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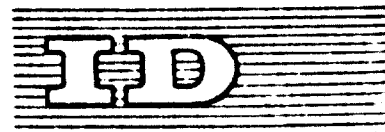
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Agenda item III/lk/iv

SUMMARY

NITROPHOSPHATE PROCESS USING DIRECT COOLED CONTINUOUS CRYSTALLIZATION^{1/}
(CHEMOPROJEKT-BAMAG PROCESS)

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One approach to nitrophosphate manufacture is the conversion of the phosphorus content of phosphate minerals to a plant available form by lowering the calcium content in the acidulation slurry from the nitric acid attack of phosphate rock by cooling and separation of crystallized calcium nitrate tetrahydrate (CN₄).

The use of direct heat transfer for cooling the acidulation slurry by means of an insoluble heat transfer medium converts the original Odda process to a fully continuous and automatized process with a minimum of equipment and maintenance. According to the requirements, it is possible to produce mother liquor -- i.e. crystallization process phosphoric acid -- which permits the production of NP/NPK fertilizers having a water soluble P₂O₅-content as high as 90 per cent (or even more), total nutrient content of about 50 per cent and a N : P₂O₅ ratio higher than 0.5.

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High purity of by-product CN_4 enables its further processing to nitrogen fertilizers by means of known processes.

The flowsheet and relevant process description of the Chemoprojekt-Bamag process is introduced and its principal process features are explained. Specific consumption figures of utilities per ton of P_2O_5 in mother liquor depend on the degree of CaO separation. Some examples for the incorporation of the crystallization process into fertilizer plants are discussed.

The second part of the paper deals with the use of the continuous direct cooled crystallizer within a NPK fertilizer plant which has been put on stream recently. The plant has a capacity of 60 tons per day of P_2O_5 (80 per cent water-soluble) as fertilizer using Morocco phosphate and 56 per cent nitric acid as feedstocks.

The plant is designed to produce three NPK formulas:

- a) 12 : 21 : 12 capacity 250 mtpd
- b) 16 : 16 : 16 capacity 375 mtpd
- c) 12 : 12 : 24 capacity 500 mtpd

According to the overall nitrogen balance a corresponding amount of ammonium nitrate solution is produced as by-product, which is, together with simultaneously produced calcium carbonate, processed into calcium ammonium nitrate in an existing facility.

A detailed process description is given and illustrated by a flowsheet.

The plant consists of the following main process steps:

nitric acid attack of phosphate rock, two-stage direct-cooled crystallization (Chemoprojekt-Bamag process), ammoniation and concentration of the mother liquor, pugmill granulation, drum drying and fluidized bed cooling for the NPK line, CN_4 is converted into ammonium nitrate and calcium carbonate using carbo-ammoniation and filtration of calcium carbonate (CFK-process) for the by-product line.

Typical examples show the high flexibility of this type of process with respect to the production of different NPK formulas in a given plant with only slight modifications practically not affecting the overall investment costs. The raw material and utility requirements are given for some typical NPK formulas. Based on average European conditions, capital investment and production costs are demonstrated.

Finally, possibilities are shown for using P_2O_5 mother liquor originating from a nitric acid attack slurry after crystallization of CN_4 using the Chemoprojekt-Bamag process, for example: NP or NPK production based on existing granulation technologies or production of phosphoric acid equivalent to super-phosphoric acid.



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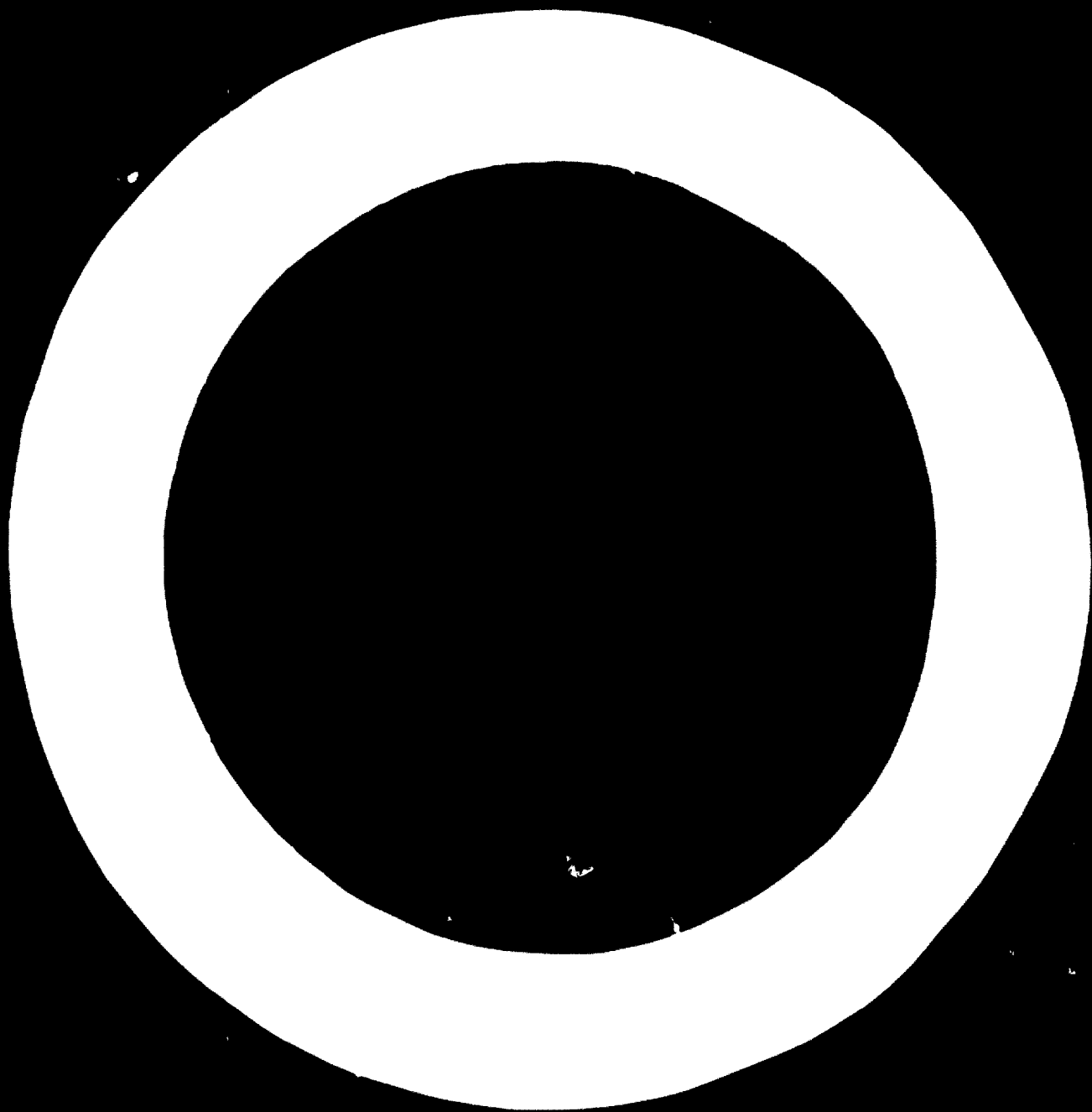
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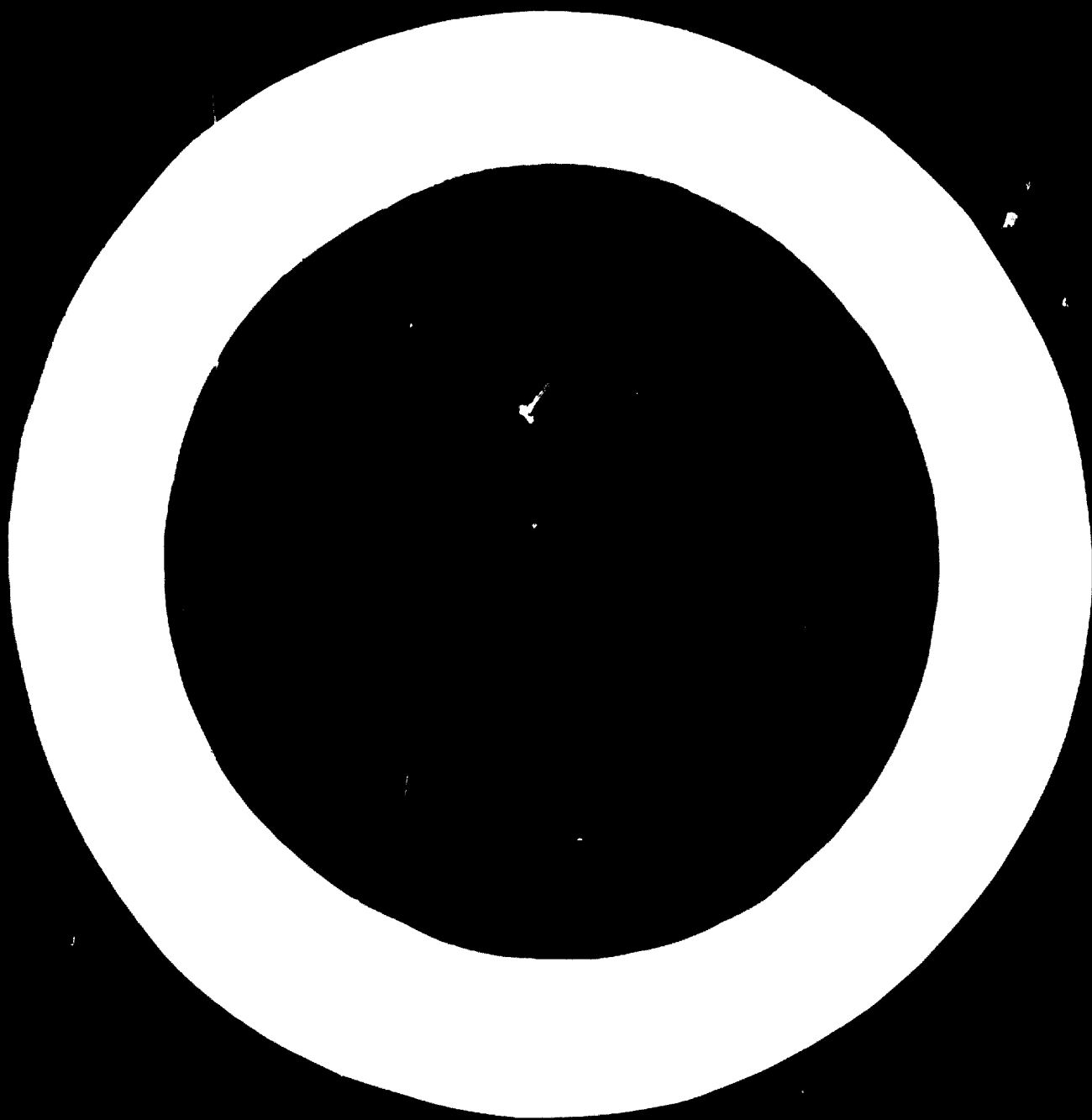
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Introduction

