

Granulation of High-Analysis Fertilizers

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Methods for production of granular, high-analysis fertilizers were developed in which the TVA-type continuous ammoniator was used in conjunction with auxiliary equipment. Combining the ammoniation and granulation steps permitted economies in equipment, in formulation based on increased proportions of lower cost nitrogen sources such as ammonia and nitrogen solutions, and in operation by granulating at low moisture content and using the heat of the ammoniation reactions to dry the products. In several formulations sulfuric or phosphoric acid was used to increase the heat of reaction and the proportion of ammonia or nitrogen solution. Artificial drying appeared unnecessary for some grades, and the extent of drying needed for other grades was decreased. Typical grades studied were 12-12-12, 10-10-10, 15-15-0, 10-20-20, 5-20-20, and 8-16-16. Factors that affected granulation included formulation, moisture content, temperature, proportion of recycle, addition of air in the ammoniator, and particle size of raw materials. Physical properties of the products, effects of short periods of curing, and the use of conditioners on bag-storage properties were evaluated. The agronomic effect of granule size was studied in tests, with fertilizers having four degrees of water solubility of the phosphorus in three particle sizes, in the greenhouse on two soils and on corn, cotton, and vegetable crops under field conditions.

MANY CHANGES IN FERTILIZER TECHNOLOGY and rapid expansion in the production and use of fertilizers have occurred in the past 15 years. The consumption of fertilizers has more than tripled in terms of primary plant nutrients. About 70% of the plant nutrients are supplied in the form of mixed fertilizer. The concentration of plant food in mixed fertilizer has increased steadily and now averages about 27%. In some areas the trend toward high-analysis fertilizers has been much stronger than the average—for instance, in the west north central states the concentration of mixed fertilizers averages 35%.

Granulation of mixed fertilizer is increasing rapidly. Granulation greatly decreases the caking tendency of high-analysis fertilizers, prevents segregation of fertilizer ingredients, facilitates more uniform distribution in the field, and decreases dust losses.

The purpose of TVA's work on granulation of high-analysis fertilizers was to develop low-cost, effective methods and equipment for granulation, to study the use of low-cost formulations for granular products, and to evaluate the physical and agronomic properties of the products. This is a joint project in which TVA is

cooperating with the U. S. Department of Agriculture; the department is doing the small scale work and TVA is doing pilot plant work. Valuable suggestions have been received from a panel of industry representatives appointed by the National Fertilizer Association, and from other representatives of industry.

In seeking to reduce the cost of manufacturing granular fertilizers, methods of combining ammoniation and granulation were studied.

The TVA-type continuous ammoniator (5) proved to be an excellent means of granulation. Combining the ammoniation and granulation steps permitted economies in equipment. Economies of formulation were based on use of increased proportions of the lower-cost nitrogen sources, ammonia and nitrogen solutions. Economies in operation were based on granulating at low moisture content and utilizing the heat of the ammoniation reactions to dry the products.

This paper describes the TVA ammoniation-granulation pilot plant, discusses methods for controlling granulation, and presents pilot plant data obtained in studies of the production of a variety of grades of granular fertilizers. Data also are presented on storage properties, including the effects of a parting agent and short periods of curing, and on the effects of water solubility and particle size on crop response.

Raw Materials

The raw materials used in the pilot plant were intended to be typical of those available to commercial producers of fertilizers. Types and typical analyses of these materials are shown in Table I.

The nitrogen solutions were prepared in the pilot plant because only small quantities were used at any one time, there were no facilities for storage of tank car lots, and the necessary ingredients were readily available from TVA plant operations. The procedure used in preparing the solutions in 400-gallon lots was as follows:

The required amounts of ammonium nitrate and water for a given solution were charged to a stainless steel tank, which was designed for a working pressure of 50 pounds per square inch. After the tank had been sealed, the required weighed amount of anhydrous liquid ammonia was introduced through spargers in the bottom of the tank. The tank was equipped with an agitator and with water-cooled coils to control the vapor pressure below 25 pounds per square inch. Usually, the ammonia could be added at a rate of about 300 pounds per hour without excessive increases in temperature and pressure.

Anhydrous liquid and gaseous ammonia were obtained from TVA opera-

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Table I. Typical Analyses of Raw Materials

Raw Material	Chemical Composition, %						Screen Analyses (Tyler Mesh), %									
	N	P ₂ O ₅			H ₂ O	K ₂ O	+4	-4	+6	-6	+28	-28	+48	-48	+100	-100
		Total	C.I. ^a	W.S. ^b												
Ordinary superphosphate	...	20.4	0.7	18.2	7.6	...	0.1	4.4	41.2	32.8	15.9	5.6				
Concentrated superphosphate	...	50.9	0.9	45.7	1.9	...	0.3	3.8	33.9	17.5	28.3	16.2				
From electric furnace acid (TVA)	...	48.6	1.0	41.0	2.2	...	0.0	0.1	40.4	22.4	27.6	9.5				
From wet-process acid				
Potassium chloride	0.1	62.4	0.0	0.0	0.1	15.5	68.4	16.0				
Recrystallized (white)	0.3	61.0	0.0	0.1	22.6	27.7	30.9	18.7				
Flotation (red)	0.1	60.2	0.0	0.0	67.6	21.4	10.2	0.8				
Granular	0.1	...	0.0	0.0	28.9	32.9	32.7	5.5				
Ammonium sulfate (nongranular)	20.7	0.1	...	0.0	0.0	73.4	22.6	3.7	0.3				
Ammonium nitrate (crystalline, TVA)	33.5	0.1	...	0.0	0.0				

Nitrogen Solutions (Prepared in Pilot Plant)	Chemical Composition, %		
	NH ₃	NH ₄ NO ₃	H ₂ O
Type X	21.7	65.0	13.3
Type Y	26.0	55.5	18.5

^a Citrate-insoluble.
^b Water-soluble.

tions. The liquid ammonia was transported to the pilot plant in a trailer tank. The gaseous ammonia was piped to the pilot plant.

