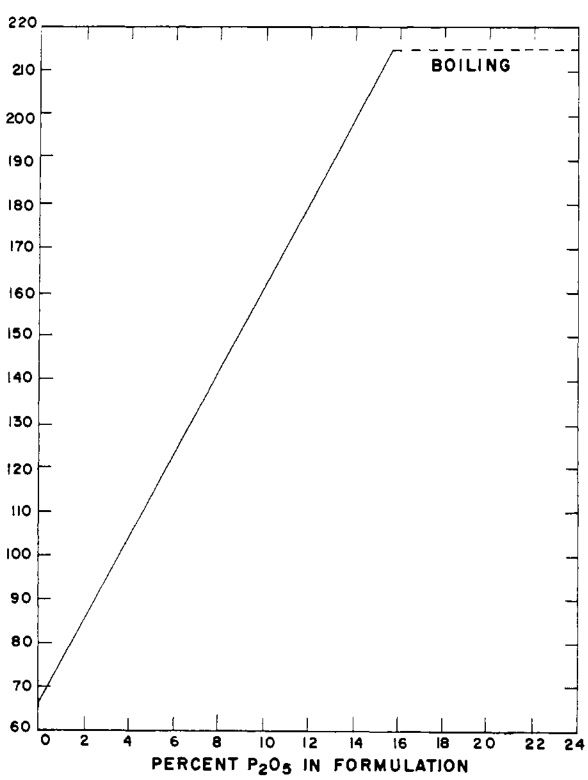
[a] Diammonium phosphate

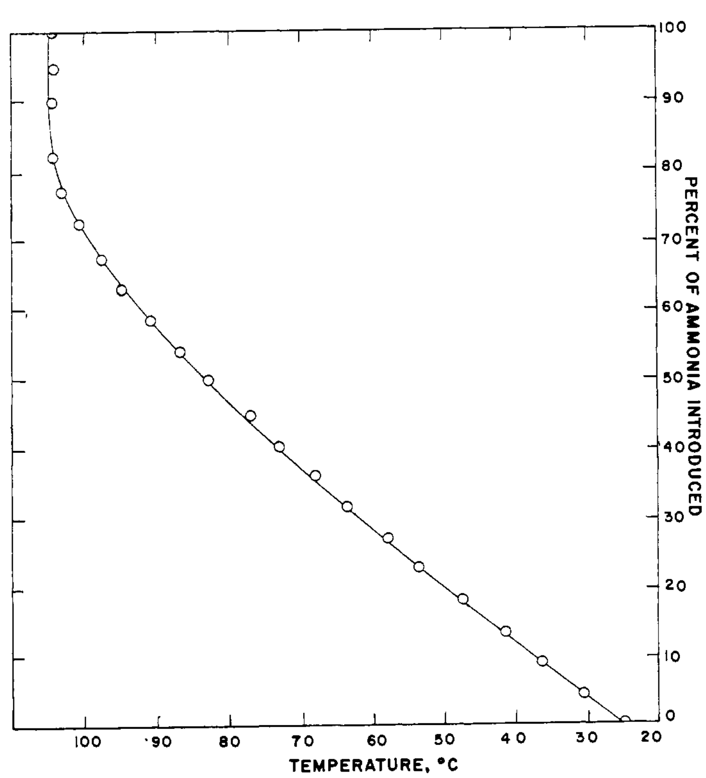
Table V. Nutrient Analysis, Total Nutrient Content, and Crystalline Phase for 1-1-x Base Ratio Formulations

Base Ratio	Nutrient Analysis		Total Nutrient Content		Crystalline Phase	
	Urea	NH_4NO_3	Urea	NH_4NO_3	Urea	NH_4NO_3
1-1-0	15-15-0	13-13-0	30	26	DAP[a]	DAP[a]
2-2-1	12-12-6	10-10-5	30	25	DAP[a]	KNO_3
1-1-1	9-9-9	6-6-6	27	18	KCl	KNO_3
1-1-2	5-5-10	4-4-8	20	16	KCl	KNO_3
1-1-4	3-3-12	3-3-12	18	18	KCl	KNO_3

