

Figure 1. Approximate location of liquid mixed fertilizer plants

Production and Use of

Liquid Fertilizers

A. V. SLACK, Tennessee Valley Authority, Wilson Dam, Ala.

PPLICATION OF FERTILIZER in liquid A^{pplication} of the growing rapidly in this country in the last decade. The most striking growth has been in use of liquids such as anhydrous ammonia and various nitrogen solutions. The rapid increase in application of anhydrous ammonia has been especially noteworthy. In less than 10 years the amount used annually has increased almost twenty-fold until today it is estimated that about 18% of all fertilizer nitrogen is applied in this way. This phenomenal increase-and the continuing growth-is an outstanding development in modern fertilizer practice.

With this substantial background in application of nitrogen in liquid form, it is conceivable that solutions corresponding to standard mixed fertilizers may have a considerable impact on fertilizer proA. V. Slack joined TVA in 1941, the same year he received an M.S. from the University of Tennessee. He is now Chief of exploratory research, division of chemical development at Wilson Dam. He has done plant control work in the ammonia plant, handled technical liaison in

patent matters for the research and development branches, and coordinated engineering of major plant projects.

duction in the future. Such solutions have the same advantages that ammonia and nitrogen solutions have over standard solid fertilizer practice—the costs of evaporating water and of bagging are eliminated and application to the soil is simplified. Moreover, use of liquid mixed fertilizer eliminates difficulties with segregation and caking often encountered in shipping and storing solid mixtures. However, the liquid mixes have some outstanding shortcomings. Raw material cost is relatively high, storage is expensive, the solutions are corrosive, and concentration is limited—for generally available materials—to a plant food content on the order of 30%.

The use of liquid mixes is not particularly new, but growth has been very slow as compared to the liquid nitrogen field. Possibly the first plant for producing liquid mixes in this country was the G & M Liquid Fertilizer Co., established in Oakland, Calif., in 1923 (10). Although other plants were built thereafter,

Table I. Estimated Sales of Liquid Mixed Fertilizers in the U. S.

(Vear ended June 30, 1954)

(Year ended June 30, 1954)							
	Ferti	ertilizer					
Region and State a	Sold, Region	Tons, State					
New England	91						
Massachusetts		51					
Middle Atlantic	229						
Maryland		30					
New Jersey		26					
New York Pennsylvania		89 55					
South Central	161	55					
Florida	101	25					
Georgia		30					
Virginia		64					
East North Central	1,879						
Illinois		532					
Indiana		827					
Michigan		25					
Ohio		435					
Wisconsin	410	60					
West North Central	412	117					
Iowa Kansas		31					
Minnesota		56					
Missouri		86					
Nebraska		90					
East South Central	117						
Kentucky		65					
Tennessee		38					
West South Central	1,385						
Louisiana		45					
Oklahoma		75					
Texas	1 025	1,262					
Mountain Arizona	1,035	896					
New Mexico		890 56					
Pacific	22,239	50					
California	22,237	20,654					
Oregon		20,001					
Washington		1,500					
Total		27,548					
^a State not listed if fewer than 25 tons are sold.							

the practice did not grow very fast, and as late as 1943 less than 1000 tons of liquid mixed fertilizer was reported sold in California. Probably the main reason for this slow growth was the relatively high cost of the raw materials, which tended to restrict the liquids to special uses such as foliar spraying, flower and garden fertilization, irrigation, and correction of unusual soil deficiencies. In recent years, however, use for more general purposes has taken a decided upturn. In California, for example, consumption had increased to 22,234 tons in 1953, or about $9\frac{C_{C}}{C}$ of all mixtures used. One reason for such increase, of course, was the over-all increase during the period in use of fertilizers; another was the fact that electric-furnace phosphoric acid became available for the first time at a price low enough to allow its use in fertilizer formulation, thereby making possible the ammoniation of the acid as a basic and economical step in manufacture of liquid complete fertilizers. The furnace acid became available not only on the West Coast but also in other major fertilizer regions of the country, so that by early 1954 production of liquid mixtures had begun in the Midwest (7).

It is a natural consequence in a fast growing industry that practice tends to move ahead of full investigation of problems in production and use. Little published material is available in the liquid mixed fertilizer field on raw material usage, problems in manufacture and distribution, and agronomic value of the product. To obtain more information on these points, a survey has been made by correspondence with state officials and experiment stations and by both correspondence and visits to producers and equipment suppliers. Information was obtained from more than 75 companies and from about 65 state organizations.