The solid raw materials were either obtained from the TVA plant or purchased from commercial sources. If the solid materials were caked, they were crushed to pass a 4-mesh screen; otherwise, they were used as received. Finer grinding was not necessary or advantageous. In some tests, when the ordinary superphosphate had been on hand for some time and dried out, the moisture content was increased to normal (6 to 7%) by treatment with steam in a rotary tumbler. In other tests the amount of moisture that would be required to bring the superphosphate to normal was added during processing. The use of dried-out superphosphate in this manner had no apparent effect on the results.

Three types of potassium chloride—recrystallized (white, 100% -28 mesh), flotation (red, 23% +28 mesh), and granular (68% +28 mesh)—were used in studies of the effects of size of potassium chloride on segregation of potash and on degree of granulation. Differences when the first two materials (smaller sizes) were used generally were not considered significant; in some formulations significantly better granulation was obtained with the granular material.

Sulfuric acid was purchased as 66° Bé. acid and used mostly at this concentration. Most of the tests with phosphoric acid were made with TVA electric furnace acid; commercial wet-process phosphoric acid was used in a few tests. The concentrations of the acids used ranged from 76 to 85% H₃PO₄. The kind of phosphoric acid used had no apparent effect on the results.

Description and Operation of Pilot Plant

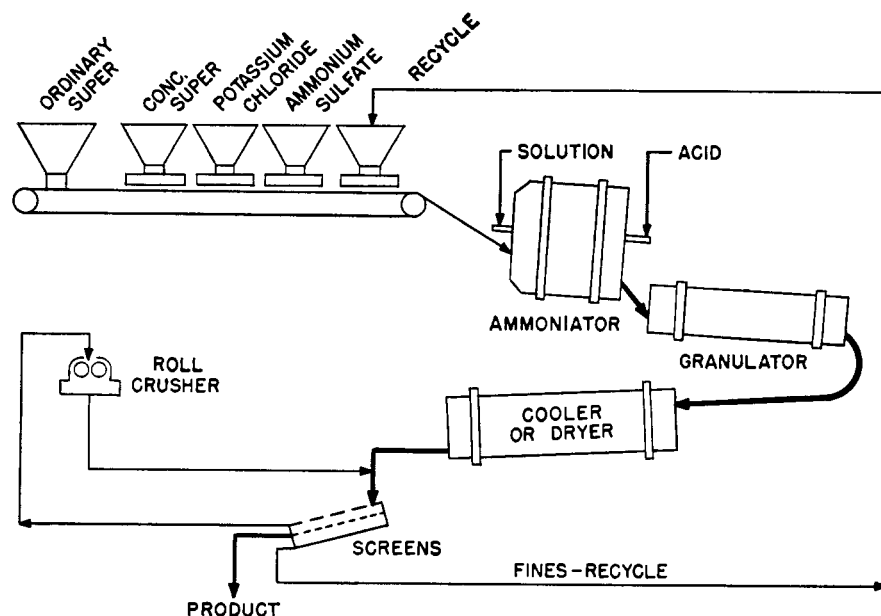
A flow sheet of the pilot plant is shown in Figure 1. It consisted of a TVA-type continuous ammoniator with auxiliary equipment for feeding raw materials, a rotary granulator, a rotary dryer which was used alternately as a cooler, and a size-classification system.

The ammoniator, shown in detail in Figure 2, was described earlier (5). It consisted of a mild steel cylinder, 3 by 3 feet, which was pitched 1 inch per foot from horizontal and usually was operated at a speed of 15 r.p.m. There were no flights in the ammoniator. The depth of the bed of solids was main-

tained at about 9 inches by means of retaining rings. A scraper bar of 2-inch angle iron was provided for continuous cleaning of the inside wall. A mild steel perforated pipe was positioned in the ammoniator parallel to the axis and about 4 inches above the surface of the bed of solids, so that jets of air could be directed onto the bed of material to control the size of the granules.

A stainless steel distributor, 30 inches long, was positioned 7 inches below the surface of the bed, so that nitrogen solution or ammonia could be introduced under the rolling bed of materials. The details of the distributor were given by Yates, Nielsson, and Hicks (5). Another distributor, for acid, was about

Figure 1. Flow diagram of TVA pilot plant for granulation of high-analysis fertilizer



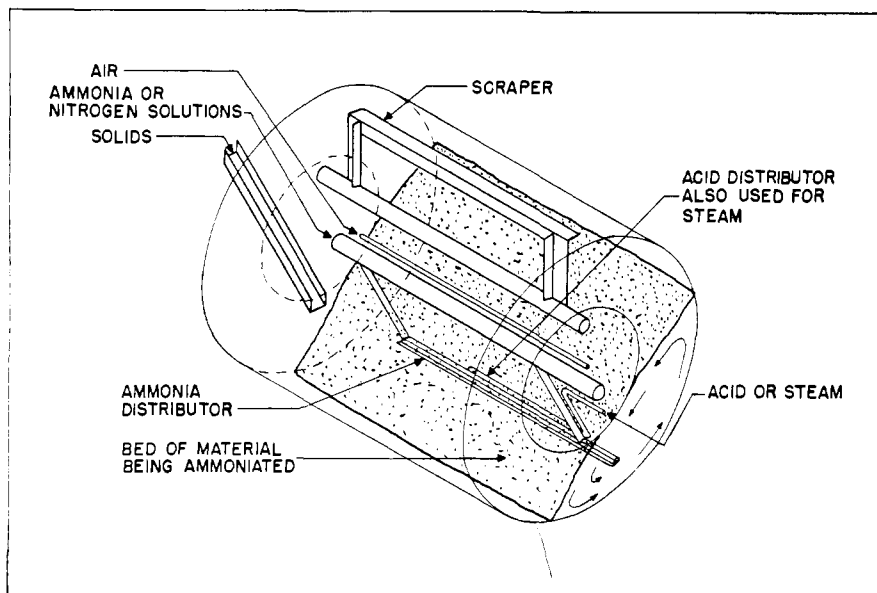


Figure 2. Continuous ammoniator

15 inches long and was fastened to the middle section of the ammonia distributor and positioned directly behind it. A typical acid distributor was made of $\frac{1}{4}$ -inch stainless steel pipe and contained twenty $\frac{5}{64}$ -inch holes spaced $\frac{3}{4}$ inch apart. When water was used to promote granulation of formulations containing nitrogen solution, the water and solution were introduced together through the solution distributor. Otherwise, the water usually was introduced as a spray on the surface of the bed. When steam was used to promote granulation, it was introduced beneath the bed through the acid distributor. When steam and acid were used simultaneously, the steam was introduced through a perforated pipe above the surface of the bed. A hood was provided for removal of exhaust gases from the discharge end of the ammoniator.