1. The purpose of this paper is to describe the technology of production, transportation, and distribution of liquid fertilizers, not including anhydrous or aqua ammonia which is the subject of another paper. Also, the present paper will not attempt to cover ammoniating solutions which are primarily intended for use in the production of granular solid fertilizers. The practices that will be described will be mainly those used in the United States, but practices in other countries will also be described insofar as the author's knowledge permits.
2. The principal liquid fertilizers used in the United States, other than anhydrous and aqua ammonia, are nitrogen solutions and liquid mixed fertilizers. Nitrogen solutions used for direct application are mainly nonpressure solutions containing no free ammonia. Liquid mixed fertilizers are those that contain at least two of the three primary plant nutrients, N, P_2O_5 , and K_2O . The term "liquid fertilizers" is used to include clear liquids containing no undissolved solids and suspensions which contain solids.

History of Liquid Fertilizers

3. Liquid fertilizers are often regarded as a modern development. However, waste liquid organic materials have been used as fertilizers for many centuries.
4. Sir Humphrey Davy experimented with solutions of inorganic salts as fertilizers as early as 1808 (1). Especially good results were reported with weak solutions of ammonium carbonate. Prior to 1840, Sir James Murray produced and marketed liquid mixed chemical fertilizers in Ireland. The

mixtures were sold in 30-gallon casks. In 1840, Liebig suggested that bones be dissolved in dilute sulfuric acid and the solution sprinkled on the soil before the plow. This advice was followed by some farmers (2). Gas liquor, an ammoniacal byproduct of coal gas manufacture, has been used for fertilizer in Great Britain since 1843.

5. Probably the first liquid fertilizer plant in the United States was built in Oakland, California, in 1923. Growth was slow in the next 25 years because of scarcity and high cost of suitable materials.

6. After World War II, increased supplies of nitrogen materials from synthetic ammonia and furnace-grade phosphoric acid favored expansion of liquid fertilizer production and use. By 1953, 22,000 tons of liquid mixed fertilizer was produced in California, constituting 9% of all mixed fertilizer in that state.

7. In the eastern and central parts of the United States the first known commercial production of liquid mixed fertilizers (other than packaged or bottled specialty products) was in a plant in Indiana. In 1955, 147 companies were reported to be making liquid mixed fertilizer in the United States. Of these, only 72 produced bulk liquid fertilizer for farm use, and only 25 were east of the Rocky Mountains.

Growth in Use of Liquid Fertilizers in the United States

8. Since 1955, production and use of liquid fertilizers in the United States have grown at a spectacular rate. One indication of the rate of growth of liquid mixed fertilizers in the United States is the increase in the number of plants which is shown in Figure 1. The number of plants increased from 335 in 1959 to over 1700 in 1968, and according to recent information, there are now over 2700. Official statistics indicate that the tonnage of liquid mixed

fertilizer has approximately doubled every 4 years during the last 12 years (1957 to 1969). Thus, in 1969, the latest year for which official data were available, the consumption was slightly over 2 million metric tons, about double the 1965 consumption. The rate of increase in consumption of nitrogen solutions has been equally rapid, from less than 200,000 tons in 1959 to 2.5 million tons in 1969. Incomplete data for 1970 and 1971 indicate that use of liquids is continuing to grow much faster than that of solids.

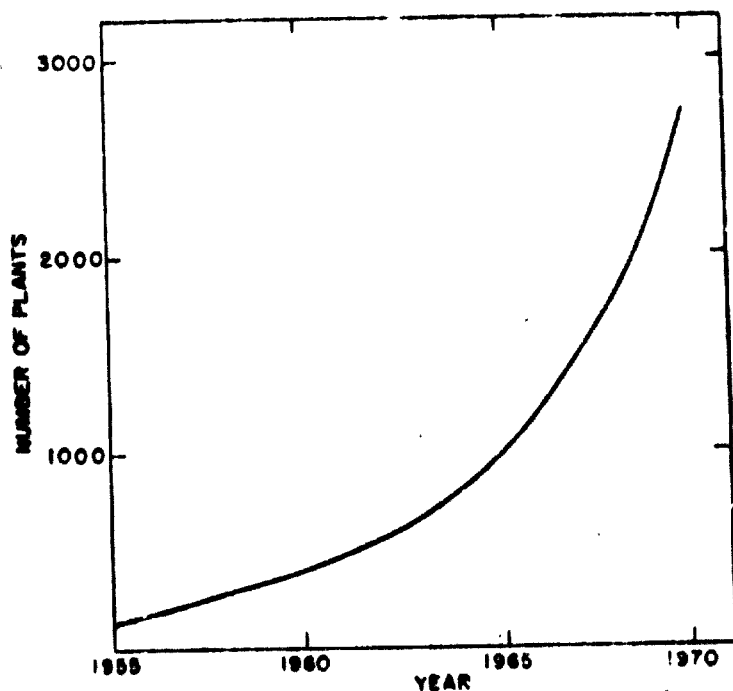


FIGURE 1
GROWTH OF LIQUID MIXED FERTILIZER INDUSTRY IN UNITED STATES

9. Data for 1969 show that consumption of liquids in all forms, anhydrous and aqua ammonia, nitrogen solutions, and liquid mixed fertilizers, constituted 24% of the total fertilizer use; on a plant nutrient basis, 28% of the N, P_2O_5 , and K_2O were in liquid form. Estimates for 1970 indicate that liquids account for 25% of the gross tonnage and 30% of the plant nutrient use.
10. The rapid growth of liquid mixed fertilizers is particularly interesting in view of the fact that the development was not planned by major industrial

organizations or by Government agencies. Instead, the growth resulted from the needs of farmers and the efforts of small, local industries to supply those needs. TVA participated by generating technological information when the need became evident. Major industry responded by making available the basic materials, although their response has lagged somewhat behind demand in the case of phosphatic materials.

11. The popularity of liquid nitrogen materials usually is ascribed in part to their lower cost as compared with solids, and no doubt cost is a factor, particularly in the case of anhydrous ammonia. Liquid mixed fertilizers, on the other hand, usually sell at a higher price than their solid counterparts, so some other explanation must be sought for the growing popularity of liquids.

12. The most frequently mentioned advantages of liquids are convenience, ease of application, and labor saving. Convenience means adaptability to rapid mechanical handling and absence of manual labor. The farmer need not lift anything heavier than the end of a hose. Liquids are dependably free flowing and can be accurately metered. Precise placement and even distribution are more easily attained with liquids than with solids. The time required for fertilizing a given area is often less for liquids than solids. Gardner (2) has presented an economic analysis which indicates that use of liquids may be economically advantageous in England when the costs of handling and spreading are taken into account.

13. Liquid fertilizers are adaptable to combination with many herbicides and insecticides; by using such mixtures, further saving in labor can be obtained. Micronutrients can be mixed with liquids; the small size of the local plants makes prescription mixing feasible.

14. Another favorite labor-saving combination of operations is irrigation and fertilization. Liquid fertilizer is injected into irrigation water.