147 Companies in the Field

On the basis of information obtained in this survey, it appears that about 147 companies produce liquid fertilizers of one type or another, or have registered them for sale. The approximate locations of these companies are given in Figure 1. It should be noted that for a rapidly growing industry such as liquid fertilizers, an accurate listing of producers is almost impossible to obtain. For one thing the terminology in the industry is still somewhat confused; anhvdrous and aqua ammonia, nitrogen solutions, liquid mixtures, and neutral ammonium phosphate solutions are all called liquid fertilizers, so that it is difficult to separate the first two from the last two as was intended in this survey. Even water-soluble dry mixtures are confused by some with liquid fertilizers. Moreover, it is difficult to separate producers from distributors, and in some cases state officials stated that they do not distinguish between liquid and drv fertilizers in their reporting and, therefore, are unable to identify liquid producers.

It is also difficult to distinguish between those who produce on a bulk tonnage basis in competition with dry fertilizers and those who make and package the liquids as specialties. A few companies do both, and any specialty producer, of course, is a potential bulk producer. An approximate division between the two groups has been made in Figure 1. A total of 72 bulk producers was identified, and several others were in process of building plants at the time of the survey (April 1955).

The position of California as a center of the industry is quite evident from Figure 1. Other centers of activity are in the Pacific Northwest (Washington), the Corn Belt (Indiana, Illinois, Iowa, and Nebraska), and the Southwest. Only limited activity, at least on a bulk basis, is evident as yet in other parts of the country.

It is interesting to note that most of the bulk producers east of the Rockies have gone into production within the past year. This makes it especially difficult to get an accurate picture of the consumption situation since most official figures are more than a year old. The best information available (Table I) is that compiled recently by Walter Scholl of the U. S. Department of Agriculture (13). For all states except California, Arizona, and Texas-which list liquid tonnage separately-the amounts were estimated from reports of manufacturers. The estimates include specialty products as well as bulk tonnages and probably are subject to the same difficulties as encountered in identifying producers, because of respondents confusing nitrogen liquids or soluble dry mixtures with liquid mixed fertilizers. However, the figures are a useful indication of the trend in the industry. It appears that current production in the Midwest-with over 25 bulk liquid plants now in production in the area-should be much higher than the estimate shows for 1953-54. Production on the West Coast is also on the increase. The figures in the table do not include sales from the new plants of Brea Chemicals, Inc., for production of ammonium phosphate solutions. The first of these started operation in September 1954, the second in the early part of 1955, and a third is scheduled for production later. Total capacity of these plants is reported as 50,000 tons per year.

Liquid fertilizer mixes have substantial future and are growing fast. If their sales potential is to be realized, attention must be given to two technical problems—development of ways to use more economical raw materials and determination of solubility relationships in the systems involved Information on grades produced (or registered) was obtained both from the state agencies and from the producing companies and is presented in Table II. The grades cover a wide range and, in general, follow quite closely the standard dry grades.

For nitrogen-phosphate combinations, some of the popular grades are 17-7-0, 10-20-0, 12-15-0, and 8-24-0. The 8-24-0 is especially noteworthy since it is produced in California in large quantities. A total of 38 nitrogen-phosphate grades was reported. Seven phosphatepotash grades were reported—ranging from 0-5-5 up to 0-18-8—but only one nitrogen-potash grade was found.

A total of 54 nitrogen-phosphate-potash grades was reported. This includes only those with more than 15% total plant food. In addition to these there are a number of grades—mainly in California and Washington—which are based on fish residues and which generally contain less than 15% plant food. These grades have not been included in this survey.

Raw Materials of 3 Types

Raw material usage in the liquid mixed fertilizer field is of three general types. The most important and most prevalent practice is to use phosphoric acid to supply P₂O₅, ammonia (either anhydrous or aqua) to neutralize the acid, a nitrogen material such as urea or ammonium nitrate to furnish additional nitrogen if needed, and potassium chloride to supply any potash required. A second type, restricted mainly to California and Washington, is use of the same materials except for the ammonia. The acid is left unneutralized because of the basic nature of the soils on which the mixtures are used. In the third type, both ammonia and acid are omitted and only salts are used. The raw materials are more expensive, and the practice is restricted mainly to very small producers and to manufacturers of specialty fertilizers.