Solid ingredients were fed to the system through volumetric feeders, which consisted of hoppers with adjustable discharge gates and variable-speed belts; these belts delivered the solid ingredients to a collector belt which discharged into the ammoniator. Stainless steel rotameters were used to measure the quantities of ammonia, nitrogen solution, acid, and water fed. Air pressure applied to the storage tanks was the means by which the acid and nitrogen solutions were delivered to the ammoniator. Feed rates sometimes were not very accurately adjusted and varied as much as 10% from the desired values. No special attempt was made to formulate to exact grades, and most of the formulations exceeded the nominal grade by a greater percentage than would be desirable commercially. Thus, most of the formulations left room for small percentages of filler or conditioner.

The granulator was a horizontal ro-

tary cylinder 24 inches in diameter and $6\frac{1}{2}$ feet long. Eight $\frac{1}{4}$ -inch rods were welded evenly spaced and longitudinally along the inside of the first $4\frac{1}{2}$ feet of the granulator to promote rolling of the bed of fertilizer. No retaining ring was used in the discharge end of the granulator, as it was found that improved firming and compacting occurred when the depth of the bed in the granulator was at a minimum. The usual rate of rotation of the granulator was 20 r.p.m.

The granulator discharged material into another rotary cylinder which was used as a cooler or a dryer, depending on the moisture content of the undried fertilizer. The cooler-dryer was 3 feet in diameter by 24 feet long. It contained eight 8-inch flights and had a 4-inch retaining ring at each end. When it was used as a cooler, the flow of air was countercurrent to the flow of solids. The air rates used were in the range 700 to 1500 cubic feet per minute (N.T.P.). The temperatures of the products usually were lowered by 60° to 80° F. and were in the range of 95° to 125° F. When used as a dryer, the flow of gases was concurrent. Heat for drying was supplied by combustion of natural gas in a brick-lined chamber adjacent to the dryer. The drying gas temperature ranged from 300° to 500° F. and the rate of flow was 1000 to 2000 cubic feet per minute (N.T.P.). The holdup of material in the cooler-dryer amounted to about 1 ton.

Material from the cooler-dryer was conveyed to a double-decked vibrating screen that had slotted openings approximately equivalent in width to 6- and 28-mesh Tyler screens. Crushing rolls were used to break down the oversize material (+6 mesh). A belt conveyor returned the crushed material to the screens.

No difficulty with corrosion has been encountered in the pilot plant, except for the acid distributor. Most of the corrosion occurred on the outside surfaces of the distributors. Because the materials used for construction of the distributors normally are resistant to corrosion by sulfuric or phosphoric acids, it is believed that the corrosion was caused by intermediate products such as hydrochloric acid. Tests are being made to find a satisfactory material for this service. Typical corrosion rates encountered when sulfuric and phosphoric acids are used in various formulations are shown below.

Distributor	Inches Penetration/ Year with Formula- tions Containing	
	Sulfuric acid	Phosphoric acid
A.I.S.I. Type 316 stainless steel	1.30-8.74	0.54
Hastelloy B	0.19-1.10	0.075
Red brass	...	0.31-0.78

Carpenter 20, which would be considered a logical material for the conditions encountered with sulfuric acid, was reported by others to be unsatisfactory and therefore was not tested. A stainless steel acid distributor sheathed in Teflon tubing is being tested and shows promise.

Prior to the start of each test the belt feeders for solid ingredients and the rotameters for liquids were checked and adjusted to ensure correct rates of delivery. At the beginning of a test, no liquids were fed to the ammoniator until it was filled to at least half its capacity with solid raw materials. During this period of start-up a flow of air was maintained in the submerged distributors to prevent them from becoming plugged.

Granulation did not occur during the first few minutes of a test, because of the low initial temperature. When material for use as recycle was not available from a previous test, the material leaving the granulator during the early part of the test was recycled. As the temperature of the material in the ammoniator increased, steps were taken to regulate granulation.

After the start of a test or a change in operating conditions, a period of about 20 minutes was allowed for reaching steady-state conditions before test data and samples were collected. Temperatures and flow rates were recorded at 10- to 15-minute intervals. The temperatures reported in the text and in the tables are temperatures of the materials as discharged from the units named. In the ammoniator there were areas of higher temperature due to heat of reaction of the charge materials. Temperatures as high as 50° F. above the discharge temperature were recorded in some tests in which the formulation included sulfuric acid. The high-temperature area in

these tests usually was close to the downstream end of the acid distributor. For each test, spot samples were taken of the solution and acid fed, and composite samples were taken of the solid raw materials and of the materials discharged from the ammoniator, granulator, dryer or cooler, screens, and crusher.

Loss of ammonia was based on the concentration of ammonia in the exhaust gas from the ammoniator. The rate of flow of exhaust gas was determined by measurements made with an orifice meter. The concentration of ammonia was determined by passing a measured portion of the exhaust gas through an absorption train containing dilute sulfuric acid. The resulting solution was titrated to determine the amount of alkaline material absorbed.

In calculating formulations, the standard degrees of ammoniation were 5.8 pounds of free ammonia per unit of available phosphorus pentoxide in ordinary superphosphate and 3.8 pounds per unit in concentrated superphosphate; early work had indicated that loss of ammonia should not be excessive under these conditions. Additional ammonia nitrogen in the formulation was fixed through the use of sulfuric or phosphoric acids.

The capacity of the ammoniator appeared to be about 3 tons of product per hour for most of the formulations tested. However, a large number of the tests were made at a production rate of 1 ton per hour, because the pilot plant facilities were not entirely suitable for the preparation and handling of the large quantities of materials required.

