0-187

0-187
AN-~~9489~~ 5196
RN-3149

PRODUCING AND MARKETING SUSPENSION FERTILIZERS FROM SOLIDS

Hubert L. Balay and David G. Salladay
Chemical Engineers
Division of Agricultural Development

For Presentation at the TVA-TFI Fertilizer Conference
Kansas City, Missouri
July 26-27, 1977

TENNESSEE VALLEY AUTHORITY
Muscle Shoals, Alabama

PRODUCING AND MARKETING SUSPENSION FERTILIZERS FROM SOLIDS

Hubert L. Balay and David Salladay

Fluid fertilizers are reported to have several advantages over solid fertilizers. Probably the most clear-cut advantage is the ease in mixing and uniformly applying pesticides, thus saving the farmer from one to three trips over the field during the busy spring planting season. Other properties frequently listed, but which may be more debatable, are accuracy of application, low salt index, easy and accurate application of clear solution grades through gravity flow starter equipment, ability to stay on analysis, ability to mix and apply secondary and micronutrients uniformly, lower labor requirements, lower plant investment, and speed of application.

Most advantages listed can be matched by solids but only with more effort. The advantages of fluids have always had to be sold to the farmer along with the product to justify the higher prices he has generally paid for fluids. Traditionally fluid fertilizers have been considered premium fertilizers, not only because of the advantages listed above but also because of the higher prices made necessary by higher costs of the phosphate materials used to produce them. Raw materials that contain low levels of impurities have been required to produce fluids that do not precipitate solids, a necessity to avoid storage and application problems.

This was the situation faced by most fluid producers until 1974. At that time, the growing price spread between fluid phosphates and bulk blend phosphates was shrinking profit margins for many fluid dealers. Both high production costs and comparative low analysis of the usual fluid fertilizer ingredients contributed to the problem. Only the fertilizer shortage kept many fluid people from turning entirely to bulk blending.

Freight costs on low analysis materials also began to increase. Between April 1974 and March 1976, freight rates on TVA phosphate solution increased 64%. It was apparent that if this situation continued, the growth rate of fluids would level off and possibly begin to decrease. The situation demanded that cheaper raw materials be found for fluids. One solution was found during the phosphate shortage when a few plant operators made fertilizer suspensions successfully from diammonium phosphate (18-46-0) and orthophosphoric acid in existing plants. These plant operators probably did not realize it at the time, but they had started a new trend—one that would allow the fluid manufacturer to compete with bulk blends, not only because of the advantages of his product, but also on price because he was using the same raw materials.

The use of solids to produce fluids, however, is not new. William E. Funk in his presentation to the 39th annual meeting of the Council on Fertilizer Application in 1963, ''Slurry Fertilizer, Equipment, and Application Costs,'' said:

> The demand for low cost liquid fertilizer has brought about new techniques in the formulations of the heavy colloidal suspension called slurry. The choice of phosphate to supply the need can be greatly varied. It is practical to utilize a choice of conveniently available low cost types of triple superphosphate or acid and rock phosphate, or phosphoric acid, or superacid, or diammonium phosphates. This has brought us to today's situation where solids are just beginning to be used on a routine basis to produce fluid mixtures.

Probably the first solid phosphate used in any quantity to produce fluid fertilizer was TVA's ammonium polyphosphate (APP; 15-62-0), made by reacting phosphoric acid with ammonia under moderate pressure and at elevated temperature.

Production began in 1969. Because the product was made from furnace superphosphoric acid, contained few impurities, and had about 50% of the phosphate in the polyphosphate form, it was well adapted to the production of clear 10-34-0 liquid fertilizer. Enough ammonia and water was added to reach the desired $N:P_2O_5$ ratio and to dissolve the solid. Some suspensions were made from this product, but it made such a satisfactory clear liquid that very little of it was ‘‘wasted’’ this way. Data developed from this product led directly to TVA's experimental ammonium polyphosphate, 11-55-0, which is made from wet-process orthophosphoric acid.

Monoammonium Phosphate

Nearly every phosphate-containing dry raw material has been tried for fluids, including phosphate rock, triple and normal superphosphate; however, the most popular solid fluid fertilizer base today is monoammonium phosphate (MAP). Until about 2 years ago, monoammonium phosphate was available only in limited quantities and had little market impact, however, it is now available in quantity, and fluid fertilizer producers have seized (with little help from their suppliers) on MAP as an ideal product for the production of suspensions.

Monoammonium phosphate alone is comparatively insoluble; only about 25 pounds will dissolve in 100 pounds of water at 32°F. But if ammonia is added to raise the $NH_3:H_3PO_4$ mole ratio (from 1.0) to 1.5, about 110 pounds of MAP will dissolve per 100 pounds of water at the same temperature (figure 1). Since the amount of solid that can be suspended is roughly the same regardless of how much material may have been dissolved, ammoniating to the eutectic point (maximum solubility point) maximizes the total amount of plant food in a given amount of fluid fertilizer.

Some producers sacrifice solubility slightly by ammoniating past the eutectic point to mole ratio of 1.65 because the usual crystallizing phase at that mole ratio is diammonium phosphate. Diammonium phosphate crystals are less dense and shaped better for suspensions than monoammonium phosphate crystals. Photos of monoammonium phosphate and diammonium phosphate crystals are shown in figures 2 and 3. Monoammonium phosphate crystals are usually precipitated at the eutectic point.