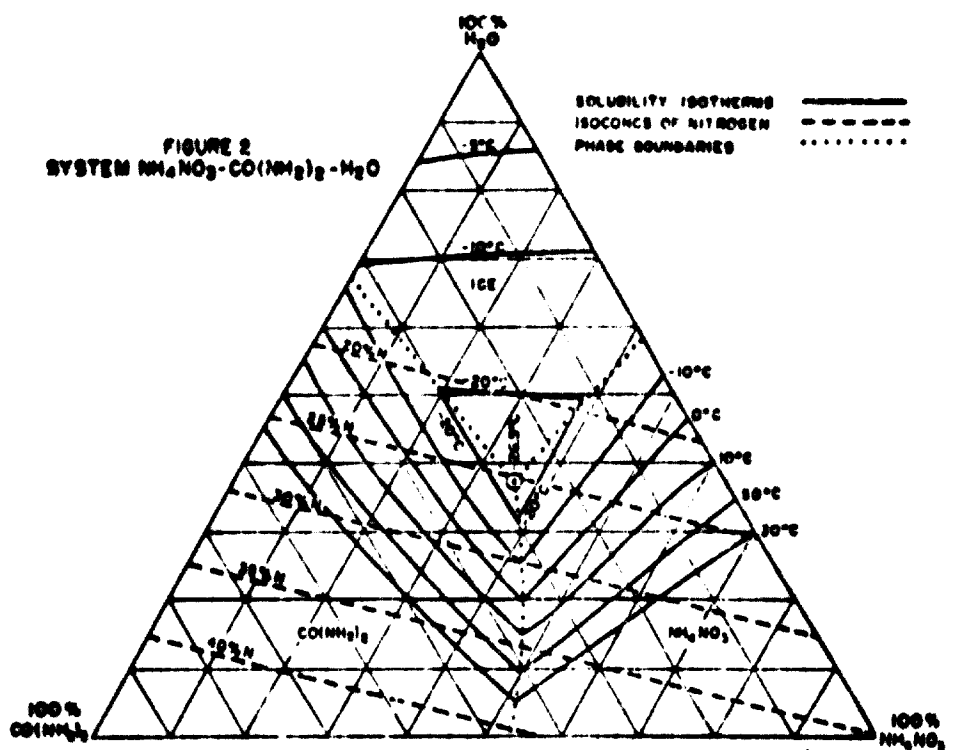
15. Liquid fertilizer is free from several faults that are often present in solids. Liquids are dependably free flowing, they are not dusty, they do not cake, they are unaffected by humid weather or even rain. They are (usually) homogeneous. They are adaptable to foliar application after suitable dilution.

16. From the viewpoint of manufacturers, the mixing equipment is simple and inexpensive. Problems of dust and fume which are prevalent in granulation operations are absent in liquid manufacture. Storage, handling, and loading for shipment are less expensive for liquids than solids. Pumps and piping for liquid handling are cheaper than conveyors, elevators, and power shovels, both in capital and operating costs.

17. Unlike granulation processes, a large-scale operation is not necessary for economic success in liquid fertilizer manufacture. Whereas the economic minimum scale for the manufacture of granular diammonium phosphate may be about 100,000 tons per year, a 10-34-0 liquid can be produced economically at one-tenth this output. However, this is possible only when the basic materials (urea, ammonium nitrate, ammonia, and phosphoric acid) are supplied from large-scale operations.

Nitrogen Solutions

18. By far the most common nitrogen solutions are the urea - ammonium nitrate (UAN) solutions. These solutions contain approximately equimolar proportions of urea and ammonium nitrate which give maximum solubility. Figure 2 is a phase diagram of the system urea - ammonium nitrate - water in which the components are indicated in percentage by weight.



19. The common grades of typical UAN solutions sold in the United States and their properties are shown below.

Composition, % by weight				Salting-out temperature, °C	Specific gravity at 15°C
N	Ammonium nitrate	Urea	Water		
32	44.3	35.4	20.3	0	1.33
30	42.2	32.7	25.1	-10	1.30
28	38.8	31.0	30.2	-18	1.28

20. In some countries a UAN solution containing 26% N is marketed; it has a salting-out temperature of about -25°C. As shown by Figure 2, the minimum possible salting-out temperature is -25.5°C which occurs at the ice - ammonium nitrate - urea triple point. The solution grade is about 25% N.

21. UAN solutions are often produced merely by mixing ammonium nitrate and urea solutions and water. Several plants produce urea solution by a "once-through" process and utilize the unreacted ammonia to make ammonium nitrate. When the ammonium nitrate and urea facilities are not at the same location,

prilled urea may be transported to the source of the ammonium nitrate solution and added to the solution while it is hot. Flaked urea has been used for this purpose, since flaking is less expensive than prilling.

22. Figure 3 is a diagram showing continuous production of UAN solution. Ammonium nitrate solution is produced continuously by neutralization of nitric acid with ammonia. The hot ammonium nitrate solution is mixed with hot urea solution from an adjacent urea synthesis unit. Water is added if necessary to dilute the solution to the desired grade. The solution is cooled to minimize corrosion of storage tanks.

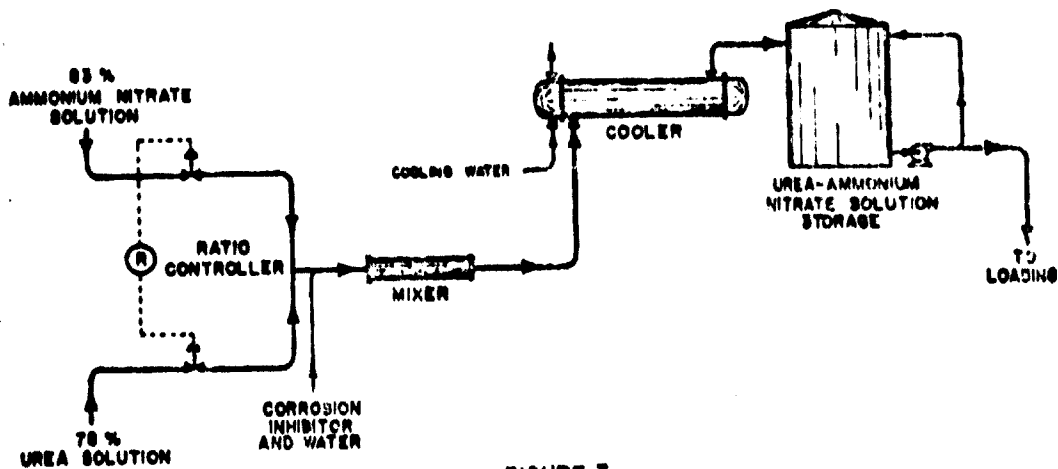


FIGURE 3
FACILITIES FOR PRODUCING UREA-AMMONIUM NITRATE SOLUTION

23. UAN solutions are somewhat corrosive to carbon steel tanks, but the life of steel tanks is long enough to make their use practical. The corrosion rate is decreased by adding enough free ammonia to keep the pH above 7. Also, various other corrosion inhibitors sometimes are used. Storage tanks at retail stations are often made of aluminum, which is more resistant to corrosion.

24. There is some use of straight ammonium nitrate solution for direct application; a solution containing 54.3% NH_4NO_3 and 45.7% water has a salting-out temperature of 1°C and contains 19% N. The solution is not popular because of its low concentration and because it is more corrosive than UAN solutions.

25. Since the costs of concentrating and prilling or granulating are avoided, it is logical that nitrogen solutions should be less expensive than solid nitrogen materials. The wholesale list price of UAN solutions delivered in the midwestern part of the United States in the spring of 1971 was equivalent to about \$149 per metric ton of N, whereas bulk ammonium nitrate or urea was priced at about \$161, about 8% higher. Various discounts from list price are often in effect on both solid and liquid nitrogen materials.

Liquid Mixed Fertilizers

26. The liquid mixed fertilizer industry in the United States consists of a large number (over 2700) of small plants¹ that compound mixtures, using materials supplied by larger manufacturers. The annual production per plant ranges from less than 500 tons to over 25,000 tons and probably averages less than 2000 tons. The smaller plants sell directly to farmers. Many of the plants also mix and sell solid fertilizers, and sell nitrogen solutions or anhydrous ammonia. Also, many of them are engaged in other agricultural services; sale of seeds and pesticides, purchasing grain, compounding and selling animal feed, ginning cotton, etc.

27. Liquid mixed fertilizer plants are classified as "hot mix" or "cold mix." A hot mix plant is one that uses phosphoric acid and ammonia; the heat of reaction gives this type of plant its name "hot mix." The cold mix plant uses ammonium phosphate solution and mixes it with other ingredients; no heat of reaction is involved. Such plants may be very simple and inexpensive. A "semihot mix" plant is one that derives part of its ammonium phosphate from

¹ The term "plant" denotes any facility that is equipped to produce mixtures whether by mechanical or chemical processes. It does not include dealers or merchants who only sell or distribute mixtures or materials.

phosphoric acid and ammonia and part from purchased ammonium phosphate (solid or solution). The proportion is such that little cooling is required, and the heat of reaction is helpful in dissolving solid materials such as potassium chloride and urea.

28. Liquid mixed fertilizers are often made to order and applied soon after mixing. For this reason the salting-out temperature is less important than that of the base solutions from which they are made. A salting-out temperature of 0°C is often used as a standard, although obviously the requirements depend on climate, season, and length of storage.