About 20 to 45% of the product from the cooler or dryer was larger than 6 mesh in size. After crushing, about 75% of this material was minus 6 plus 28 mesh. In Tables II and III the proportion of the final product shown as on-size (-6 +28 mesh) product after the oversize had been crushed was calculated to include 75% of the oversize material. Actual and calculated values check closely.

The rate of recycle used in the tests usually was based on anticipated production of fines. The difference between the rate used and the rate of production of fines usually was not very great. Data from special tests indicated that the difference did not have an important effect on the degree of granulation obtained. In plant scale operation the rate of recycle would be adjusted to equal the rate of production of fines.

Results of Pilot Plant Tests

Data for typical tests of the production of granular fertilizers in the TVA ammoniation-granulation pilot plant are given in Tables II and III, grouped under headings designating the N:P₂O₅:K₂O ratios of the products—i.e., 1:1:1,

1:2:2, 1:4:4—and grades containing only two of the three major plant nutrients. The individual tests are not described in detail. Instead, the results are discussed from the viewpoint of the factors affecting granulation and ammonia absorption.

Factors Affecting Granulation

One of the most important factors governing the granulation of fertilizer mixtures is the proportion of liquid phase. Too little liquid phase may result in an excessive amount of fines; too much liquid phase may cause excessive agglomeration and attendant mechanical difficulties.

The amount of liquid phase is dependent on the formulation and on the temperature and moisture content of the mixture. Mixtures containing soluble salts may be granulated at very low moisture content if the temperature is high. In order to granulate mixtures at a moisture content sufficiently low to allow omission of artificial drying, temperatures in the range of 180° to 250° F. are often required. These temperatures are higher than those usually obtained through ammoniation of the superphosphate in most mixtures. A convenient means of attaining the higher temperatures is by reaction of additional ammonia with sulfuric or phosphoric acid. This is also an economical means of increasing the nitrogen content of the mixture.

The extent to which the heat of reaction of ammonia with superphosphate and acid is utilized depends in part upon heat losses. Because a smaller percentage of heat is lost in plant scale than in pilot plant scale equipment, more of the heat may be utilized for granulation and drying than in the current work. Observation of some plant scale operations indicates that this effect may be appreciable. As a result, similar formulations may be granulated at somewhat lower moisture content in large scale plants and more moisture may be evaporated in cooling. In many plants the superphosphate taken from the curing pile may contain an appreciable amount of sensible heat, whereas in the pilot plant the superphosphate and other materials were at room temperature.

The methods used to obtain and control granulation in the pilot plant were (1) changing the formulation, (2) blowing a controlled amount of air on the bed of material in the ammoniator, (3) varying the amount of cooled fines recycled to the ammoniator, (4) adding water or steam in the ammoniator, and (5) varying the particle size of the solid raw materials. Usually, during a given run, granulation was controlled by varying the amount of cooling air or the amount of water or steam. If the formulation provided too much plasticity, granulation was controlled by cooling with air; if it provided too little plas-

ticity, granulation was controlled by the addition of water or steam. In either case, the control during a run was based on visual observation of the extent of granulation. If these means were not effective, other runs were made in which the formulation was changed or other conditions were varied to obtain the desired results.

Effect of Formulation. The formulation was found to be an important factor affecting granulation. For some grades, several exploratory tests were necessary to find formulations that would provide the most satisfactory granulation. One such grade was 5-20-20.

In preliminary tests with 5-20-20 (not shown in Table II), ammoniating solution Y (26% free ammonia, Table I) was used to supply all of the nitrogen; water addition was the only means of granulation control. The heat released by the ammoniation reaction was not sufficient to permit granulation at low moisture content. It was necessary to add water to increase the moisture content to about 13% to obtain granulation. The efficiency of granule formation was satisfactory, but the percentage of both oversize and undersize increased during drying, leaving only 42% in the desired size range. After the oversize had been crushed, only 72% was on size. The dried granules were weak and dusty.

The need for artificial drying was eliminated and the stability of granules was improved by adding sulfuric acid to the formulation. The heat generated by the reaction of the acid with the free ammonia increased the temperature in the ammoniator. At the higher temperature, more liquid phase was formed by the solution of soluble salts, and no water addition was needed for granulation. This use of acid to promote granulation is illustrated by test JC-1 (Table II). Best operation was obtained when the acid rate was 143 pounds of acid per ton of product. Fifty-seven per cent of the granulator product was on size. There was very little breakdown of particles in the cooler. On-size material, including the crushed oversize, amounted to 80% of the total product. The moisture content of the product was only 1.7%, even though artificial drying was not used.

During a part of test JC-1 the acid rate was increased to 170 pounds per ton of product. Overagglomeration resulted, and operation was inferior at the higher acid rate. When the acid rate was reduced to 90 pounds per ton, there was too little granulation.

The foregoing tests showed that operation with nitrogen solution as the source of nitrogen was much improved when sulfuric acid was added to supply heat by reacting with the free ammonia. Additional tests were made to determine whether similar results could be obtained