Several grades of monoammonium phosphate are produced, varying with the quality of the acid and the process used. Most companies produce the ratio that suits their own production methods. Some methods used to produce MAP are:

1. Ammoniating acid to the $NH_3:H_3PO_4$ mole ratio of 1.4 to 1.5 in a preneutralizer and adding acid in a TVA ammoniator-granulator or blunger to return the mole ratio to 1.
2. Ammoniating acid to the $NH_3:H_3PO_4$ mole ratio 0.5 in a preneutralizer and adding ammonia to a TVA ammoniator-granulator or a blunger to increase the mole ratio to 1.
3. Two-step neutralization under pressure followed by flash ejection of hot concentrated slurry into a receiving tower.
4. Direct reaction of ammonia and phosphoric acid followed by flash ejection into a receiving tower.
5. Reaction of phosphoric acid and ammonia in a pipe-cross reactor in the presence of a small amount of sulfuric acid with subsequent flash ejection onto a rolling bed of solids in a TVA ammoniator-granulator.

Methods 1 and 2 are most frequently used to produce monoammonium phosphate for suspension fertilizer. Usually fairly low quality acid is used to produce granules suitable for bulk blending, but when mixed with the proper amount of water, suspending clay and ammonia, and broken down by suitable agitation, they produce a good suspension. Method 3 is not used in the U.S. The product is powdered and is intended only as an ingredient for further granulation in combination with other solid plant food ingredients. No data are available on the use of this product to produce fluid fertilizers.

Method 4 produces a powdered product. This is an economical process now being used to produce MAP being sold by several U.S. companies, primarily as an ingredient for granulation plants. It is, however, being used successfully as a base for fluids. A granule is not produced, so the product is unsuitable for bulk blending. When the impurity content is kept low by the use of quality acid, the product is especially suited for fluids because the powder will ammoniate easier than granules and less power is required than with granular products. Due to economics in its production, it may become an important fluid base.

Method 5 is a new process for producing monoammonium phosphate and only a small amount has been used in fluids. The product usually is not a true MAP, but a combination of monoammonium phosphate, diammonium phosphate, and ammonium sulfate which is 80% to 90% monoammonium phosphate. The usual grade is granular 12-48-0, a grade suitable for the production of 1:4:X bulk blends and suspensions. In some areas the small amount of sulfur present can be an asset.

Diammonium Phosphate

As mentioned by Mr. Funk, fluids made by breaking down diammonium phosphate with water and adding urea-ammonium nitrate solution, potash, and clay have been around for many years. The literature indicates, however, that the early grades produced were low in analysis and that mixing was slow. Adding acid to diammonium phosphate to bring the mixture to near the eutectic point has been used only in recent years, but the use of diammonium phosphate and phosphoric acid, along with a little ammonia to provide heat and liquid phase, predates the use of monoammonium phosphate. This was probably because diammonium phosphate was readily available while monoammonium phosphate was not.

Formulas for several grades of suspensions made from 18-46-0 are shown in table 1. The base grades 10-30-0 and 11-33-0 are usually made for storage, and some problems have developed during long-term (2 months) storage. In many cases it has been found, especially with 11-33-0 and in grades to be stored, that 10% to 15% polyphosphate from 10-34-0 or superacid improves handling of the product. Anyone making grades from DAP or MAP should expect some variation in the physical properties between batches. This is not usually an important consideration unless the product is to be stored.

Diammonium phosphate (usually 18-46-0) is probably the most widely used phosphate base in bulk blend plants. Most DAP is manufactured by the TVA process, which consists of ammoniation of the phosphoric acid to mole ratio of 1.45 in a preneutralizer (the same eutectic point used in fluid fertilizer) and discharging the slurry into a rotating TVA ammoniator-granulator where it is further ammoniated to mole ratio 2.0 and pelletized.

Triple Superphosphate

Triple superphosphate was one of the first solids to be tried as a phosphate source in fluid fertilizers. Many difficulties were encountered with the equipment available at the time. Mr. Funk reported some early work by TVA which ‘‘allows greater quantities of triple superphosphate to be used than previously.’’ He was referring to work done by Julius Silverberg of TVA’s Applied Research Branch. Mr. Silverberg had developed a technique for ammoniating triple superphosphate which allowed it to be used to make suspensions. The process, described in reference 10, includes slurrying 20% of the triple superphosphate with the water in the formulation, then adding urea-ammonium nitrate solution (if required), potassium chloride, ammonia (Mr. Silverberg used aqua ammonia), and the balance of the triple. Satisfactory grades as high as 5-15-15 and 12-12-12 were made in the laboratory. These laboratory procedures were tested in the field with varying results and were not widely developed because of the general availability of low-cost phosphoric acid. It was found that the higher the ammoniation rate, the higher the quality of the products. Tests with ammoniation rates as high as 8 pounds of ammonia per unit P_2O_5 were successful.

Triple superphosphate is again of some interest, not so much as a low cost source of phosphate, but as a way to produce 0-X-X suspensions. An 0-13-13 grade with 1% attapulgite clay made in the laboratory stores fairly well for short periods, and an 0-14-14 without clay, which it appears could easily be taken to the field and applied, has been made. The pH of these products is usually in the range of 2 to 4, and they should be handled only with stainless steel equipment. High-shear mixing equipment now available would allow these grades to be made from run-of-pile or even granular triple superphosphate, although granules of triple made by the slurry process are sometimes hard and more difficult to reduce than granules of DAP and MAP, especially when no heat can be generated by a chemical reaction.