29. The principal materials used in liquid mixed fertilizers are ammonium phosphates (including polyphosphates), UAN solutions, "white" (fully soluble) potassium chloride, and solid urea. As mentioned previously, the nitrogen solutions are simple to produce and relatively inexpensive. White potash is available from several sources in the United States and Canada; its price is about 8% higher than "standard" fine potash that contains insoluble impurities, but 6% lower than granular potash. When sulfur is required, it is usually supplied as ammonium thiosulfate solution; ammonium sulfate or elemental sulfur is sometimes used in suspensions. The most common micronutrient is zinc; it may be supplied as the oxide, carbonate, or sulfate. All of these forms are soluble in ammonium polyphosphate solution, but not in orthophosphate. The zinc sulfate and oxide are also soluble in UAN solutions if sufficient ammonia is added to maintain the pH in the range of 7 to 8.

30. The main difficulty has been in getting an adequate supply of good-quality phosphatic material, and it is in this field that major technical developments have occurred and will occur. For this reason a large part of this paper will be devoted to phosphatic materials for liquid fertilizers.

Superphosphoric Acid and Ammonium Polyphosphates

31. When the liquid fertilizer industry was getting started, the principal phosphatic material was electric-furnace orthophosphoric acid. The usual practice was to neutralize the acid with aqua ammonia to produce an 8-24-0 ammonium phosphate solution and then add UAN solutions and potash as required.

32. The available supply of electric-furnace acid for fertilizer purposes was limited. Also, the concentration of mixtures obtainable in the ammonium orthophosphate system was rather low.

33. The use of superphosphoric acid caused a major breakthrough in the technology of liquid fertilizers. "Superphosphoric acid" is a term generally applied to phosphoric acid containing a substantial percentage (usually 40 to 80%) of its P_2O_5 in the form of polyphosphoric acids. The use of superphosphoric acid has the following advantages.

- a. Higher analysis base solutions can be prepared because of the high solubility of ammonium polyphosphates.
- b. Since polyphosphates will sequester the impurities in wet-process acid, this acid can be used in the preparation of clear solutions.
- c. Substantial amounts of micronutrient elements can be dissolved in ammonium polyphosphate solution, whereas many of these elements are essentially insoluble in ammonium orthophosphate solution.
- d. The high concentration of superphosphoric acid (over 70% P_2O_5) results in freight savings if the acid is shipped.

34. Although superphosphoric acid has been known for many years, its first known commercial use in making liquid fertilizers was in 1957 when superphosphoric acid produced by the Tennessee Valley Authority was shipped to the West Kentucky Liquid Fertilizer Company, at Hopkinsville, Kentucky, where it was

ammoniated to make a base solution (11-33-0). The superphosphoric acid contained about 76% P_2O_5 , and about 50% of the P_2O_5 was present as polyphosphoric acids, mainly pyro. This concentration was chosen because it was near a eutectic between orthophosphoric and pyrophosphoric acid which occurs at 75.4% P_2O_5 and 16°C. TVA had only limited success in promoting the use of superphosphoric acid by liquid fertilizer manufacturers. The main drawbacks were the scarcity and high cost of tank cars for transporting the acid and occasional difficulty with crystallization of the acid. Also, few liquid fertilizer manufacturers had suitable tanks for storing acid.

35. In 1959, TVA started manufacture of the 11-33-0 base solution from acid of about 76% P_2O_5 content. The grade was changed in 1960 to 10-34-0 which had a lower salting-out temperature. This solution became quite popular with liquid fertilizer manufacturers; it was shipped in mild steel tank cars or trucks and stored in mild steel tanks. Also, it relieved the manufacturers of the need for carrying out any chemical reactions. In 1962 the grade was changed again to 11-37-0, which was made from acid of 79 to 80% P_2O_5 content with a polyphosphate content of 70 to 75%. A typical sample of 11-37-0 contained 27% of P_2O_5 as orthophosphate, 42% as pyrophosphate, 20% as tripolyphosphate, and 11% as higher polyphosphate. The solution has a pH of 5.8 to 6.2. Its viscosity is 80 centipoises, and its specific gravity is 1.4 at 21°C.

36. Several advantages of the 11-37-0 over earlier solutions soon became evident. Its higher polyphosphate content increased its sequestering ability. The solubility curve is relatively flat in the region of maximum solubility, allowing more latitude in N: P_2O_5 ratio and pH (see Fig. 4, 12). The 11-37-0 could be stored for several months at -18°C without crystallization. When crystals form, they are small, thin crystals of $(NH_4)_5P_3O_{10} \cdot 2H_2O$ that

redissolve readily when the solution warms up; crystallization of solutions of lower polyphosphate content yielded large, thick crystals of $(\text{NH}_4)_2\text{HPO}_4$ that were difficult to dissolve.

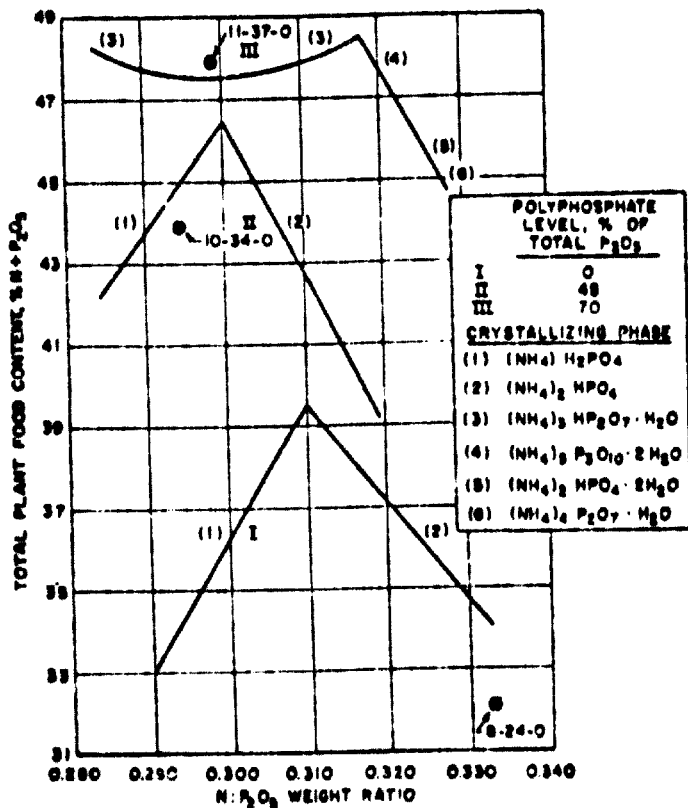


FIGURE 4
EFFECT OF POLYPHOSPHATE LEVEL AND N:P₂O₅ WEIGHT RATIO ON SOLUBILITY OF AMMONIUM POLYPHOSPHATES AT 0°C

37. Advantage was taken of the good cold weather storage properties of 11-37-0 to store substantial quantities in the northern Midwest States. Demand for liquid fertilizer is highly seasonal, and a shortage of tank cars often develops in the peak season. To ensure an adequate supply and to take advantage of seasonal discounts, some producers purchased 11-37-0 in the autumn and stored it through the winter. Winter temperatures in the northern states often go as low as -29°C and may average as low as -18°C for as long as a month. Winter storage of 11-37-0 under these conditions has proved entirely satisfactory.

38. More recently TVA has increased the polyphosphate content of 11-37-0 to 75% minimum (usually about 80%) and has introduced a new grade, 12-44-0, also containing a minimum of 75% of the P_2O_5 in the polyphosphate form. These solutions contain increased proportions of tripolyphosphate and longer chain polyphosphates which are more effective for magnesium sequestration than pyrophosphate.

39. These high-polyphosphate solutions have a strong tendency to supercool, so much so that determination of salting-out temperature is difficult. The supercooling is sufficiently dependable that use can be made of it in commercial practice. "Stability" tests are made in which the samples are stored at $0^\circ C$ for 1 to 6 months. Approximate data showing stability of ammonium polyphosphate solutions containing about 70 to 80% of their P_2O_5 in polyphosphate forms are shown in Figure 5. For the 80% polyphosphate level, the highest concentration stable at $0^\circ C$ is obtained at a relatively low N: P_2O_5 ratio (12-44-0 = N: P_2O_5 ratio of 0.27). This solution has a lower pH than 11-37-0 (about 5.6 vs. 6.2). The low pH causes relatively rapid hydrolysis at temperatures above $20^\circ C$, so it should be well cooled or used soon after production. It may be converted to 11-37-0 by addition of water and ammonia, or it may be utilized in sequestration of wet-process acid.

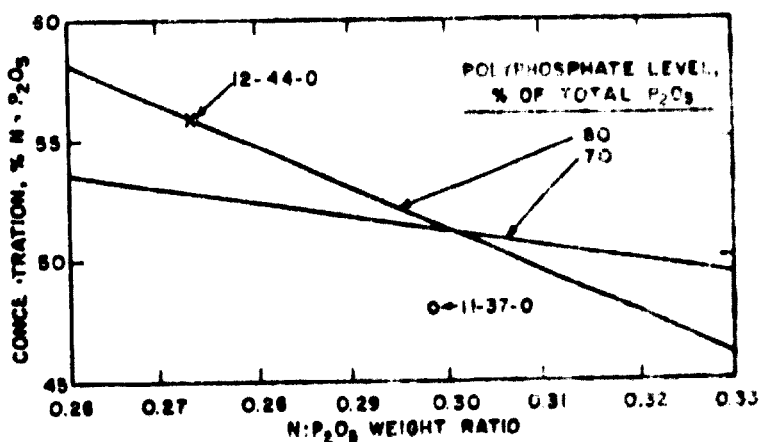


FIGURE 5
STABILITY OF AMMONIUM POLYPHOSPHATE SOLUTIONS AT $0^\circ C$

40. In 1966, TVA started production of a solid ammonium polyphosphate, 15-62-0, containing a minimum of 50% of its P_2O_5 in the form of polyphosphates. The solid material has an obvious advantage in reducing shipping cost; it is used to make liquid fertilizer by dissolution in water and addition of ammonia to produce 10-34-0 base solutions. Typical analyses of these TVA products are shown below.