In the acid neutralization practice, the most important variations are in use of a nitrogen material to adjust the nitrogen content. For some grades--notably 8-24-0-no added material is needed. The ammonia used to neutralize the acid supplies all the nitrogen required. For the higher nitrogen grades either urea or ammonium nitrate usually is added. Urea is preferable from the formulation standpoint because more phosphate and potash can be kept in solution with it than with ammonium nitrate. Other reasons advanced by producers in favor of urea were: longer availability in the soil, no storage hazard, less corrosion, better plant physiological response, and better stability during application in very hot weather. However, urea is not as generally available as ammonium nitrate and the price in some areas is higher.

For grades of 1:1:1 type (8-8-8 and

Table II. Liquid Mixed Fertilizer Grades Produced in the U. S. and Canada

Туре			Grades		
N-P	2-8-0 4-40-0 5-7-0 5-20-0 6-8-0 6-12-0 6-15-0 6-18-0	7-21-0 7-24-0 8-8-0 8-10-0 8-16-0 8-24-0 8-25-0 9-4-0	9-12-0 9-28-0 10-10-0 10-12-0 10-15-0 10-20-0 11-15-0 12-12-0	12-15-0 12-16-0 12-18-0 13-13-0 13-15-0 13-17-0 13-20-0 14-6-0	14-14-0 15-5-0 15-10-0 16-10-0 17-7-0 17-10-0 20-10-0
N-K	6.3-0-5.5				
N-P-K	$\begin{array}{c} 2\text{-8-16} \\ 3\text{-10-10} \\ 3\text{-12-12} \\ 4\text{-10-8} \\ 4\text{-10-10} \\ 4\text{-12-4} \\ 4\text{-12-8} \\ 4\text{-12-10} \\ 4\text{-12-12} \\ 5\text{-5-10} \\ 5\text{-10-5} \end{array}$	5-10-10 5-14-9 5-15-5 5-20-5 6-8-8 6-8-10 6-9-6 6-12-4 6-12-6 6-12-8 6-12-8 6-18-6	7-6-19 7-9-5 7-11-5 7-13-5 7-14-7 8-8-4 8-8-8 8-10-12 8-12-4 8-16-8 8-16-16	9-5-4 9-9-9 9-12-7 10-5-5 10-5-10 10-6-4 10-6-5 10-10-5 10-10-10 12-6-3	12-6-6 12-8-4 12-12-3 12-12-6 14-7-7 15-5-5 15-5-10 15-8-4 15-10-5 16-8-8
P-K	0-5-5 0-8-4	0-9-6 0-10-5	0-10-10	0-10-12	0-18-8

10-10-10), urea is almost a necessity in order to keep the crystallization temperature down. Ordinarily ammonium nitrate is used only for lower nitrogen or lower potash grades such as 5-10-10 or 10-10-5. Many of those reporting use both urea and ammonium nitrate in the formulation.

Urea and ammonium nitrate are used both in the dry form and in the form of standard ammoniating solutions. The latter, however, are available in only four or five ammonia-ammonium nitrate or ammonia-urea ratios. Therefore most producers use some dry urea or nitrate to give flexibility in formulation. Some use of ammonium nitrate liquor and of urea-ammonium nitrate solution was also reported.

A variation in means for adjusting the nitrogen content is use of sulfuric acid to form ammonium sulfate in the finished mixture. Limited use of this method was reported.

Phosphoric acid used is both of the wet-process (green) and electric-furnace (white) type. The former, however, is used mainly for formulations in which the acid is not neutralized. It contains impurities which would precipitate on neutralization and perhaps cause trouble by clogging handling and distribution equipment. Only two companies are reported to be using wet-process acid in a neutralization process and in both these cases the impurities are removed at some stage of the process.

The potash material used almost exclusively is muriate of potash. Although it is an economical source of potash it leaves something to be desired in the way of solubility. Many producers recommend that the K_2O content should be limited to 10% if muriate is used. The white grade of muriate is generally preferred since the red grade contains some insoluble material. Other potash materials reported were potassium sulfate, potassium hydroxide, potassium carbonate, potassium nitrate, and potassium phosphate. Ordinarily these are used only in specialty products.

Many other materials such as trace elements, herbicides, and insecticides are added to liquid fertilizer by some producers. Trace elements reported were iron, zinc, manganese, molybdenum, and boron. Magnesium and sulfur additions were also reported. Calcium polysulfide is added in some instances as a soil conditioner.

Those who use salts only as raw materials ordinarily use monoammonium or diammonium phosphate as the P_2O_5 source. Other materials are the same as those used in the neutralization method, except that there is more usage of potash salts other than muriate. Many of the salt solution producers aim at high analyses—up to 40% plant food content—and, therefore, must have a material more soluble than muriate.