Ammonium Polyphosphate

Between 1967 and 1972, TVA produced about 190,000 tons of ammonium polyphosphate from electric-furnace phosphoric acid. This product has been discontinued due to the high cost of electric power. TVA now is producing from wet-process orthophosphoric acid and ammonia granular APP having 15% to 30% of its phosphate in the polyphosphate form. The polyphosphate improves the properties of suspensions made from APP just as the polyphosphate from liquid sources enhances the storage properties of products produced from it. The polyphosphate in ammonium polyphosphate dissolves quickly and helps disintegrate the solid. Production rates with APP at one time were better than with monoammonium phosphate or diammonium phosphate. Monoammonium phosphates have improved, and the average dissolution rate for APP is about the same as with MAP in high-shear equipment, although there is still some advantage to ammonium polyphosphate. Field tests show, however, that ammonium polyphosphate dissolves quicker than MAP in low-shear equipment.

Granular APP (presently 11-55-0) is made by ammoniating merchant-grade wet-process phosphoric acid in the pipe reactor and granulating the melt in a pug mill. It is expected that as solid phosphate bases become more popular as raw materials for fluid fertilizer and as low-cost products are produced expressly for both fluids and solid fertilizer, TVA ammonium polyphosphate will be used as the model.

Comparative Production Costs

Little has been published on the comparative costs of producing monoammonium phosphate, diammonium phosphate, and ammonium polyphosphate. A TVA study based on January 1974 costs shows that diammonium phosphate can be produced slightly cheaper than ammonium polyphosphate. The same study shows, however, the production of diammonium phosphate requires about 907,000 more Btu's per ton. No one has to be reminded that rising energy costs can have significant impact on production costs. No studies comparing ammonium polyphosphate and monoammonium phosphate have been published. It can be assumed that the production cost of the granular products are similar to the costs of diammonium phosphate and ammonium polyphosphate, especially when products suitable for fluid fertilizers are made.

Mixing Equipment

There are many agitators capable of reducing solids to produce suspensions. Some of the most popular ones are shown in figure 4. Most users of high-shear agitators are pleased with the equipment, but the equipment usually has been installed for only a short time.

No suitable study has been made as to the effectiveness of equipment, and the claims that one type or another is superior have not been established. Thus, the only recommendation which can be made is that the purchaser consider all aspects of the equipment, including purchase price, energy requirements, simplicity of operation, availability of spare parts, prior use, installation cost, and possible maintenance problems.

The time required to produce an 11-33-0 suspension base from MAP varied from 25 to 45 minutes for a 10-ton batch in different plants, even with the same equipment and all variables apparently the same. Variables sometimes included in mixing times but which may have nothing to do with mixing are problems with solid handling equipment. Everything from bucket elevators to drag and screw conveyors is used to add solid material to a mix tank. Hopper designs also vary, and bridging of solids in a hopper is a frequent bottleneck making it difficult to establish accurate mixing times for various systems. Attention to proper design of solids handling equipment can make the production of suspensions from solids more pleasant and more profitable.

Considerable variation in raw materials also makes it difficult to establish criteria for mixing equipment. Shipments of monoammonium phosphate from the same supplier may vary enough in impurity content to cause the production of a 10-ton batch of 11-33-0 with a given piece of equipment to vary 5 to 7 minutes.

Mixing Procedures

Recommended mixing procedures also vary among suppliers of base materials. TVA recommends the following procedures for ammonium polyphosphate. We also use these same procedures when we work with mixers that are using monoammonium phosphate.

1. Add the required amount of water to the mix tank, add and gel the clay, add half of the ammonium polyphosphate, all of the ammonia, and last, the remaining APP with continuous mixing.
2. Add the required amount of water, add and gel the clay, add part of the ammonia (about 25%), add the ammonium polyphosphate, and finally add the remaining ammonia.
3. Add the required amount of water to the mix tank, gel the clay in it for about 5 minutes, then add the APP and ammonia simultaneously.

The required dissolution and mixing time for all three procedures is from 20 to 40 minutes depending upon the amount of mixing and recirculation available. A rise in temperature of about 60° F is obtained during ammoniation. After ammoniation of the ammonium polyphosphate, the finished base suspension has a pH of about 6.3, a specific gravity of about 1.42, and a viscosity of 300 centipoises at 80° F. When diammonium phosphate is used, orthophosphoric acid usually is added to bring the $NH_3:H_3PO_4$ mole ratio back to 1.65 or to the eutectic point, 1.5. Usually a small excess of acid and some anhydrous ammonia are added to provide heat and liquid phase to hasten the disintegration of the DAP pellets. In most cases about 70% of the P_2O_5 is obtained from diammonium phosphate.

TVA usually uses the following procedure with diammonium phosphate. Add the required amount of water to the mix tank. Add and gel the clay. Add diammonium phosphate. Add phosphoric acid. Mix for approximately 5 minutes. Add ammonia and, finally, urea-ammonium nitrate solution (if required) and potash. Usually the maximum temperature reached by the fluids in the mix tank is about 160° F; after adding all the potash, the temperature drops to about 100° F.

Other Solid Materials

There are many other solid materials which will probably come into use as the trend to the use of solid materials in fluid fertilizer increases and as mixing equipment improves. Each of these materials presents interesting possibilities and, if covered as deserved, would each require papers of their own.