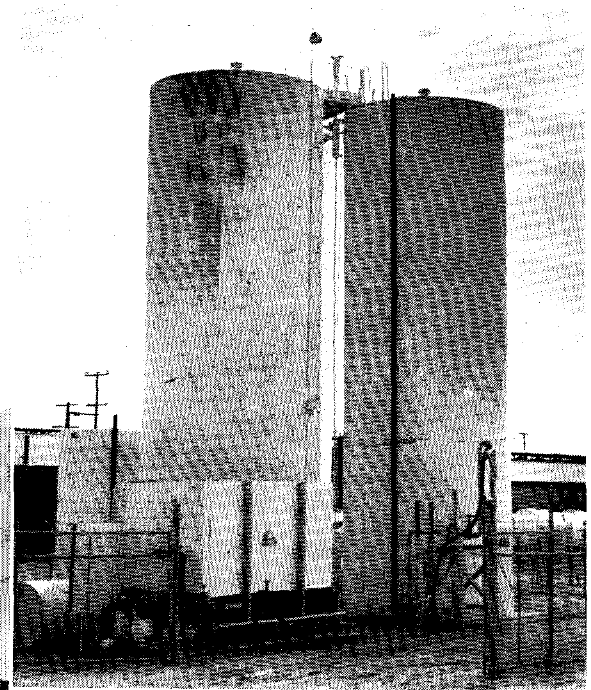
[a] Diammonium phosphate

Left. Figure 5. Maximum temperatures expected from ammoniation of phosphoric acid as a function of P_2O_5 content of finished formulation. Right. Figure 6. Temperature of solution as a function of the percentage of the total ammonia introduced for the manufacture of a 6-18-6 formulation





Right. Pacific Guano Co. converts anhydrous to aqueous ammonia in this unit at Holtville, Calif. Aqueous is used to formulate its liquid fertilizers



Bottom. Right grade of liquid fertilizer can be hauled from distributing station to the field with nurse trucks such as this. Truck loads simply by backing under the tanks, the driver then raising tank legs for travelling. Proper spacing of tanks at end of furrows by gaging application rate permits truck to deliver tank to just the right spot. Operator of tractor applicator drops off empty tank, backs under full tank, and is under way again in a short time

can be used in lieu of anhydrous ammonia but were not investigated in this study because this process merely requires the mixing of the liquids. The neutralization process can be carried out faster with these solutions than with anhydrous ammonia since the solutions can be pumped rapidly into the reactor. This would mean an increase in production capacity over the quantity produced using anhydrous ammonia.

The equations representing the neutralization of phosphoric acid with anhydrous and aqueous ammonia, and the quantities of heat liberated when 100 pounds of 75% phosphoric acid is neutralized with anhydrous and 29.6% aqueous ammonia, assuming the same total water content in each case, are given in Table VI.

The difference in heat content of the two systems is given by the difference between the heat of vaporization of the liquid ammonia and the heat of solution of gaseous ammonia since the heat of reaction of aqueous ammonia with phosphoric acid is common to both systems. Table VI shows that about 20% greater heat is liberated when liquid anhydrous ammonia is used for the neutralization.

Heat of formation data for liquid anhydrous ammonia, phosphoric acid, monoammonium and diammonium phosphate and estimated specific heat data for the resulting solutions have been used to calculate the maximum temperatures that can be expected from the ammoniation of the acid, assuming a temperature of 65° F. for the water. These values have been plotted as a function of the percent P_2O_5 in the finished formulation (Figure 5). From this plot it can be seen that formulations having a P_2O_5 content greater than 16% will boil before the ammoniation is complete unless external cooling is employed. A further reduction in these temperatures may be realized from the endothermic dissolution of any solid form nutrient materials required in the formulation by adding them to the reactor after about 75% of the ammoniation has been completed. These materials are not added previously to this since they may react with some of the unneutralized phosphoric acid. Lower temperatures than those shown in Figure 5 will be realized if aqueous ammonia or an ammoniating solution is used.

The relationship of temperature to the percentage of total ammonia introduced during the processing of a 6-18-6 formu-

Table VI. Comparison of Heats of Reaction Involved with Anhydrous and Aqueous Ammonia

$$1.7\,NH_3\,(liq) + H_3PO_4\,(aq) \rightarrow 0.3\,NH_4H_2PO_4\,(aq) + 0.7\,(NH_4)_2HPO_4\,(aq)$$

$$1.7\,NH_4OH\,(aq) + H_3PO_4\,(aq) \rightarrow 0.3\,NH_4H_2PO_4\,(aq) + 0.7\,(NH_4)_2HPO_4\,(aq) + 1.7\,H_2O$$

Description of Heat	Heat Liberated (or Absorbed), B.T.U./100 Lb. of 75% H_3PO_4 Using	
	Anhydrous ammonia	29.6% Aqueous ammonia
Heat of vaporization of liquid NH_3	13,000 absorbed	...
Heat of solution of gaseous NH_3	19,000 liberated	...
Heat of reaction of aqueous NH_3 with H_3PO_4	35,700 liberated	35,700 liberated
Total	41,700 liberated	35,700 liberated

lation in the pilot plant is shown in Figure 6. No external cooling was used. The boiling temperature of this solution was reached after the ammoniation was about 75% complete. The solution was cooled to about 160° F. by the addition of potassium chloride after the ammoniation was completed.