Manufacturing Problems

Manufacturing practice in the liquid fertilizer industry appears to be in a state of flux. The process is a relatively simple one—the only operation beyond simple mixing is neutralization of the acid—but there are several points on which both practice and opinion differ. The principal differences are: batch vs. continuous neutralization, methods of proportioning raw materials, and means for preventing ammonia loss during neutralization. Flow diagrams for three of the major process variations are given in Figure 2. In variation A, the neutralizer rests on a scale and the raw materials are

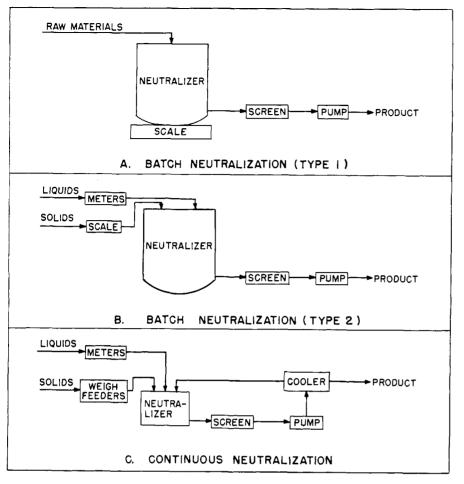


Figure 2. Process variations in liquid mixed fertilizer production

weighed in stepwise. The usual order of addition is water, acid, ammonia, other nitrogen, and muriate. The purpose of the screen in this and other processes is to remove foreign objects such as fragments of paper and wood.

In variation B, the raw materials are weighed or measured outside the neutralizer and may be fed in simultaneously if desired. The use of liquid meters seems to be the prevalent practice; however, some producers weigh the liquids and others measure the change of depth in a feed tank.

Variation C is a continuous process throughout and is therefore well suited to large-scale production. The use of a cooler as shown is the normal practice, but it is reported that some plants are operated without one.

The advantages and disadvantages of these variations seem to be about as follows. Variation A is quite simple in design and probably costs less to install than any of the others, but the stepwise addition of materials is time consuming and conducive to ammonia loss. In B the use of several measuring devices rather than one complicates the process somewhat, but some of the materials can be added simultaneously to speed up the operation. This is especially helpful during the last stages of ammoniation, when addition of the solid salts helps to cool the solution and thereby reduces ammonia loss.

Variation C has the usual advantages of continuous operation but also the usual drawbacks—higher initial cost and greater care required in operation. The continuous process appears to be especially suitable for plants which produce relatively few grades.

Producers have pointed out several problems connected with manufacture of liquid mixed fertilizers. They are listed in the order of frequency of mention.

Salt crystallization Corrosion of equipment Loss of ammonia during mixing Cost of raw materials Availability of raw materials Control of product composition Low solubility and incompatibility of additives Insoluble impurities Rate of solution Dissipation of heat of neutralization Cost of raw material storage

Salt Crystallization

An objective in the industry is to make the liquid fertilizer as concentrated in plant nutrients as are solid mixtures, which are reported to have averaged over 26% in plant food concentration in 1953-54. In comparison, most of the producers consider that the danger of salt crystallization sets the upper limit at about 25% for liquid fertilizer, with perhaps 30% if urea is used.

Thus liquid fertilizer can be made about as concentrated as the average solid mixed fertilizer. However, many solid mixtures exceed the average and it is in this higher analysis area that salt crystallization becomes a major problem in the formulation of liquid fertilizer, especially when nitrogen or potash content is high. Some producers avoid this problem by restricting combined nitrogen and K₂O content to 15%.

The practical limit of concentration is governed by the maximum crystallization temperature which can be tolerated under field conditions. Most producers gave 32° F. as the highest safe temperature. The range of temperature given was from -20° F. for winter to 52° F. for summer.

One of the most important factors in salt crystallization is the degree to which phosphoric acid is ammoniated. Solubility in the monoammonium phosphatediammonium phosphate-water system is such that an approximately equimolar mixture of diammonium phosphate and monoammonium phosphate is considerably more soluble than other mixture ratios or the pure salts. Thus for highest solubility it is desirable to ammoniate to a degree which will give the optimum ratio of the two salts. The relatively narrow range in which the producer must operate is shown in Figure 3, which is based on the work of Brosheer and Anderson (2). The very highest solubility is obtained at an N: P2O5 weight ratio of about 0.3; on either side of this value the total plant food content of the solution drops off rapidly. It is desirable to add as much nitrogen as possible in the form of ammonia because of its relatively low cost and because it reduces corrosion by raising the pH of the solution. The limiting factors are reduced solubility and increase in ammonia vapor pressure over the finished solution. Most producers find the best balance among these factors to be at a ratio of about 0.33, which gives such popular grades as 8-24-0 and 6-18-6.