Urea

As the supply of urea increases, it is likely that its use as a supplementary nitrogen source in fluid fertilizers will increase. Urea-ammonium nitrate solution is the major source of supplementary nitrogen in liquid fertilizers but the ammonium nitrate in this solution lowers the plant food content in some formulations containing potash. Ammonium nitrate reacts with the potash in liquid fertilizers to produce potassium nitrate and ammonium chloride. Potassium nitrate is relatively insoluble at ordinary temperatures and increases the viscosity of suspensions. Urea does not react with potash, and grades made with urea usually contain more nutrients than grades made with urea-ammonium nitrate solution. The same granular or prilled urea can be used in bulk blending.

Sulfur

Suspensions containing up to 40% sulfur have been made from flowers of sulfur. Viscosities ranged from 500 to 600 centipoises. These suspensions have been made and applied successfully to correct sulfur deficiencies.

Ammonium Sulfate

Cost is the major factor determining the extent of use of ammonium sulfate as a supplementary nitrogen source, since grades produced from it are lower in analysis than those produced using urea or urea-ammonium nitrate solution. When prices are low, it is widely used. Ammonium sulfate, however, supplies some sulfur, which gives it an advantage where sulfur is needed.

Potassium Sulfate

Finely divided potassium sulfate suspends about like ammonium sulfate and makes good suspensions. It has been used to replace potassium chloride in suspensions intended for crops where chlorine cannot be tolerated. The lack of a dependable supply of fine potassium sulfate suitable for suspensions has been a problem, however.

Limestone

Suspensions containing up to 60% finely ground limestone (-100 mesh) are being used successfully in some areas. Ordinary mixing equipment along with tetrasodium pyrophosphate or some other dispersing agent is normally used with these suspensions.

Phosphate Rock Suspensions

Finely ground phosphate rock from certain sources has been used successfully as a phosphate source for many years. Finely ground phosphate rock, however, is very dusty and very difficult and annoying to handle. TVA has produced suspensions of finely ground phosphate rock suitable for direct application in laboratory equipment. The rock can be suspended in water using attapulgite clay and tetrasodium pyrophosphate as a dispersant. The suspension can be applied through conventional fluid fertilizer application equipment.

Fine Standard Potash

A few suspension manufacturers have used standard (red) potash to save money. However, they have used fluid grinders to reduce the portion of the standard potash which was too large to suspend. Finely ground standard potash has been available for some time from some potash manufacturers, but it has not been widely used for fluids. A large amount of this potash has recently come onto the market at a very low price, and manufacturers with high-shear mixing equipment are using it with excellent results.

There is some evidence that suspensions made from this potash will gel if stored too long, but few (if any) of these manufacturers are storing their products. Somewhat lower grades often have to be produced from the fine standard since the K_2O content usually is about 2% lower than that of white liquid grade potash. This product has been well received by suspension manufacturers and will continue to be used as long as it is less expensive than white liquid grade.

Application Equipment

The quality of fluid fertilizers produced from solids using modern mixing equipment is usually equal to the quality of suspensions produced from fluid raw materials. Generally, no changes are needed in application equipment to handle suspensions made from solids, except when they contain limestone and phosphate rock. Larger nozzles are required for phosphate rock and limestone.

Conclusion

The only reason to use solids to produce suspensions is to save money. In 1975 prices of monoammonium and diammonium phosphates were low, indicating rapid payout on high-shear equipment. Before some equipment could be purchased and installed, however, the prices of base phosphate products had risen so that the payout extended far longer than anticipated. Prices of these solid bases have fluctuated recently. Before payout calculations are made, some thought should be given to possible long-term prices of the raw material to be used and their relation to future prices of conventional raw materials.

Nearly every solid used to produce bulk blended fertilizers can be used to produce fluids. This allows the production of a fertilizer with the unique advantages of fluids and the raw material cost of solids. It is expected that many future plants will be constructed for both bulk blending and suspension fertilizers using the same ingredients for both operations. Plants similar to the one in figure 5 already exist, and we will see more of them in the future.

Freight rates may increase even more as energy costs continue upward. This could encourage greater use of solids for suspension production as the shipping of low-analysis fertilizer ingredients containing water becomes more prohibitive. Plants constructed for the use of solids can easily use conventional raw materials, although they may be overdesigned for this purpose.

Production and marketing of suspension fertilizer made from solids will become a major way of getting fertilizer on to the farmer's field in an effective and efficient way.

Bibliography

1. F. P. Achorn, J. I. Bucy, and J. S. Lewis, Jr., ''Granular Diammonium Phosphate in Formulation of Fluid Fertilizers,'' *Solutions Magazine*, July-August 1973).

2. H. L. Balay, ''Savings Big Attraction for Using Solids in Suspension,'' *Fert. Solutions* (March-April 1977).

3. H. L. Balay ''Storage and Handling of Urea,'' Proceedings of the Florida Fertilizer and Limestone Conference (1976).

4. H. L. Balay and D. G. Salladay, ''Recent Developments in the Production and Use of Monoammonium Phosphate,'' paper presented at the Fertilizer Industry Round Table, October 26-28, 1976.

5. *Effects of Increased Energy Costs on Fertilizer Production Costs and Technology,* TVA Bulletin Y-84, November 1974.

6. W. E. Funk, I. H. Lehman, and T. Clements, ''Slurry Fertilizer: Equipment and Application Costs,'' thirty-ninth annual meeting, Council of Fertilizer Application, American Society for Horticultural Science, University of Massachusetts, Amherst, Massachusetts, August 28, 1963.

7. H. E. Mills, ''Slurry Fertilizers: Formulations, Handling and Application,'' *Fert. Solutions* (November-December 1962).