Table II. Production of Granular Fertilizer in TVA Pilot Plant

Nominal grade	1:1:1 Ratio					1:2:2 Ratio					1:4:4 Ratio							
	10-10-10	12-12-12	15-15-15	6-12-12	8-16-16	10-20-20	3-12-12	4-16-16	5-20-20	10-10-10	12-12-12	15-15-15	6-12-12	8-16-16	10-20-20	3-12-12	4-16-16	5-20-20
Test No.	A-10	A-11	K-20	441(X)	431(X)	441(X)	329(Y)	386(Y)	405(Y)	499(X)	362(X)	147(Y)	...	252(Y)	...	180(X)	...	JP-2
Production rate, tons/hr.	1	1	3	1	2	1	1	1	3	1	2	3	1	1	2	2	2	1
Formulation, lb./ton product	514(X)	542(X)	431(X)	441(X)	441(X)	329(Y)	386(Y)	405(Y)	499(X)	362(X)	147(Y)	...	252(Y)	...	180(X)	...	JP-2	
Nitrogen solution ^a
Anhydrous ammonia ^a	61(G)
Ammonium sulfate, or nitrate ^a	206(AS)	547(AS)	746(AN)	192(AN)
Ordinary superphosphate	1059	1031	647	1156	1265	1059	992	1183	1329	260	278	293	774	
Concentrated superphosphate ^b	252	282	693	854	851	741	769	810	...	
Acid ^c	122(S)	126(S)	126(S)	323(P)	211(P)	241(P)	93(S)	112(P)	143(S)	139(S)	...	380(P)	
Potassium chloride ^a	390(F)	354(F)	383(R)	509(R)	488(F)	447(F)	414(R)	522(F)	515(F)	620(F)	655(R)	374(R)	493(R)	669(F)	643(F)	630(F)	645(F)	
Filler, sand	219
Subtotal	2085	2053	2045	2102	1988	1900	2008	2178	2153	2066	2060	1923	2043	2065	1958	1963	1926	
Water	0	0	0	0	0	175	22	0	0	0	0	232	319	0	140	112	149	
Steam	0	0	0	0	0	0	150	0	0	0	38	0	0	0	0	0	0	
Recycle, lb. ^c	0	215(9)	465(19)	281(12)	0	431(18)	601(22)	402(16)	392(16)	576(22)	465(20)	645(24)	397(16)	304(14)	356(15)	829(30)	...	
Total	2085	2268	2510	2383	1988	2075	2611	2779	2555	2458	2674	2620	3007	2462	2402	2431	2904	
Air for control of granulation, cu. ft./ton product	600	0-900	5160	2400	432	0	0	0	3480	750	0	0	0	0	2816	0	0	
Input degree of ammoniation, lb. NH ₃ /unit available P ₂ O ₅ from superphosphate and acid	6.6	7.6	4.2	5.7	3.8	6.4	6.1	6.1	6.1	3.9	3.7	3.3	6.8	1.0	3.9	3.9	6.9	
Moisture and temperature conditions	
Moisture, %	5.7	5.0	4.5	5.1	0.5	13.2	11.5	7.1	6.6	3.6	4.7	14.4	15.7	4.4	8.1	7.0	11.0	
Input to ammoniator	1.7	2.4	2.4	3.7	1.3	11.6	7.3	4.7	4.6	2.9	4.8	13.9	12.5	4.4	5.9	7.5	9.0	
Ammoniator product	
Granulator product	
Cooler product	1.8	...	1.6	9.3	4.8	1.1	1.9	4.2	4.9	...	
Dryer product	6.5	6.1	
Temperature, ° F.	203	200	199	178	194	137	187	183	192	197	180	108	144	206	207	176	176	
Ammoniator product	190	178	187	158	179	120	162	160	177	179	167	106	125	188	191	156	156	
Granulator product	115	...	105	93	95	105	90	90	95	...	
Cooler product	
Dryer product	197	183	163	...	213	145	137	

Losses, %	11.1	6.9	8.0	4.0	1.2	0.5	3.0	0.1	0.2	0.1	0.1	1.4	3.0	0.3
Free NH ₃ by gas analysis	4.6	1.4	0	0.2	3.3	0.0	0.4	0	0.1	0.1	0	1.0	1.3	1.2
P ₂ O ₅ availability	0.8	0	2.7	0.2	0	0.0	0.4	0	0.1	0.1	0	1.0	1.3	1.2
Screen analysis (Tyler), %														
Granulator product														
Oversize (+6 mesh)	14	29	34	17	37	26	31	18	44	35	29	29	31	31
On size (-6 +28 mesh)	76	66	61	71	49	62	55	70	48	57	68	68	65	58
Undersize (-28 mesh)	10	6	5	12	14	12	14	12	8	8	3	3	4	11
Dryer or cooler product														
Oversize (+6 mesh)	12	26	43	6	35	31	39	26	30	31	25	25	21	...
On size (-6 +28 mesh)	77	69	43	76	52	63	41	42	41	56	72	72	68	...
Undersize (-28 mesh)	11	5	14	18	13	6	20	32	29	13	3	3	11	...
On-size (-6 +28 mesh) product after crushing	86	88	75	80	78	86	70	62	63	80	91	91	84	81
oversize, %														
Chemical analysis of product (-6 +28 mesh), %														
Total N	10.5	11.6	14.7	6.0	6.9	7.8	8.0	10.4	4.8	5.0	4.8	4.8	6.1	...
NH ₃ -N	7.5	8.9	12.2	4.6	5.2	5.9	6.0	7.3	7.3	3.8	5.2	...
Total P ₂ O ₅	10.9	13.0	15.5	12.5	13.7	17.0	17.0	20.2	20.2	21.4	21.8	21.8	22.0	...
Available P ₂ O ₅	10.6	12.6	15.4	12.4	13.1	16.7	16.6	19.1	19.1	21.7	21.7	20.8	21.1	...
W.S. P ₂ O ₅	2.4	6.7	13.0	9.8	3.5	9.6	9.2	11.9	11.9	12.8	12.8	11.3	10.7	...
K ₂ O	12.7	11.3	15.7	12.6	12.3	15.6	17.3	19.6	19.6	15.1	20.9	20.9	19.9	...
H ₂ O	1.8	2.1	0.9	9.3	4.2	0.9	0.9	1.1	5.9	1.7	3.9	3.9	4.5	...

^a AN, Ammonium nitrate. AS, Ammonium sulfate. F, Flotation. G, Gas. L, Liquid. P, 76-85% phosphoric acid. R, Recrystallized. S, Sulfuric acid 66° Bé. X, Y. See Table I.

^b TVA concentrated superphosphate produced with electric furnace acid.

^c In parentheses, % of total feed, excluding water and steam.

by adding part of the nitrogen as anhydrous ammonia. Thus, the amount of free ammonia available to react with the superphosphate was increased, and more heat from this source was released in the ammoniator. The nitrogen solution (solution X in these tests), anhydrous ammonia, and water required for granulation were all injected through the same distributor. In one test (not listed in Table II), about 4 units of nitrogen were supplied as anhydrous ammonia, and slightly over 1 unit was supplied as solution. Ninety-two pounds of sulfuric acid were added per ton of product in order to reduce the degree of ammoniation to about 4 pounds of free ammonia per unit of phosphorus pentoxide. Good operation was obtained under these conditions. Almost two thirds of the material from the granulator was on size, and there was practically no undersize. There was little breakup of particles in the cooler. Eighty-eight per cent of the product was on size after the oversize was crushed. The moisture in the product was 2%. The ammonia loss was only 1.8%.