Since the solubility relationships effectively limit the ammonium phosphate portion of the solution to an N: P_2O_5 ratio of approximately 1:3, neutral fertilizer solutions are restricted to this as a minimum. In other words, it is not feasible to make a lower ratio (such as 1:4, e. g., 3-12-12) without reducing solubility greatly and increasing acidity and corrosiveness of the product solution.

For higher $N:P_2O_5$ ratios urea or a nitrogen salt such as ammonium nitrate or ammonium sulfate is used to bring up the nitrogen above the amount that can be supplied as ammonia. Here the solubility relationships are not so well known as they are for the simple ammonium phosphate solutions. The crys-

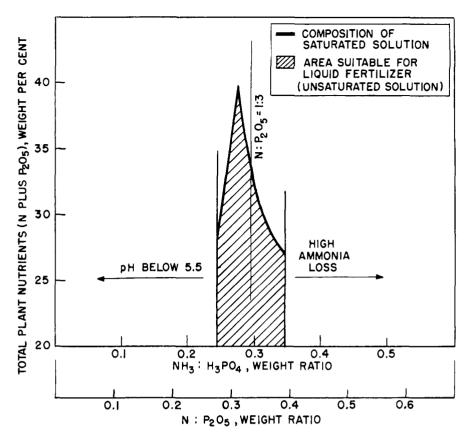


Figure 3. Ammonium phosphate solution. Effect of $NH_3:H_3PO_4$ ratio on solubility at 32° F.

tallization temperatures of some of the more common formulas have been determined by Arvan et al. (1); beyond this there apparently is no information other than that from plant experience in the industry.

Supersaturation is an additional factor in the salting out of product solutions, and some producers take advantage of this to make high concentrations. For example, a 10-10-10 solution (made with urea, ammonia, phosphoric acid, and muriate) should crystallize at 64° F. (1). However, solutions made up by neutralization tend to supercool and will sometimes remain stable for long periods at a temperature considerably below the normal crystallization point. The 10-10-10 has been known to survive a 32° F. cold spell without crystallization. For colder weather, however, most producers drop back to a 9-9-9 or 8-8-8.

In depending on supercooling for protection, producers are helped by the fact that their product is distributed mainly on a bulk basis, and therefore ordinarily goes directly from producing plant to the field without any long period of storage.

Supercooling can be enhanced or stabilized to some degree by use of a small amount of an additive such as a hydrophilic colloid. A few producers are reported to be using such an additive but no information was obtained on its efficacy. In the specialty field, potash-containing formulas with over 30% total plant food almost always require some potash compound other than muriate in order to avoid salting out. Materials reported for such use were potassium phosphate, potassium carbonate, and potassium hydroxide.

Corrosion an Outstanding Disadvantage

One of the outstanding disadvantages of liquid fertilizer as compared to dry products is the corrosive nature of the liquids. This is a problem during formulation and in storing, handling, and distributing the finished product.

The acidity of the solution is the most important single factor. The majority of producers reported that a pH of 6.5 to 7.5 is optimum in this respect. For unneutralized solutions the pH is quite low; typical values reported were 1.5, 2.0, and 3.0. Reported pH values ranged from 1.5 to 11.0.

The use of ammonium nitrate and potassium chloride is also reported to contribute to corrosion. Urea is considered to be superior to ammonium nitrate in this respect.

Corrosiveness of the solutions dictates choice of construction materials, which range from stainless steel to wooden barrels. For solutions with a pH of about 6.0 or higher, ordinary mild steel is generally considered to be satisfactory for storage and handling. For lower pH's either stainless steel or mild steel coated with some resistant material ordinarily is used. A few producers report use of a corrosion inhibitor.

For specific pieces of equipment, the following general practice was reported.

Acid storage and handling

Rubber-lined steel or stainless steel (preferably No. 316)

Ammoniating solution storage and handling Aluminum

Reactor

Stainless steel

Finished solution storage and handling Ordinary steel or wood (coated steel for lower pH's)

Although use of these materials constitutes general practice a number of exceptions were found. For example, one company uses stainless steel all the way through, from raw material storage to field application. On the other extreme, one instance was found of the use of mild steel for the neutralizer, accomplished by keeping the neutralizer partially filled with product liquor and adding ammonia and acid simultaneously, thereby keeping the pH at a safe level throughout the neutralization.