8. *New Developments in Fertilizer Technology.* 11th Demonstration, TVA Bulletin Y-107, 1976.

9. J. Silverberg, ''Suspension Fertilizers,'' *Commercial Fertilizer and Plant Food Industry*, August 1966.

10. J. Silverberg and H. K. Walters, Jr., ''Slurry Fertilizers - TVA Progress Report,'' *Commercial Fertilizer and Plant Food Industry,* April 1964.

11. R. D. Young and G. C. Hicks, ''Monoammonium Phosphate in a TVA-Type Ammonium Phosphate Granulation System,'' *Commercial Fertilizer and Plant Food Industry*, February 1967.

12. R. D. Young, G. C. Hicks, and C. H. Davis, ''TVA Process for Production of Granular Diammonium Phosphate,'' *Agricultural and Food Chemistry,* November-December 1962.

Table 1

Suspension Grades from 18-46-0 and Phosphoric Acid

		Pounds Per Ton of Product						
Ratio	Grade	Water	Clay[a]	10-34-0[b]	Ammonia (82.2-0-0)	Acid (0-54-0)	18-46-0	UAN Soln (32-0-0)	Potash (0-0-62)
1:3:0	11-33-0	524	30	95	47	349	955	-	-
1:3:0	10-30-0	679	30	-	44	334	913	-	-
1:3:1	8-24-8	678	30	-	35	267	731	-	259
1:3:3	6-18-18	615	30	-	26	200	548	-	581
1:2:2	8-16-16	599	30	-	24	178	487	165	517
1:1:1	12-12-12	566	30	-	18	134	365	499	388
2:1:1	16-8-8	534	30	-	12	89	244	832	259
3:1:1	18-6-6	518	30	-	9	67	183	999	194

[a] Amount varies with differences in properties of raw materials.

[b] 70 percent of phosphate as polyphosphate. Amount may change if amount of polyphosphate or impurity level changes.