In another test (test JB-1, Table II), about 2 units of nitrogen were supplied as anhydrous ammonia; the balance was added as solution. With these proportions the degree of ammoniation was 3.9, and no sulfuric acid was added. Water was added in the quantity that appeared to give the best granulation. Granulation was not quite as good as in the previous test, but was considered satisfactory. Eighty-three per cent of the product was on size after the oversize was crushed. The moisture in the product was 4.5%. The ammonia loss was 3.0%.

In another series of tests, of which test J-19 (Table II) is typical, all of the nitrogen was supplied in the form of anhydrous ammonia. It was necessary to add sulfuric acid to prevent excessive ammonia loss and to add water to give enough liquid phase for agglomeration. In some of the tests the water was added through an air-atomized spray on the surface of the bed of material in the ammoniator. Liquid ammonia and acid were distributed under the bed. Operation was poor because of frozen lumps which formed on the ammonia distributor and interfered with the rolling action of the bed. Much rodding was required. Fuming was severe. Granulation was fair but erratic. The ammonia loss was also erratic and reached as high as 15%, although the degree of ammoniation was only 3.7 pounds of free ammonia per unit of phosphorus pentoxide. Increasing the acid rate from 158 to 179 pounds per ton did not improve operation.

In further tests, including test J-19, the water was premixed with the ammonia by teeing the water line into the ammonia line just upstream from the

ammonia distributor. This change eliminated the formation of lumps on the distributor. The heat of solution of ammonia in the water raised the temperature in the vicinity of the distributor above the freezing point.

As illustrated by test J-19, operation under these conditions was very good.

The material from the granulator contained only 2 or 3% fines. The cooled product was 91% on size after the oversize was crushed. Loss of ammonia was only 1.5%. There was no fuming when 5500 cubic feet of air and 190 pounds of water were used. There was only slight fuming when the air rate was

reduced to 2800 cubic feet and the water rate was reduced to 140 pounds per ton of product.

In all of the tests in which all of the nitrogen was supplied as anhydrous ammonia, the moisture content was less than 5.0% without artificial drying. The moisture ranged from less than 1% up to about 4.5%, depending largely on the input moisture content.

Several tests were made in which phosphoric acid rather than concentrated superphosphate was used to supplement the phosphorus pentoxide from ordinary superphosphate. Nitrogen was added as anhydrous ammonia. Water, which was required for granulation, was added in an air-atomized spray on top of the material in the ammoniator.

Test JP-2 is typical of operation with phosphoric acid and anhydrous ammonia. Operation was generally satisfactory, except that frequent rodding was required to remove lumps which formed around the distributor. The lump formation was similar to that when anhydrous ammonia was used. It probably could have been prevented as before by premixing the water with the ammonia. Granulation was fairly good; 58% of the granular product was on size. The moisture content of the material from the granulator was 9%. The material was not processed farther than the granulator. Artificial drying probably would have been required to decrease the moisture content enough to prevent caking in storage.

Considering all of the formulations tried for 5-20-20, the one using sulfuric acid and anhydrous ammonia (test J-19) gave the best granulation. It would also be one of the least expensive formulations in most locations, and the operating cost should be low because drying would not be needed.

Change of formulation as a means of obtaining satisfactory granulation was also demonstrated in tests with 15-15-0. In one series of tests (not shown in Table II) 12.5 units of nitrogen were supplied as solution X and the remainder was supplied as ammonium sulfate. About 180 pounds of sulfuric acid was required to obtain good ammonia recovery. With this formulation, granulation was difficult to control; either large amounts of cooling air or recycle were required to prevent overagglomeration. When the formulation was changed to include 10 units of nitrogen from solution X, 5 units from ammonium sulfate, and 129 pounds of sulfuric acid (test WB-1, Table III), granulation was readily controlled with a moderate amount of air and an amount of recycle sufficient only to dispose of the fines that were produced.

When solution Y was substituted for solution X in the formulation for 15-15-0 (test WA-1, Table III), it was necessary to increase the sulfuric acid content of

Table III. Production of Granular Fertilizer in TVA Pilot Plant

Nominal grade	Two-Component Fertilizers				
	15-15-0	14-0-14	0-20-20		
Test No.	WB-1	WA-1	Y-2	Q-1	Q-2
Production rate, tons/hr.	3	3	3	2	1
Formulation, lb./ton product					
Nitrogen solution ^a	485(X)	461(Y)	182(X)
Anhydrous ammonia
Ammonium sulfate	494	489	1042
Ordinary superphosphate	564	505	...	842	222
Concentrated superphosphate ^b	390	452	...	467	563
Sulfuric acid 66° Bé.	129	191	139	...	196
Potassium chloride ^a	516(F)	665(R)	617(R)
Kaolin or phosphate rock ^a	161(K)	...	316(P)
Subtotal	2062	2098	2040	1974	1914
Water	0	0	60	279	92
Steam	0	0	61	0	45
Recycle, lb. ^d	340(14)	390(16)	510(20)	340(15)	...
Total	2402	2488	2671	2593	2051
Air for control of granulation, cu. ft./ton product	3190	4078	0	0	0
Input degree of ammoniation, lb. NH ₃ /unit available P ₂ O ₅ from superphosphate and acid	3.8	3.6	1.83 ^e	0	...
Moisture and temperature conditions					
Moisture, %					
Input to ammoniator	5.5	6.2	6.6	14.1	7.3
Ammoniator product	4.2	3.8	3.2	13.0	...
Granulator product	3.7	3.6	2.9	12.6	...
Cooler product	2.8	2.2	1.1
Dryer product	5.0	...
Temperature, ° F.					
Ammoniator product	190	215	193	69	161
Granulator product	174	199	180	71	143
Cooler product	103	126	98
Dryer product	142	...
Losses, %					
Free NH ₃ by gas analysis	0.6	4.7	4.1
P ₂ O ₅ availability	1.2	0.2	...	0	...
Screen analysis (Tyler), %					
Granulator product					
Oversize (+6 mesh)	37	38	29	33	44
On size (-6 +28 mesh)	60	58	50	61	55
Undersize (-28 mesh)	3	4	21	6	1
Dryer or cooler product					
Oversize (+6 mesh)	36	42	28	12	30
On size (-6 +28 mesh)	60	50	48	70	63
Undersize (-28 mesh)	4	8	24	18	7
On-size (-6 +28 mesh) product after crushing oversize, %	87	82	69	79	86
Chemical analysis of product (-6 +28 mesh), %					
Total N	15.6	14.8	14.1
NH ₃ -N	12.8	12.7	13.1
Total P ₂ O ₅	15.2	16.4	...	20.1	22.0
Available P ₂ O ₅	14.6	15.9	...	19.7	21.5
W.S. P ₂ O ₅	8.4	9.2	...	17.8	20.4
K ₂ O	15.7	20.4	20.0
H ₂ O	2.6	2.2	0.8	5.0	4.3