Grade	Liquids				Solid
	<u>10-34-0</u>	<u>11-37-0</u>	<u>12-44-0</u>	<u>15-62-0</u>	
Concentration of acid, % P_2O_5	76	79-80	80-81	80-81	76.5
Species of distribution, % of total P_2O_5					
Ortho	49	29	20	16	39
Pyro	42	42	37	36	36
Tripoly	8	21	23	24	3
Tetrapoly	1	5	10	13	2
Higher	0	3	10	11	2

41. The high-polyphosphate materials are especially useful in sequestration techniques which will be described later.

42. All of the TVA materials described above were made from elemental phosphorus that was produced by the electric-furnace process. In 1958, TVA and others started experimental studies of production of superphosphoric acid by concentrating wet-process phosphoric acid. This work ultimately resulted in several commercially successful processes.

43. The TVA pilot plant (5) produced superphosphoric acid by concentrating wet-process acid in a direct-fired evaporator. At least two companies in the United States now use this process in large-scale production facilities. Several similar commercial-scale units are in operation in Europe (6).

44. Some other firms use vacuum evaporators heated by high-pressure steam (7) or Dowtherm (8).

45. Production of superphosphoric acid from elemental phosphorus in the TVA plant has been described (9). A modification of this plant permits production of "mixed superphosphoric acid" from elemental phosphorus and wet-process acid (10). TVA and one other organization now produce mixed superphosphoric acid. Usually 20 to 40% of the P_2O_5 in this product is derived from wet-process acid.

46. Current production of wet-process superphosphoric acid in the United States is estimated at about 450,000 metric tons of P_2O_5 per year. In addition, superphosphoric acid produced from electric-furnace or mixed acid for fertilizer use is estimated to amount to at least 150,000 tons per year.

47. Thus, the current annual production rate of superphosphoric acid is estimated at about 600,000 metric tons of P_2O_5 , and additional capacity is planned. Most of this production goes into liquid fertilizers.¹ In addition, perhaps as much as 200,000 tons of orthophosphoric acid is used in liquids through techniques such as sequestration, direct production of polyphosphates, and orthophosphate suspensions.

48. The conversion of superphosphoric acid to ammonium polyphosphate solution is relatively simple. Figure 6 shows a sketch of the TVA plant. Superphosphoric acid, ammonia, and water are metered continuously to the reactor. The concentration of the solution is controlled by monitoring the specific gravity, and the $N:P_2O_5$ ratio is controlled by holding the pH in the desired range (5.8 to 6.2 for 11-37-0). The temperature in the reactor is held at about

¹ Substantial amounts of superphosphoric acid that are known to be used for production of animal feed supplement are excluded from this estimate. However, some unknown amount of ammonium polyphosphate solution is used in animal feed, for control of forest fires, and other uses.

75°C by circulating the solution through the cooler. The solution drawn off from the reactor is cooled by water to about 35°C in a heat exchanger and stored in mild steel tanks. The production rate is about 15 tons of 11-37-0 per hour. The solution in storage is further cooled by refrigeration to about 20°C to minimize hydrolysis of polyphosphate to orthophosphate that would otherwise occur at summer temperatures.

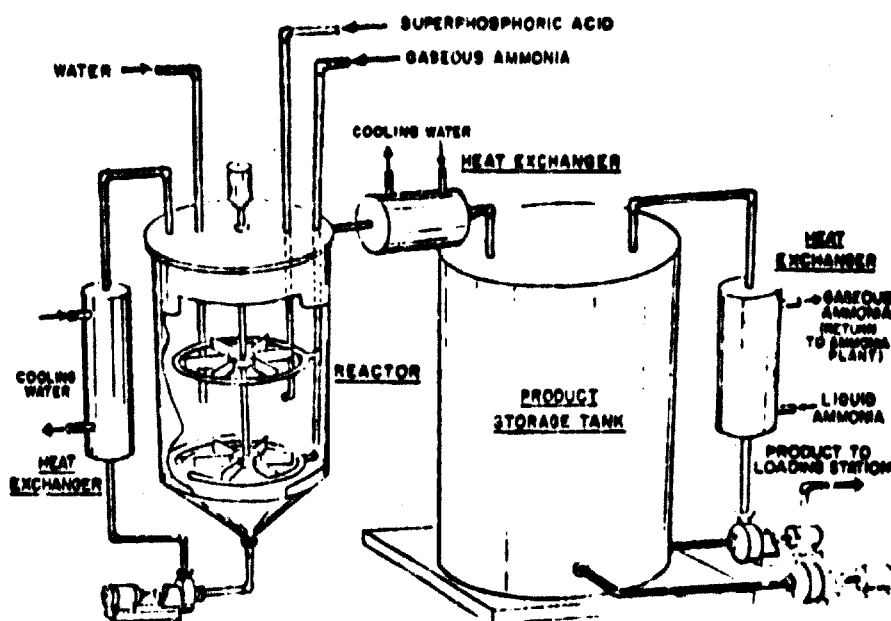


FIGURE 8
TVA PLANT FOR PRODUCTION OF 11-37-0 AND 12-44-0 LIQUID FERTILIZER

Distribution Patterns

49. Some companies sell superphosphoric acid as such, and some convert it to base solution, usually 10-34-0, for sale to liquid mixed fertilizer manufacturers. In either case, nearly all superphosphoric acid is converted to base solution soon after it is made, either by the manufacturer or by the purchaser. Very little superphosphoric acid is stored. Superphosphoric acid is shipped by rail in insulated, stainless steel-lined tank cars. The base solutions 10-34-0, 11-37-0, etc., may be shipped by rail or barge and stored in plain steel tanks. Recently one company has transported 10-34-0 and UAN solution by pipeline.

50. According to a recent estimate, at least 75 plants produce base solutions; most of them use purchased superphosphoric acid. Many of them sell at least part of their production to small cold mix plants.

Quality of Superphosphoric Acid

51. The industry recognizes three types of phosphoric acid; black, green, and white. Black acid is produced from uncalcined phosphate rock (usually Florida rock). The black coloration is caused by carbonaceous matter. Green acid is made from calcined rock and usually is transparent. In some cases the carbonaceous matter in black acid is oxidized by treatment with nitrates or nitric acid or other oxidizing agents. Such acid may be yellow, amber, green, or other colors, depending on the treatment. Electric-furnace acid is generally referred to as "white acid." Green or white acid is preferred to black acid and usually sells at a premium of about \$5 per ton of P_2O_5 . The color classification applies to both orthophosphoric and superphosphoric acids and base solutions made from them. Some phosphate rocks yield green acid without calcination or other treatment, but all phosphate rocks commonly used in the United States require treatment if a transparent acid is desired.

52. Naturally the color of a clear wet-process acid depends on its impurities. It is possible that some phosphate rocks may yield products of some color other than green. The green color in most commercial acids is attributed to its iron and chromium content.

53. The impurity content of wet-process acid naturally depends on the phosphate rock from which it was made and the extent of sludge removal. Phosphoric acid intended for superphosphoric acid is first concentrated to about 54% P_2O_5 , and insoluble impurities are partially removed by settling or centrifuging. The sludge is utilized in production of triple superphosphate or other solid fertilizers, and the clarified acid is further concentrated to superphosphoric acid. Most of the fluorine (and silicon) is eliminated during

the concentration step as SiF_4 . Since magnesium is a particularly troublesome impurity, some companies have developed methods for partial removal of magnesium. The details of the methods are not common knowledge.

54. The following tabulation gives analyses of superphosphoric acid prepared from various phosphate rocks.

Type of rock	Florida	Western U. S.	North Carolina	Morocco	Togo	Taiba
Calcination	No	Yes	Yes	No	No	No
Composition, % by weight						
Total P_2O_5	72.9	72.5	71.2	72.4	73.0	72.1
Ortho P_2O_5	31.8	34.0	37.6	25.1	35.3	27.1
Fe_2O_3	2.2	1.2	1.4	0.6	1.9	2.4
Al_2O_3	1.8	3.0	1.3	0.4	0.9	0.5
F	0.3	0.3	0.4	0.1	0.1	-
SO_3	2.0	2.1	3.4	2.7	1.7	3.3
MgO	0.3	0.8	0.6	1.1	0.1	0.1
Color	Black	Green	Green	Green	Dark	Dark
Polyphosphate content, % of total P_2O_5	56	53	47	65	52	62.5

Pricing of Phosphoric Acids and Base Solutions

55. List prices of wet-process phosphoric acid in the spring of 1971, delivered in the midwestern area of the United States, were about \$166 per metric ton of P_2O_5 for orthophosphoric acid and \$177 for superphosphoric acid. These prices include freight charges which may amount to as much as \$38 per metric ton of P_2O_5 .