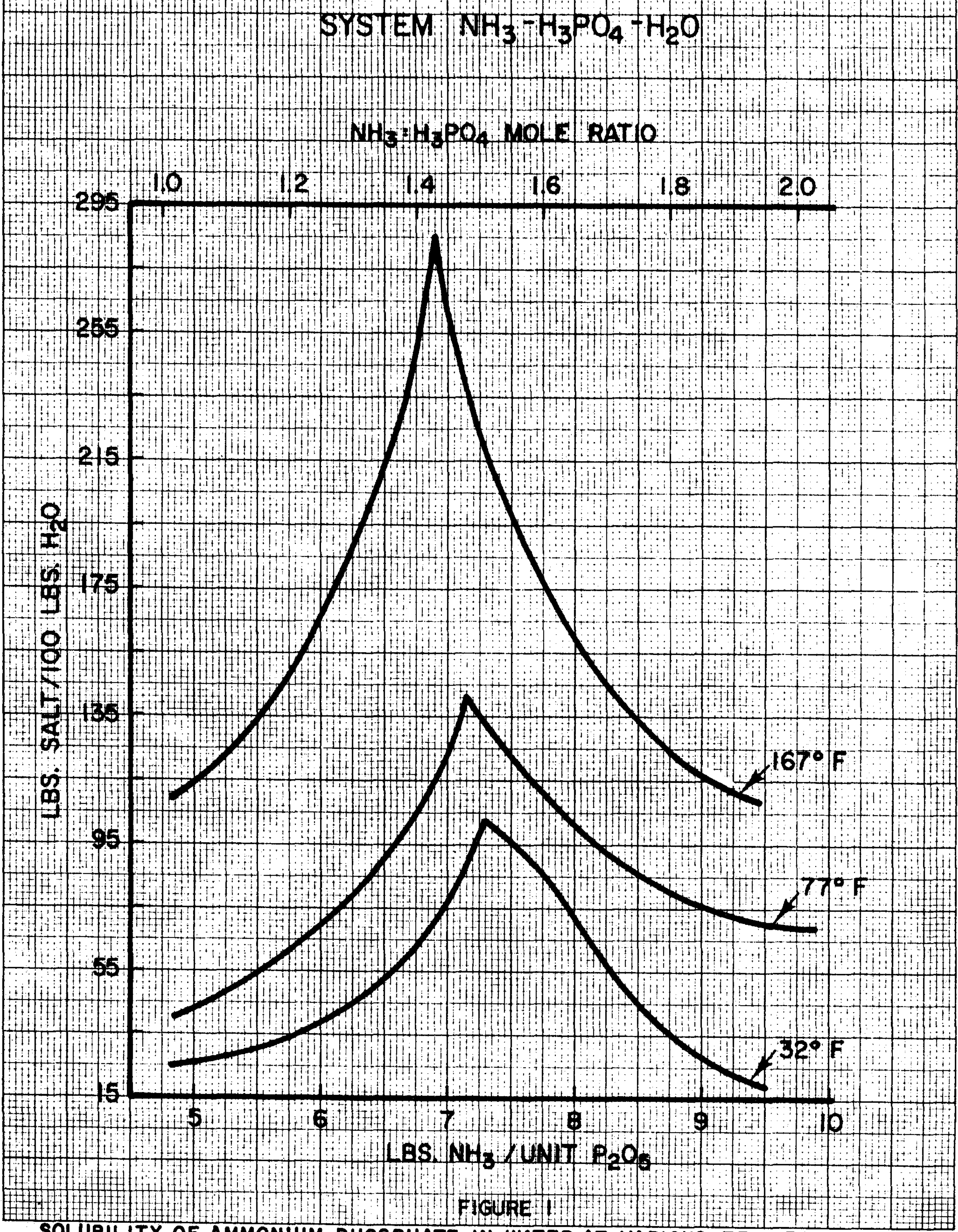

FIGURE 1

SOLUBILITY OF AMMONIUM PHOSPHATE IN WATER AT VARIOUS TEMPERATURES AND VARIOUS $NH_3:P_2O_5$ RATIOS

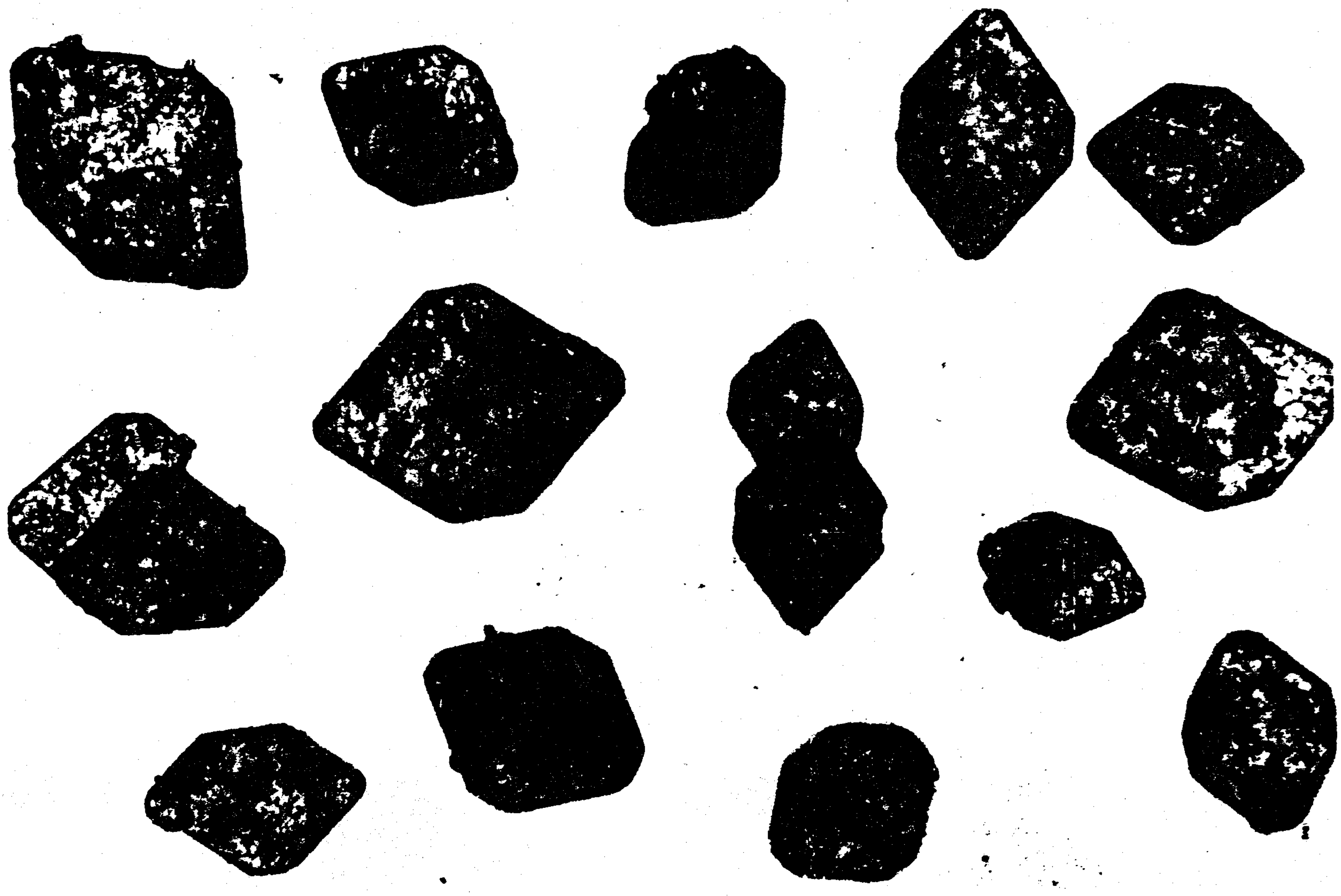