^a F. Flotation. K. Kaolin. P. Phosphate Rock. R. Recrystallized. X, Y. See Table I.

^b TVA concentrated superphosphate produced with electric furnace acid.

^c NH₃:H₂SO₄ mole ratio.

^d In parentheses, % of total feed excluding water and steam.

the formulation from 129 to 191 pounds. This change increased the heat of reaction and required more cooling air to prevent overagglomeration.

In general, in formulations in which sulfuric acid and ammonia or ammoniating solutions were used, optimum granulation was obtained when the amount of sulfuric acid was in the range of 100 to 150 pounds per ton of product.

A further illustration of the effect of formulation on granulation is provided by tests on 0-20-20. In test Q-1, 0-20-20 was formulated from ordinary and concentrated superphosphates and potassium chloride. With no heat of reaction, granulation was dependent entirely on the addition of moisture. Good granulation was obtained when the moisture content of the charge was raised to 14% by the addition of 279 pounds of spray water per ton of product, even though the material tended to stick to the equipment and occasionally plugged the feed chute to the dryer. The product from the granulator contained 12.6% moisture and was dried to 5% moisture. The dried granules were rather weak. About 79% of the final product was minus 6 plus 28 mesh in size.

In test Q-2, 0-20-20 was formulated from ordinary and concentrated superphosphates, phosphate rock, sulfuric acid, and potassium chloride. The heat of reaction of sulfuric acid with phosphate rock assisted in granulation and the fresh superphosphate formed by these materials provided plasticity. Steam and water also were added to assist in granulation. Good granulation was obtained at much lower moisture content than in test Q-1, and the need for artificial drying was eliminated. The granules appeared to be stronger than those from test Q-1. The final product contained only 4.3% moisture after cooling. About 86% of the final product was minus 6 plus 28 mesh in size. In this test, the weight ratio of sulfuric acid to phosphate rock was about 0.6, which is about the same as that used in manufacturing superphosphate. Conversion of the phosphate rock to a citrate-soluble form was 97% complete without curing. About 25% of the available phosphorus pentoxide in the product was supplied from phosphate rock.

Effect of Cooling Air. The use of cooling air to control granulation was demonstrated by a test of the production of a 15-15-0 fertilizer in which 12.5 units of nitrogen were supplied as solution and 2.5 units were supplied as ammonium sulfate; the other constituents of the formulation were ordinary and concentrated superphosphates and sulfuric acid (about 180 pounds per ton). The test, made at a production rate of 1 ton per hour, was started with air at a rate of 6300 cubic feet per ton of product. Cooled product fines were recycled to

the ammoniator at a rate of about 350 pounds per ton of product, which was about equal to the usual rate of production of fines. However, the liquid phase in the ammoniator was too high, and overagglomeration occurred to the extent that 80% of the product from the ammoniator was larger than 6 mesh in size. The tabulation below shows that, as the flow of air was increased, the temperature and the proportion of plus 6-mesh material decreased; with air at a rate of 17,100 cubic feet per ton of product, only 22% of the material was plus 6 mesh in size.

Air Rate, Cu. Ft. (N.T.P.)/ Ton Product	Product from Ammoniator				
	Temp., °F.	Screen Analysis (Tyler Mesh), %			
		+6	-6	+28	-28
6,300	182	79.9	18.6	1.5	
8,700	174	50.8	47.0	2.2	
9,900	170	36.8	58.3	4.9	
17,100	163	21.7	64.8	13.5	

The use of cooling air was considered the most satisfactory method of controlling granulation when the formulation was such that overgranulation would occur without some means of control. Table II shows the amount of cooling air used for several grades.

Effect of Recycle. The effect of the proportion of cooled fines recycled to the ammoniator on degree of granulation also was demonstrated in a test of the production of 15-15-0 fertilizer with the formulation mentioned above, in which 12.5 units of nitrogen were supplied as solution. In this test the production rate was 2 tons per hour and air was used at a rate of 8550 cubic feet per ton of product. The data below show that, when the recycle rate of cooled product fines was 772 pounds per ton of product, 69% of the material from the ammoniator was larger than 6 mesh. With recycle at a rate of 1158 pounds per ton of product, the proportion of plus 6-mesh material was reduced to 54%.

Recycle Rate, Lb./Ton Product	Product from Ammoniator				
	Temp., °F.	Screen Analysis (Tyler Mesh), %			
		+6	-6	+28	-28
772	200	69.3	27.2	3.5	
1158	199	53.6	43.0	3.4	

Effect of Steam and Water. The use of steam and water to promote granulation was illustrated in the production of a 6-12-12 fertilizer from ordinary superphosphate, nitrogen solution, and potassium chloride. Without the addition of supplemental heat or moisture, no granulation occurred.

When no steam was added, 175 pounds of water per ton of product was required to obtain good granulation (test S-1). This amount of water increased the input moisture content to 13%; after cooling,

the moisture content was 9%. As this moisture content was considered too high, part of the product was dried in a separate operation for bag-storage tests.