A corrosion problem has developed in some areas in field application of the liquids. Many farmers and distributors already own aluminum equipment which they use for applying nitrogen solutions. Use of this for complete fertilizers has in some cases resulted in corrosion, apparently because of action of muriate on aluminum.

Causes of Ammonia Loss

Dissipation of heat of neutralization, loss of ammonia during neutralization, and control of product composition are all related problems. The reaction of ammonia with phosphoric acid produces a considerable amount of heat, so much so that some grades boil during neutralization. The high vapor pressure of ammonia over ammonium phosphate solution at this temperature and composition makes ammonia loss a problem. Arvan et al. (1) found that such loss could be kept below 1% in pilot-plant work with a 30-minute period for making up a batch. Some producers have reported difficulty with ammonia loss, but practice differs so much that it is difficult to generalize as to the cause. As noted previously, those producers who measure materials before introduction into the reactor are able to reduce ammonia loss by adding the solids before neutralization is complete, thereby cooling the solution. Others cool by blowing air through the solution or by recycling it through an indirect cooler. The use of

aqua ammonia is also helpful since it produces less heat of reaction. Many producers either buy aqua or make it from anhydrous.

The general problem of product composition control appears to be giving some trouble in areas where liquid fertilizer production is new. Many of the plants have no means of checking composition and must rely on correct measuring of raw materials and on keeping ammonia loss below a significant amount. Some occasionally submit spot samples to a laboratory as a check. The situation apparently tends to improve as the industry matures in an area. For example, in California during the early years of the industry the percentage of samples found deficient by the state control laboratory ran as high as 25 to 32%. In 1953, however, the percentage was down to about 12.5%, or about the same as for all fertilizers sold in California (3).

Incompatibility of Additives

As in the solid fertilizer field, many producers of liquids use additives such as trace elements, herbicides and pesticides in their formulations. They have a major advantage over solids producers in that the additives can be mixed much more quickly and thoroughly in a liquid system than in a dry one. Unfortunately, however, many of the trace elements are not very soluble in neutral types of liquid fertilizers, zinc being especially difficult in this respect. Some producers add trace elements, however, to the extent that they can be kept in solution. Boron seems to be the element added most often.

As for pesticides and herbicides, the situation in the liquids field appears to be no clearer than in solid fertilizer manufacturing (5). Several producers reported that such additives tend to separate on standing, a difficulty which they avoid by postponing addition until just before field application.

Availability of Raw Materials

Because of the unsuitability of some standard materials, the producer of liquid fertilizers has more of a problem than the solids producer in obtaining materials. For example, he needs urea for some grades rather than ammonia nitrate. He uses furnace-type phosphoric acid rather than standard fertilizer phosphates, and he prefers white muriate to the red because of insoluble impurities in the latter.

With these peculiar requirements it is not surprising that local shortages occasionally develop. Moreover, liquids producers are concerned over the future supply of phosphoric acid, which has not been available very long and which ordinarily goes into markets where it commands a higher price than in the fertilizer field.

Although suitable materials are sometimes in short supply, the problem may not be a serious one. Suppliers appear to look on liquid fertilizers as a potentially important field and seem to be moving in the direction of meeting these needs. Phosphorus producers are especially aggressive in this and have built several acid plants around the country in the past two or three years. The interest of nitrogen producers is perhaps indicated by a recent announcement that one is building a liquid mix plant to serve as a demonstration unit for users of ammonia and nitrogen solutions (8).

Cost Factors

Producers were asked how costs compare generally in their area for liquid mixes vs. bagged dry material. Nearly all of those using ammonia for neutralization stated that liquids were either competitive or lower in production cost. Those who considered liquid cost higher were mainly producers who use salts only and whose raw material cost is, therefore, much higher. Those who use acid without neutralization were divided on the question.

In respect to raw material cost, liquids producers have the advantage of being able to use a larger proportion of inexpensive ammonia than can be used in making up solid products. In liquid mixes eight pounds of ammonia per unit of P2O3 normally is used, whereas the average in the dry mixing industry probably does not exceed four pounds. This is quite a marked advantage for grades such as 8-24-0, in which all the nitrogen comes from ammonia. For higher nitrogen grades the advantage is decreased because the cost of the additional nitrogen is more nearly in line with what the dry producer pays. The cost will still tend to be less, however, if such liquid sources of nitrogen as ammoniating solutions and solutions of ammonium nitrate or urea can be used. Or sulfuric acid can be used to tie up additional nitrogen at a cost which should be less than that which the dry producer pays for ammonium sulfate.