FIGURE 2
DIAMMONIUM PHOSPHATE CRYSTALS

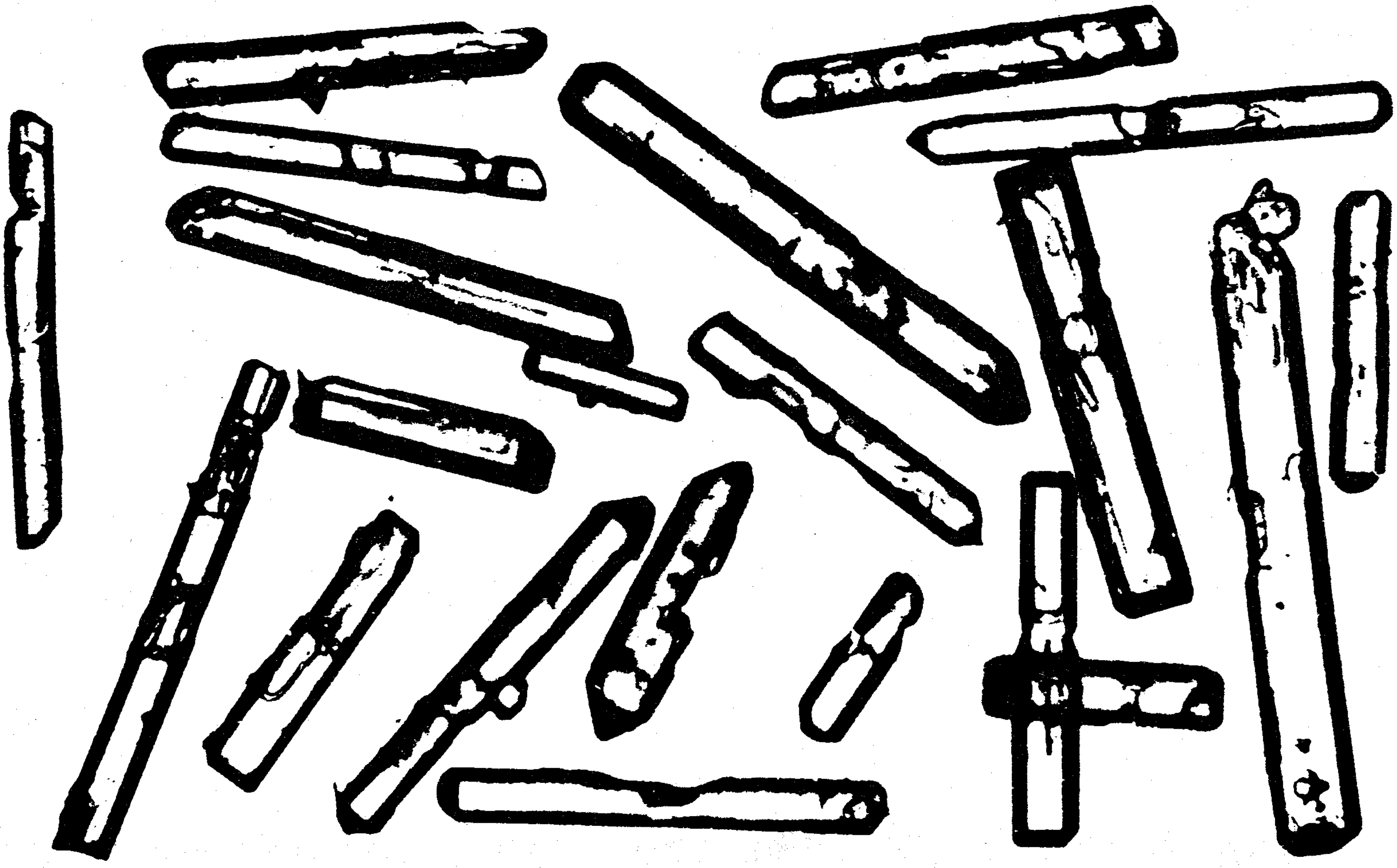

FIGURE 3
MONOAMMONIUM PHOSPHATE CRYSTALS

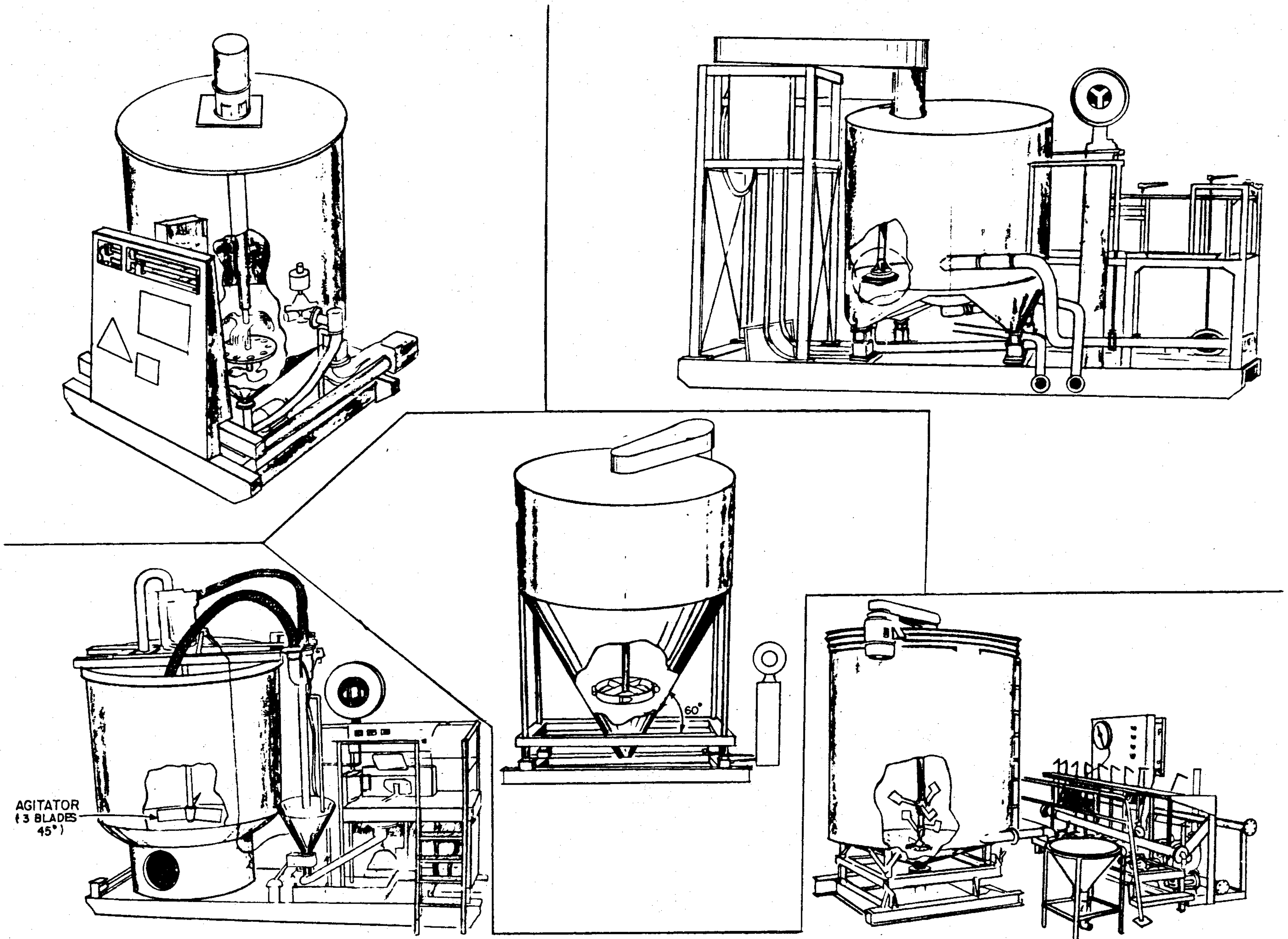