56. The midwestern area is roughly 1600 kilometers from the nearest phosphate mining area. For such distances there is an appreciable saving in freight which partially offsets the higher cost of superphosphoric acid. In areas nearer the phosphate mines, a greater cost differential between orthophosphoric and superphosphoric acid may be expected. For instance, the freight on fertilizer-grade phosphoric acid (either 54 or 70% P_2O_5) from Lee Creek, North Carolina, to Des Moines, Iowa, is about \$20.70 per metric ton of material if shipped in 50-ton carloads or \$18.30 in 100-ton carloads. There are various discounts for quantity, season, etc. Contract prices for orthophosphoric acid

in large quantities f.o.b. Florida in summer or autumn have been as low as \$88 per metric ton of P_2O_5 .

57. The list price for 10-34-0 base solution in the spring season of 1971 in the Midwest was \$78.30 per metric ton, which is equivalent to \$178 per ton of $N + P_2O_5$. For comparison, the price of granular diammonium phosphate (18-46-0) was \$88 per ton, equivalent to \$138 per ton of $N + P_2O_5$. Thus, the liquid material was about 29% more expensive than the solid.

Sequestration

58. The term "sequestration" is generally used to denote the ability of polyphosphates to hold in solution various metallic compounds that are insoluble in ammonium orthophosphate solutions. The principal impurities in phosphoric acid which are sequestered are iron, aluminum, and magnesium compounds. Various added micronutrient compounds also may be sequestered, including zinc and copper.

59. Superphosphoric acids often contain more than enough polyphosphate to sequester their own impurities, so liquid mixed fertilizer producers often use a combination of orthophosphoric acid with superphosphoric acid or more often ammonium polyphosphate solution. Base solution made from electric-furnace superphosphoric acid such as TVA's 11-37-0 is particularly useful for this purpose because it has very little impurities of its own and because of its unusually high proportion of polyphosphate.

60. Figure 7 is a sketch of a typical plant that uses the sequestration technique. The proportion of sequestrant (ammonium polyphosphate solution) may vary widely, depending on its polyphosphate content, the impurities in the orthophosphoric acid, and other factors. When using 11-37-0, as little

as 20% of the P_2O_5 from this source may be sufficient for nonpotash grades, whereas for potash-containing grades, at least 30% is required. TVA's 15-62-0 also has been used successfully for sequestration.

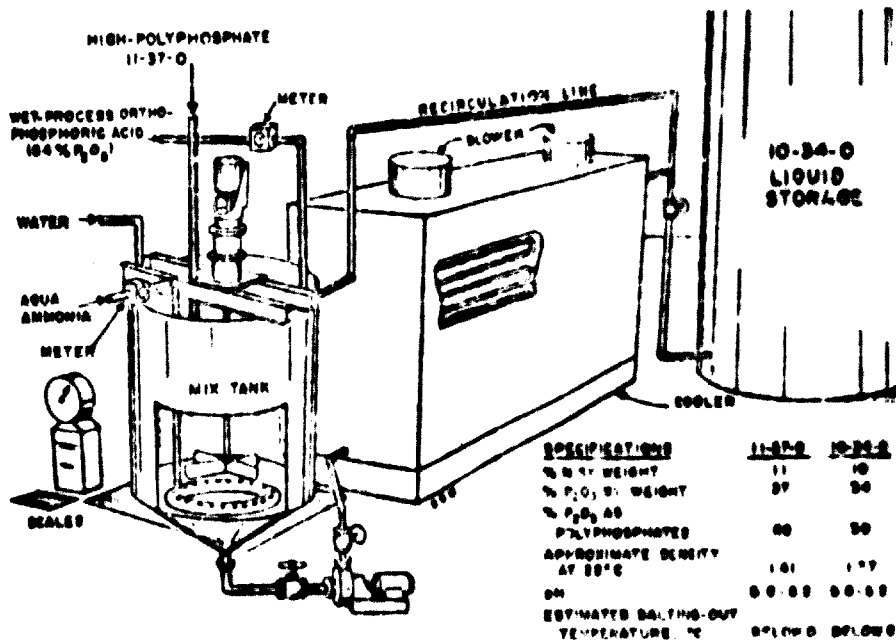


FIGURE 7
PRODUCTION OF 10-34-0 FROM MERCHANT-GRADE WET-PROCESS PHOSPHORIC ACID
AND HIGH-POLYPHOSPHATE 11-37-0

61. Small plants often use batch mixing; a common procedure is to first add water, UAN solution, and 11-37-0 to the mixing tank; then wet-process acid and aqua ammonia are added simultaneously, keeping the pH at about 6.6 to minimize hydrolysis. The potash is added last.
62. Complete mixtures usually are made to order, although in some cases a popular grade may be prepared in advance and stored.
63. "Spent" phosphoric acid from aluminum-treating processes is available at low cost in some locations. The spent acid contains aluminum compounds as its principal impurity. This acid also may be utilized by the sequestering technique.

Direct Process Ammonium Polyphosphate

64. Production of superphosphoric acid requires a substantial amount of heat, and when it is ammoniated, such heat is liberated. "Direct" processes aim to utilize the heat of reaction to produce ammonium polyphosphate without the intermediate step of superphosphoric acid production.

65. The TVA direct process pilot plant is shown in Figure 8.

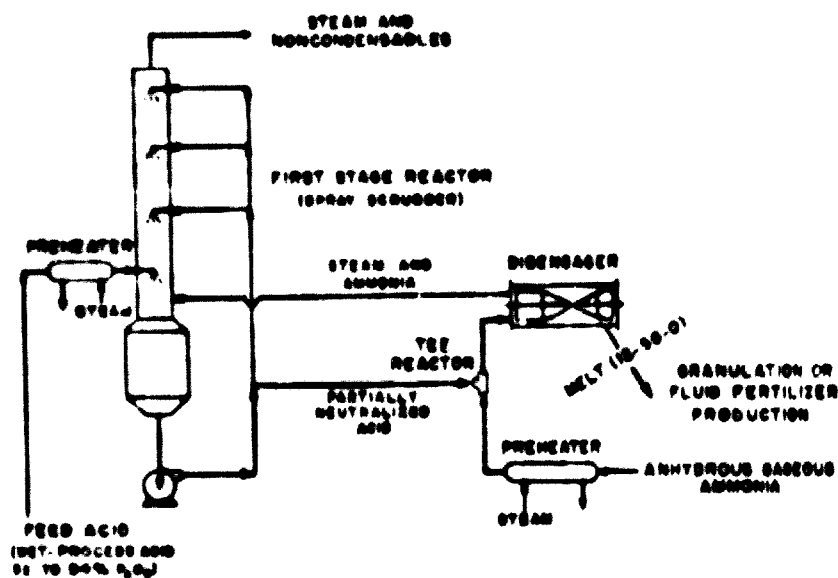


FIGURE 8
REACTION SYSTEM OF TVA DIRECT AMMONIUM POLYPHOSPHATE PROCESS

66. Merchant-grade wet-process acid (52 to 54% P₂O₅) is preheated and fed to a simple spray-type scrubber for recovery of ammonia evolved in the process. Partially neutralized acid from the scrubber is fed to one branch of a simple pipe tee reactor where ammoniation is completed by heated gaseous ammonia fed to the other branch of the tee. The rapid and vigorous reaction in the tee results in a temperature of about 230° to 240°C that drives off the remaining water to form polyphosphate melt. The melt, which is very foamy when using uncalcined Florida rock, passes to a rotary disengager where steam and excess ammonia are stripped out. Ammonia is recovered in the scrubber, and the water vapor is evolved. The fluid melt of about 12-58-0 grade has a

polyphosphate content of 35 to 50%. It can be readily converted to ammonium polyphosphate liquids and suspensions (10-34-0 and 11-37-0 grades) with about half of the phosphate as polyphosphate. Alternatively, the melt may be converted to a granular solid, although granulation is difficult at polyphosphate levels above 35%.

67. The production of clear liquids by the direct process is difficult when using phosphoric acids commonly available in the United States because of impurities that form precipitates. The most difficult problem is with magnesium compounds. The direct process has been used successfully to make clear ammonium polyphosphate liquids in France, using acid of lower impurity content.

68. The polyphosphate level of the products can be increased above 50% by using more concentrated incoming acid or by supplying more external heat.

69. In a modification of the direct process, superphosphoric acid of relatively low polyphosphate content may be converted to ammonium polyphosphate solution of high polyphosphate content. For this purpose, only the tee reactor is required; any excess ammonia and water vapor are absorbed in the ammonium polyphosphate solution. By this method, solutions with an 80 to 90% polyphosphate level were produced from acids containing as little as 10% of their P_2O_5 in the form of polyphosphate.

70. Figure 9 is a simplified diagram of the process as carried out in a TVA pilot plant. No preheat of acid or ammonia is necessary except that it may be desirable to preheat the acid to about 65°C to lower its viscosity sufficiently for pumping. The reaction between the superphosphoric acid and ammonia occurs in the tee and pipeline where the two materials mix; temperatures in this pipe range from 340° to 390°C. The reaction products--high-polyphosphate melt, steam, and excess ammonia--are quenched in the cooled solution

where the melt is dissolved and the steam and excess ammonia are absorbed. Advantages of this system are listed below.