In many cases, however, producers use solid urea and thereby incur a cost handicap. This may be due to unavailability of ammoniating solutions, lack of adequate storage, or other reasons. Also, ammonium nitrate solution is not generally available and as far as is known no urea solution is on the market as yet. Urea-ammonium nitrate solution is available, however, and is used by some producers.

The main cost disadvantage in liquid manufacture is the cost of furnace phosphoric acid. At an f.o.b. price which appears to range from \$1.48 to \$1.62 per unit around the country, the cost of P_2O_5 in this form is somewhat higher than that from solid sources. One possibility for reducing this cost is use of wet-process acid, which ordinarily costs less to produce than furnace acid. However, wet acid is not generally available and the cost of removing impurities may be a significant cost item. Pilot-plant work at TVA (4) has shown that precipitated impurities can be removed from ammonium phosphate solutions by a practical process. However, for liquid fertilizer preparation some separate use would have to be found for the precipitate, since it contains a substantial amount of phosphate. If the producer also owns a dry fertilizer plant the precipitate might be worked into the dry product. Or it might be sold separately as is the precipitate obtained in purification of wet-process acid for industrial use. There is also the possibility of using the ammoniated wet acid as a "slurry" fertilizer without removing the precipitate. This approach may have serious drawbacks from both technical and consumer acceptance standpoints.

The concensus seems to be that cost of raw materials for liquid fertilizer production will normally be higher than for solid mixtures, but that if proper materials are available the differential can be reduced in many areas to a figure which will give an over-all production cost lower than for the equivalent dry product.

The simplicity of liquid fertilizer plants and elimination of operations such as curing, crushing, and bagging make operating cost very low. Many of the batch plants use a 1000-gallon reactor and thus can produce 10 to 15 tons per hour, with only one or two men needed per shift. An especial advantage for liquids in the Midwest is that the cost of granulation is avoided. A granulated form of the dry product is demanded in this area by a large percentage of the consumers.

Another major advantage of the liquids is in the low plant cost. Equipment prices for 10- to 15-ton-per-hour plants are quoted at from about \$13,000 to \$45,000, which is considerably less than the cost of comparable dry plants. The principal differences are the smaller building requirement, reduced need for solids handling equipment, and elimination of curing, granulating, drying, and bagging.

On the other hand an outstanding disadvantage for liquids is the cost of product storage, which normally runs at least twice as much as for dry materials. Many producers avoid this handicap by making up solutions only as needed, storage being installed for only a few batches. Raw material storage in these plants usually is also limited, thus shifting the storage problem

back to the supplier. This is a growing problem for the nitrogen suppliers in the solid fertilizer field as well as the liquid, and it appears that means to cope with the problem are being worked out. Acid producers do not have as severe a problem; flexibility between industrial and fertilizer use appears better than in the nitrogen field and the P2O5 can be stored if necessary as elemental phosphorus, a relatively inexpensive method as compared to acid storage.

The distribution pattern for liquids is a further cost factor. The tendency is to build a small plant to serve an area of about a 25-mile radius. If demand from outlying areas grows, a new plant is built to serve the new area instead of expanding the old plant. Simplicity and low cost of liquid fertilizer plants make this more feasible than in solid fertilizer production. The result is that the producer retails the product and in many cases applies it on the farm, with a higher profit resulting from this integration of functions. Thus liquid mixing tends to leave only the primary producer and the mixer in the chain from original sources of plant nutrients to ultimate consumer.

The balance between various cost factors is perhaps indicated by the fact that producer-dealers are currently selling liquid mixtures in the Midwest at a price less than that charged by dealers for comparable bagged dry fertilizer. Typical prices for liquids are \$61 to \$62 for 10-10-10, \$44 to \$45 for 4-10-10, \$57 to \$62 for 12-8-4, and \$58 to \$62 for 6-18-6. The price for bagged 10-10-10, for example, runs as high as \$70 per ton in the same area.

Delivery and Application

Practice in delivery to the farm and application to the soil parallels fairly closely that of nitrogen solutions. Numerous varieties of application equipment are in use (6). Like nitrogen solutions, the liquid mixtures have a significant advantage over solid products in convenience and economy of application. A further advantage claimed is accuracy of application. Liquid producers state that the liquids can be distributed in the field with less than 5% variation and that this is better than usually is done with solid materials.