FIGURE 4
FIVE TYPES OF MIX TANKS FOR SUSPENSIONS

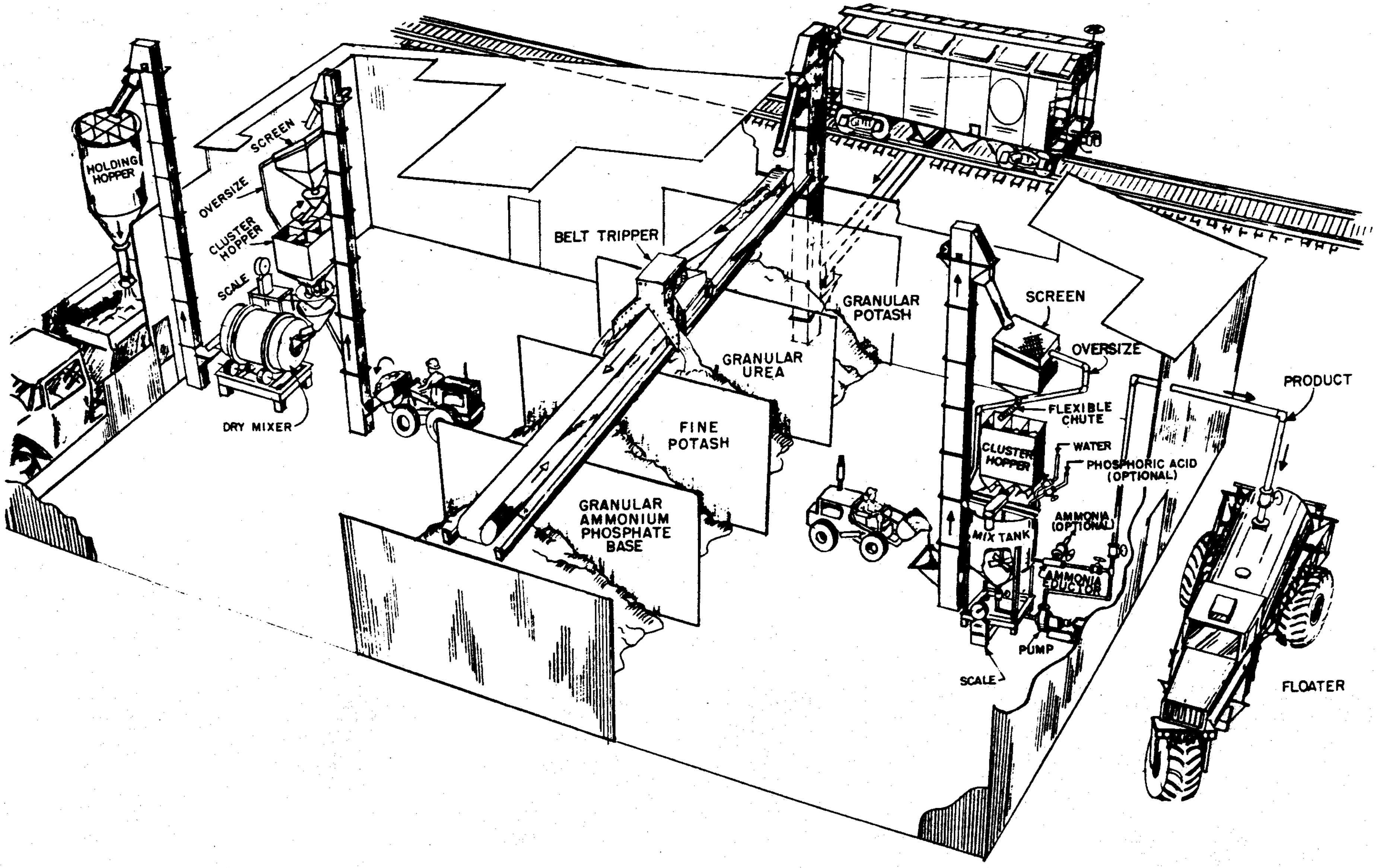

FIGURE 5

COMBINATION PLANT FOR PRODUCTION OF SUSPENSIONS AND BLENDS