- a. Superphosphoric acid of low polyphosphate content may be used which is easier to manufacture. Transportation and handling are easier because of lower viscosity.
- b. The system is very simple and inexpensive.
- c. The product containing 80% or more polyphosphate is more concentrated and has improved sequestration properties, especially for preventing precipitation of magnesium compounds.

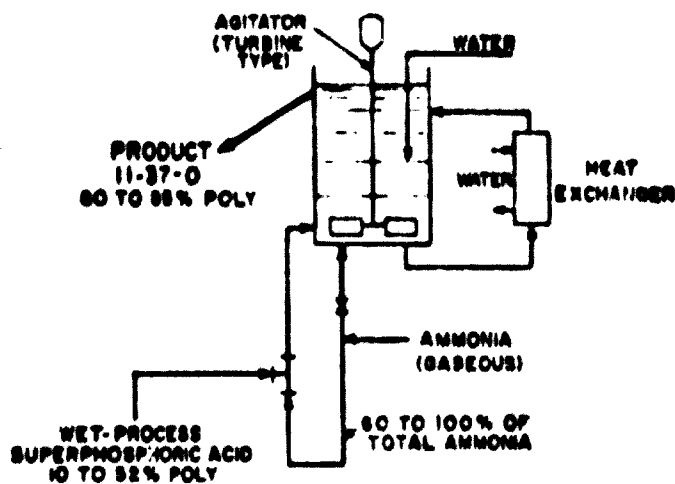


FIGURE 9
PRODUCTION OF 11-37-0 LIQUID FERTILIZER OF
HIGH POLYPHOSPHATE CONTENT USING
WET-PROCESS SUPERPHOSPHORIC ACID

Hydrolysis of Ammonium Polyphosphate Solutions

71. Ammonium polyphosphate solutions hydrolyze at rates that are strongly dependent on temperature and pH. The following tabulation shows the effect of temperature on rate of hydrolysis of TVA 11-37-0 solution (pH 6.0) initially containing 69% of its P_2O_5 as polyphosphate.

<u>Temperature,</u> <u>°C</u>	<u>Monthly decrease</u> <u>in polyphosphate content,</u> <u>% of polyphosphate initially present</u>
27	2.2
38	9.4
43	18.8
49	30.4

72. Thus, in warm climates, refrigerated storage may be necessary to prevent excessive loss of polyphosphate content and consequent precipitation of crystals or impurities. As mentioned previously, TVA uses refrigeration to keep 11-37-0 solution in storage tanks at about 20°C during the summer. At this temperature the rate of hydrolysis is inconsequential.

73. The rate of hydrolysis of ammonium polyphosphate in the soil is, in general, much more rapid and depends strongly on microbiological activity.

Purification of Phosphoric Acid or Solutions

74. The difficulty with impurities in wet-process acid has led to consideration of various schemes for purification. Calcination of the phosphate rock improves the appearance of the acid, and facilitates separation of the sludge. The cost of calcination of Florida rock is about \$5 per ton of P₂O₅, but there are compensating advantages (elimination of antifoam chemicals and increased filtration rates). Increased use of calcination is expected. Solvent extraction methods are available that will remove a major part of the inorganic impurities. Also, it is possible to ammoniate wet-process acid and separate the solid impurities by filtration or settling. One company in Canada markets an 8-24-0 ammonium orthophosphate solution that is produced in this way. Similarly, a fully soluble crystalline diammonium phosphate can be made by processes that involve removing solid impurities after or during ammoniation. One such process was developed by TVA on a pilot-plant scale (11). Commercial use of soluble diammonium phosphate in liquid fertilizers has been

reported in Europe. Studies of uses of pure diammonium phosphate in liquid fertilizer formulations have been reported by TVA (12).

75. One drawback of most of these purification processes is the utilization of the impurities which contain a substantial percentage of the P_2O_5 in the original acid. The impurities may be incorporated in solid fertilizers, but the quality of the solid products may be adversely affected. One company in Mexico is constructing facilities to purify a portion of its acid for liquid fertilizer use. The technical and financial success of this venture may determine whether other producers follow suit.

Solubility Problems

76. High-analysis nonpotash liquid fertilizers are readily prepared from ammonium polyphosphate and UAN solutions (e.g., 22-11-0, 19-19-0, and 15-30-0). However, grades containing potassium chloride are relatively low in analysis, particularly when the supplemental nitrogen is supplied as UAN solution. Potassium nitrate which has a low solubility at $0^\circ C$ is formed by reaction of ammonium nitrate with potassium chloride. Use of urea instead of UAN solution improves the solubility somewhat; for instance, a 7-7-7 is the highest grade soluble at $0^\circ C$ when UAN solution is used, whereas 9-9-9 is satisfactory when made with urea.

77. To circumvent the solubility problem, some companies encourage farmers to apply potash separately, in solid form. For instance, the potash may be applied by broadcasting in the autumn and the nitrogen and phosphate applied in the spring in liquid form. Some success in farmer acceptance of this program is reported in some areas.

78. Very high analysis potash-containing liquids are possible when the potash is present as potassium polyphosphate. One company markets a 0-26-27 solution made by reaction of potassium hydroxide with superphosphoric acid.

However, potassium hydroxide is too expensive for most fertilizer uses. Less expensive methods of producing soluble potassium phosphates for use in liquid fertilizers are under study.

Suspension Fertilizers

79. Another method of avoiding the problem of low solubility of potash-containing liquids is production of suspensions. Suspensions are liquids that contain fine solids suspended in a saturated solution. The solids are kept in suspension by addition of 1 to 3% of a gelling-type clay.

80. A further advantage of suspensions is that materials not soluble in liquid fertilizers may be added, such as magnesium and manganese compounds.

81. Handling and application of suspensions, in the present state of development, are not as simple, convenient, and trouble-free as for clear liquids. From the farmer's viewpoint, the main advantage of liquids is convenience, and this advantage is lost in going to suspensions. It is likely, therefore, that liquid fertilizers applied by the average farmer will continue to be mainly clear liquids in the immediate future, although suspensions are already being used by some farmers (13). Farmer-applied liquid fertilizers are mainly starter fertilizers which need not contain much potash and can be fairly high in analysis.

82. It is estimated that about 15% of the liquid mixed fertilizer used in the United States is in the form of suspensions.

83. On the other hand, much of the basic fertilizer application is custom-applied by broadcasting before plowing, often in the form of bulk blends. If the fertilizer is custom-applied, the farmer is not concerned with the ease of application. Custom application of suspensions offers the liquid fertilizer industry a means for competing with bulk blends. The market for broadcast

fertilizer for plow down is substantially larger than for starter fertilizer, so any success in this field will greatly increase the sales potential of liquids. Some success is already apparent.

Agronomic Considerations

84. No agronomic difference between liquids and solids would be expected when the two forms contain the same chemical compounds and when the time of application and placement is the same. The only difference would be the small amount of water required to dissolve the salts.

85. Lathwell et al. (14) compared several liquid fertilizers with water-soluble solids as sources of phosphorus for field crops and concluded that "under a wide range of conditions, liquid fertilizers are as satisfactory as equivalent solid fertilizers." However, the formulations usually are different. For instance, most nitrogen solutions contain both ammonium nitrate and urea, a combination that must be avoided in solids because of its extreme hygroscopicity. Also, liquids often contain polyphosphates, whereas solids seldom do. Most liquids are fully water soluble, whereas solids often contain insoluble materials. Placements often differ; for instance, injection of liquids, particularly nitrogen solutions, into irrigation water for spray-type irrigation systems is common, whereas this practice is quite uncommon with solids.

86. All of the factors mentioned above complicate a practical comparison of the agronomic evaluation of liquids and solids. It seems evident that liquids may be better for some uses and poorer for others. In general, most farmers buy liquids because of the convenience and labor-saving factors previously mentioned rather than any real or imagined agronomic superiority.

87. The principal area of disagreement is the value of the polyphosphate content of liquids. It may be noted that polyphosphates could be applied in solid form, but at present they seldom are. It may be further noted that "polyphosphate" is a general term which may include anything from pyrophosphate to long-chain polyphosphates. However, in the present liquid fertilizer practice, pyrophosphate is the predominant polyphosphate species, and triammonium pyrophosphate, $(\text{NH}_4)_3\text{HP}_2\text{O}_7$, probably is the most common compound. Most liquid fertilizers also contain a substantial proportion of orthophosphate.
88. Terman and Engelstad (15) summarizing studies in the United States concluded that ammonium polyphosphate usually was equal or slightly superior to monoammonium phosphate. Both were usually superior to concentrated superphosphate for early growth response. Fourcassie and Gadet (16) concluded from experiments in France that ammonium polyphosphate supplied as liquid fertilizer was consistently superior to other phosphorus sources as the result of better phosphorus utilization. Most of these tests were made on calcareous soil. Field tests at six locations in Japan indicated that response to solid ammonium polyphosphate was generally greater than to ammonium orthophosphate, although early growth was sometimes slightly delayed. There was some suggestion that better utilization of native or applied micronutrients may have been a factor in the favorable results with polyphosphates.
89. Gourny and Conesa (17) reported that liquid fertilizer containing 34 to 82% of its phosphate as nonorthophosphate was slightly inferior to ammonium orthophosphate on acid soil, but markedly superior on calcareous soil.
90. Conesa (18) demonstrated that plants can take up polyphosphate without previous hydrolysis.