Although custom application by the mixer is a prevalent practice, the survey indicates that farmer participation in the application is growing. A summary of the methods used by various producers is as follows:

Custom application	41%
Delivery of returnable field tanks to the farm	38%
Delivery to farmer-owned tanks at the farm	1207
Delivery to farmer-owned tanks	13%
at the mixing plant	8%

at the mixing plant

Some producers state that although custom application is usually a necessity at first, the farmer tends to take over local transportation and application as he becomes accustomed to the new material.

Producers Differ Widely on Agronomic Value

The agronomic effectiveness of liquid mixtures is a point on which producers differ widely. About a third of those contacted stated without qualification that liquids are superior to solid mixtures. About half of the group affirmed the superiority but included some limiting qualification. Some of the conditions listed as giving superior results with liquids were: with certain crops only, for certain fertilizer practices such as side dressing, in dry seasons, in cold weather, and on alkaline soils (for the acidic type of liquid mixtures). The remainder of the group (about 20%) stated that in their opinion the liquids have no agronomic advantage over the solid type.

Agronomic literature on the subject appears to be scant and to some extent conflicting (9, 11, 12, 14). The situation probably is confused somewhat by variation in water solubility of the solid materials considered in various comparisons. Water solubility of phosphate is regarded by agronomists as being quite advantageous under certain soil and crop conditions. It is quite possible that the complete solubility of the liquids has shown an advantage in some areas where solid fertilizers used have been only partially water soluble. There appears to be no evidence, however, that the liquids are generally superior to water-soluble solid materials such as diammonium phosphate and ammonium phosphate-sulfate.

The only agronomic criticism of liquids received was that phosphate is fixed in the soil more rapidly when it is in liquid form. Little agronomic data appears to be available on this point.

Status of the Industry

Liquid mixed fertilizer is currently a fast growing phase of the fertilizer industry, at least from the standpoint of the number of companies going into the business. The actual quantitative significance of this growth cannot be estimated very well as yet because many operations have started quite recently and some plants are still under construction. However, advantages of liquids seem to indicate a substantial future for them, although any major displacement of dry materials in the near future seems quite unlikely. One of the more important factors in the rate of growth is the probability that ammonia

and nitrogen solution distributors will move into the field of complete fertilizer solutions so that they can give a balanced fertilizer service to the farmer. The greatest deterrent probably is that a new practice is involved and consumers are slow to change. However, the growth of liquid nitrogen application in the past decade is proof that a new technique can grow at a rapid rate in the fertilizer industry.

In order to realize fully whatever potentialities exist in liquid mixtures, it is essential that the several problems in production and use be investigated fully. Two problems that appear to warrant special attention are development of ways to use more economical raw materials and further determination of solubility relationships in the systems involved.

Acknowledgments

The author appreciates the interest and cooperation of many control officials, agronomists, liquid fertilizer producers, and equipment suppliers. On the TVA staff, J. C. Driskell and H. B. Shaffer, Jr., assisted in gathering and compiling the information.

Literature Cited

- (1) Arvan, Peter G., Langguth, Robert P., and Sisler, Charles C., "The Manufacture and Properties of Liquid Fertilizers," J. AGR. FOOD CHEM., 3, No. 8, in press.
- (2) Brosheer, J. C., and Anderson, J. F., J. Am. Chem. Soc., 68, 902 (1946).
- (3) California Department of Agriculture, Bureau of Chemistry, Special Publication No. 251 (1953).
- (4) Houston, E. C., Yates, L. D., and Haunschild, R. L., J. Agr. FOOD CHEM., 3, No. 1, 43 (1955).
 (5) Jacob, K. D., *Ibid.*, 2, 970-6 (1954).
 (6) Johnston, Douglas, Proceedings of
- the 29th Annual Meeting of the National Joint Committee on Fertilizer Application, p. 151 (1953).
- (7) J. Agr. Food Chem., 2, 1156-60 (1954).
- (8) Ibid., 3, 380 (1955).
- (9) Luckhardt, R. L., Agr. Chemicals, 8, 45-7 (1953).
- (10) McCollam, M. E., and Fullmer, F. S., Better Crops with Plant Food. 32, 6-8, 46-7 (June-July, 1948).
- (11) MacIntire, W. H., Winterberg,
 S. H., Clements, L. B., and
 Johnson, H. S., Jr., J. Am. Soc. Agron., 39, No. 11 (1947).
- (12) Ohlrogge, A. J., and Warren, G. F., Purdue University Agricultural Extension Service, Leaflet 368 (1954). Extension
- (13) Scholl, W., private communica-tion, April 29, 1955.
- (14) Weldon, M. D., and Ringler, W. E., University of Nebraska, E. C. 195 (1951).