During the processing of several different formulations in the pilot plant, samples were removed directly after the ammoniation in order to determine the completeness of the absorption of liquid ammonia by the phosphoric acid at elevated temperatures, and whether ammoniation could be continued at the boiling point of these solutions without serious loss of ammonia. Table VII shows the loss of ammonia that was observed for several liquid fertilizer formulations processed in the pilot plant. The accuracy of the ammonia determinations given in the table represents the error involved in weighing the ammonia. The ammonia analyses do not correspond to the nitrogen content of the finished formulation since the samples were removed before the addition of any solid nutrient materials. Urea was added for supplementary nitrogen and muriate of potash for K_2O.

The results show that the absorption of liquid anhydrous ammonia is essentially complete. No ammonia loss is observed over the solutions which do not reach the boiling point during the ammoniation. Further, the ammonia odor was first detected over the solutions that do boil after the ammoniation was about 75% complete. Less than 1% ammonia was lost from the formulations which were allowed to boil to dissipate the heat.

Table VII. Ammonia Loss from Pilot Plant Production of Various Liquid Formulations

Nutrient Analysis ($N-P_2O_5-K_2O$)	% N Derived from NH_3	Maximum Temperature, °C.	Ammonia Analysis, %		% of Total Ammonia Lost
			Theoretical	Observed	
12–8–4	22	63°	3.85 ± 0.02	3.84	0.00
5–10–10	65	69°	4.38 ± 0.02	4.40	0.00
5–10–10	65	71°	4.38 ± 0.02	4.39	0.00
3–12–9	100	74°	4.34 ± 0.02	4.32	0.00
6–18–6	100	104° (boiling)	8.19 ± 0.02	8.11[a]	0.73
8–24–0	100	105° (boiling)	8.08 ± 0.02	7.98[a]	0.99

[a] These values were corrected for water loss from evaporation.

Anhydrous NH_3 Cheapest Source of Nitrogen for Liquids

The pilot plant described in this paper was constructed for the use of anhydrous ammonia since it is the cheapest source of neutralizing nitrogen. The use of anhydrous ammonia, however, requires greater capital investment for storage than does aqueous ammonia. Aqueous ammonia can be used by simply introducing it under the surface of the phosphoric acid in a reactor.

The use of stainless steel equipment is required where phosphoric acid is being handled at higher temperatures. Since mild steel is relatively noncorrosive in the neutral ammonium phosphate solutions, it can be used where ammonia and phosphoric acid are proportioned to maintain a neutral solution. This can be applied to either batch or continuous operations. A close control on the ammonia and acid is required and sufficient cooling should be supplied to minimize corrosion on the reactor tank from the hot solution. Supplementary nitrogen in the form of solutions could be proportioned with the ammonia and phosphoric acid, but potash has to be added as a solid since potassium chloride cannot be obtained in high concentrations in solution.

Monoammonium and diammonium phosphates may be used in place of phosphoric acid and ammonia in liquid fertilizer formulations. The manufacture of solutions from these materials involves merely dissolving the necessary solid-form nutrient sources in water. A mild steel or wooden tank is sufficient for the reactor. Since the dissolution of these solids in water is endothermic, it is necessary to have some method for introducing heat into the mixing system in order to increase the rate of dissolution. The advantage of this method is that it requires a minimum of capital investment. The main disadvantage is that the ammonium phosphates are more expensive than the same components purchased in the form of anhydrous ammonia and 75% furnace-grade phosphoric acid.

Summary

The maximum nutrient concentrations have been established for a large number of neutral liquid fertilizer formulations having crystallization temperatures less than 32° F. From these formulations it has been shown that:

Total nutrient analysis greater than 30% can seldom be obtained using the common raw materials.

Lower total nutrient analysis results from an increased potash content.

Maximum total nutrient analysis for a given base ratio is generally lower when ammonium nitrate is substituted for urea as a supplementary source of nitrogen.

Presented in part before the Division of Fertilizer and Soil Chemistry, American Chemical Society, New York, N. Y., Sept. 12 to 17, 1954.

This skid-type tank rig is easily transported on any flat bed truck. Such equipment is often used by liquid fertilizer dealers to rent or loans to customers. Stainless steel boom and nozzles are pump-fed with the liquid fertilizer