91. Singh and Dartigues (19) reported that polyphosphate was superior to ammonium orthophosphate on two zinc-deficient calcareous soils.
92. Soubies and Baratier (20) emphasize the advantage of band placement of ammonium polyphosphate solution near the seed as compared with broadcast solid orthophosphate. They claimed that the band placement used with liquids was not possible with solids.
93. Mortvedt and Giordano (21) reported that liquid polyphosphate fertilizers were effective carriers of iron sulfate in greenhouse tests for crops grown on iron-deficient soils, whereas application of iron sulfate alone or in several granular fertilizers was ineffective.
94. The agronomic value of ammonium polyphosphate may be connected with its rate of hydrolysis in the soil, which is much more rapid than in concentrated solutions. The rate of hydrolysis is affected by many variables, but micro-biological activity and temperature seem to be the most important. At low soil temperatures, hydrolysis may be delayed enough to affect phosphate availability adversely. However, most liquid fertilizer contains enough orthophosphate to minimize this effect.
95. There is a need for further research to define the conditions under which polyphosphates are agronomically superior and the cause of this effect.

Use of Liquid Fertilizer in European Countries

96. Liquid mixed fertilizers and nitrogen solutions are becoming increasingly popular in the United Kingdom; it was reported that consumption of liquid fertilizers (excluding byproduct ammoniacal liquor) more than doubled in 4 years, from about 95,000 metric tons of plant food content in 1966 to nearly 200,000 tons in 1970 (22). In 1970, liquid fertilizers supplied 3.2% of the total plant food consumption.

97. About 15 companies produce liquid fertilizers in the United Kingdom. Only one of them is known to produce ammonium polyphosphate solution. The remainder probably use soluble diammonium phosphate as the phosphorus source. Palgrave (1) noted that in contrast to U. S. practice, liquid mixed fertilizer plants in the United Kingdom had capacities up to 1000 tons per day. Lagoon storage of liquids is a common practice (23).
98. Although no official statistics are available for other countries, it is known that liquid fertilizers are growing in popularity in Belgium and France. One company in Belgium produces superphosphoric acid in a plant of 100 tons of P_2O_5 per day capacity, and converts it to ammonium polyphosphate solution. Nitrogen solutions also are available. Clear liquid N-P fertilizers are formulated from these two materials, and a range of N-P-K suspensions is also available. These materials are marketed through local distribution centers which offer prescription mixing.
99. It is estimated that about 415,000 metric tons of liquid fertilizers were consumed in France in 1970. The principal liquid materials were ammonium polyphosphate solutions made from superphosphoric acid and nitrogen solution made from urea and ammonium nitrate. Some mixtures also are produced. Use of liquid fertilizer may be approximately 10% of all fertilizers in France.
100. An interesting feature of the liquid fertilizer industry in France and Belgium is the expression of the plant food content by volume. Thus, a 15-50-0 solution contains 15 kg of N and 50 kg of P_2O_5 per 100 liters of solution. This system probably is convenient for farmers, as it is easier for them to measure volume than weight.
101. Another unusual feature in France and the United Kingdom is the popularity of on-the-farm storage of liquid fertilizers, which enables the farmer

to take advantage of seasonal discounts and to be assured that the supply is on hand when needed. Some large farms may have several storage tanks dispersed in different fields. The tanks are movable, so they can be located at the points of planned use each year.

Outlook

102. While the amount of liquid mixed fertilizer is still a rather small percentage of the total in most countries, it is growing rapidly and may become a major form of compound fertilizers in the future, particularly in countries where labor is scarce and labor costs are high. Technological improvements are expected to lower the cost of liquid materials, especially the phosphatic materials. Decreasing the relative cost of liquids should accelerate the demand.

103. The possibility of using liquid fertilizers in developing countries has often been brushed off as "too sophisticated." In the author's opinion, this conclusion should be seriously reexamined. The fact that "night soil" has been collected, distributed, and applied to field crops for many years in some developing countries indicates that distribution and application of liquids can be done with the most primitive equipment. Manufacturing facilities for liquids generally are simpler and less expensive than for granular solids. Liquids lend themselves well to production of homogeneous mixtures in local distribution centers to meet local needs--a segment of the fertilizer production and marketing system that has been sadly neglected in many developing countries. Many developing countries are located in very humid, tropical areas where even relatively nonhygroscopic solids give trouble. Hygroscopicity is never a problem with liquids. It may be significant that

liquids are particularly popular in some of the subtropical parts of the United States--Hawaii, southern Texas, and southern California.

104. Liquid nitrogen materials such as UAN solutions are substantially less expensive than solid nitrogen, especially if the solid is bagged. Liquid phosphate materials are more expensive than bulk solid phosphates, but not necessarily more expensive than bagged solid phosphates. As mentioned earlier, new technical developments now coming into use should lower the cost of phosphatic materials.

105. Shipment by rail or road tankers should provide less opportunity for pilferage. If tankers are not available, perhaps smaller tanks that can be loaded on trucks or open rail cars could be used.

106. If fertilizers are imported, liquids can be readily shipped in bulk in mild steel tankers such as those used for oil transport. Rapid loading and unloading by pumps and piping would be an advantage.

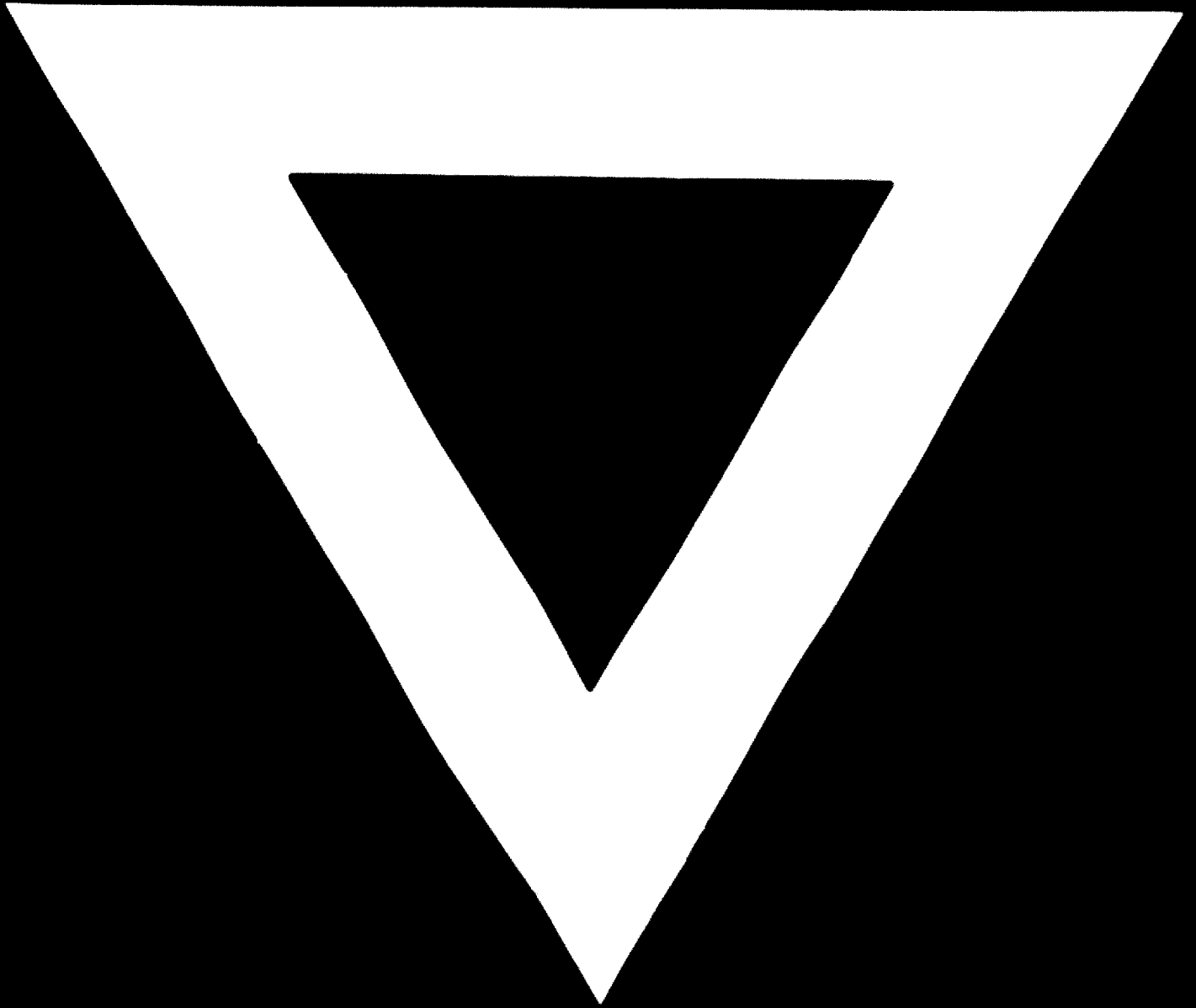
107. Obviously there would be many problems in distributing, handling, storing, and marketing of liquid fertilizers in developing countries, just as there are many problems with solid fertilizers. However, there are so many potential advantages that careful thought should be given to the liquid route.

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