When steam was used (test H-25), only a small amount of water was required for good granulation. Probably no water would have been required if the superphosphate had not been unusually dry. In this test, the final product contained only 4% water without artificial drying, which may be low enough for satisfactory bag-storage properties for this grade.

The use of steam was also found to be effective in granulation of 10-20-20 (test CA-1), 14-0-14 (test Y-2), and 0-20-20 (test Q-2). Steam was not effective in granulation of 3-12-12 (test X-1) or 4-16-16 (test O-5); in these grades water was used in the amounts shown in Tables II and III. Tests showed that the use of steam did not reduce the amount of water required for granulation of these formulations.

Effect of Particle Size of Raw Materials. The effect of particle size of the raw materials was studied in a series of three runs in the production of 8-16-16. The formulation and operating conditions in these tests were similar to those in test Z-2 (Table II). In the first test, the solid raw materials, potassium chloride and superphosphate, were ground to pass a 28-mesh screen. In the second test, 39% of the superphosphate and 11% of the potassium chloride were plus 28 mesh. In the third test, 30% of the superphosphate and 73% of the potassium chloride were plus 28 mesh. The weighed average percentage of plus 28 mesh in the raw materials was 1, 30, and 44% in the three tests.

As shown in the following tabulation, the efficiency of granulation increased as the particle size of the raw materials increased. When the raw materials were all minus 28 mesh, granulation was very poor; only 23% on-size material was formed. There were large amounts of both oversize and undersize. Granulation efficiency was highest when granular potassium chloride was used. Although most of the potassium chloride was in the desired particle size range, practically no separate particles were visible in the screened product. Examination of individual granules by splitting them open showed that most of them contained a core of granular potassium chloride coated with the other materials.

Screen analysis of granulator product (Tyler), %	Size of Raw Materials, % -28 Mesh		
	99	70	56
+6 mesh	36	31	15
-6 + 28 mesh	23	55	71
-28 mesh	41	14	14

In tests with some other grades, the particle size of the potassium chloride did not affect granulation efficiency appreciably.

Effect of Production Rate. Tests were made in which the production rate was varied from 1 to 4 tons per hour in producing 12-12-12 by the formulation shown in Table II for test K-20. Rates higher than 4 tons per hour were not tried, because the equipment for handling materials was not adequate.

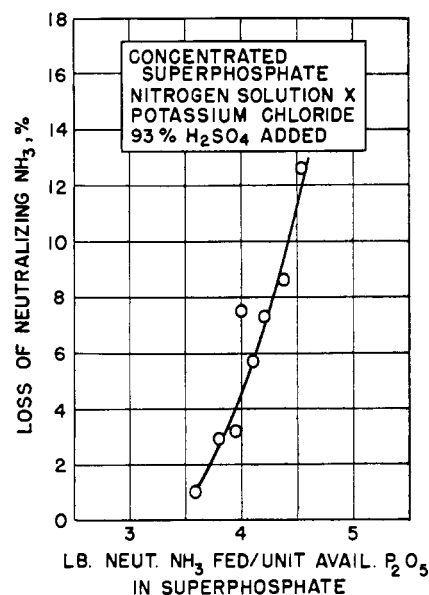


Figure 3. Effect of degree of ammoniation on loss of ammonia

10-20-20 fertilizer produced at 1 ton per hour

The amount of air required for granulation control increased from 1000 cubic feet per ton at 1 ton per hour to 3000 to 5000 cubic feet per ton at 3 or 4 tons per hour. However, neither the granulation efficiency nor the strength of the granules was affected by the production rate when the proper amount of air was used.

The effect of production rate also was studied in tests with 8-16-16 (tests Z-1 and Z-2, Table II). Increasing the rate from 1 to 3 tons per hour increased the amount of cooling air required from 0 to 3480 cubic feet per ton. The granulation efficiency was lower at 3 tons per hour, and there was more breakdown in the dryer. As a result, the recovery of on-size material was only 70% at the 3-ton-per-hour rate, as compared with 86% at 1 ton per hour. This result is apparently inconsistent with the results obtained with 12-12-12, in which granulation efficiency was unaffected by production rate. It is believed that the longer retention time in the granulator provided by the 1-ton-per-hour rate improved the strength of the 8-16-16 granules, but that this

treatment was not necessary to produce strong granules of the 12-12-12 formulation. There is not sufficient evidence to determine what difference in the character of these two materials is responsible for their different behavior.

Factors Affecting Ammonia Absorption Factors affecting the absorption of ammonia by superphosphate in the continuous ammoniator have been reported (5). Although the present work was mainly concerned with granulation, some further data on ammoniation efficiency were obtained.

Effect of Degree of Ammoniation. The results of tests of the effect of input degree of ammoniation on loss of ammonia in the production of 10-20-10 granular fertilizer at 1 ton per hour are plotted in Figure 3. As the input degree of ammoniation was increased from 3.6 to 4.6 pounds of free ammonia per unit of phosphorus pentoxide, the loss of ammonia increased from 1 to 13%. In calculating these degrees of ammoniation, the amount of ammonia required to combine with the sulfuric acid to form ammonium sulfate was not included. In these tests all of the phosphorus pentoxide was supplied in the form of concentrated superphosphate and ammonia was supplied as nitrogen solution X. The formulation was similar to that shown in test C-26 (Table II).

In formulations deriving all of the phosphorus pentoxide from ordinary superphosphate, such as 10-10-10 and 6-12-12, losses of free ammonia were less than 5% when the degree of ammoniation was 6.5 or less, and when granulation was controlled satisfactorily. When granulation was not properly controlled, and too much oversize was produced, the ammonia losses often were higher than 5%.

In formulations containing phosphoric acid and superphosphates, it was not possible to determine accurately how much ammonia was absorbed by the superphosphates and how much was absorbed by the phosphoric acid. As an empirical rule, it appeared satisfactory to assume that phosphoric acid would absorb 7.2 pounds of free ammonia per unit of phosphorus pentoxide from phosphoric acid, which is equivalent to an NH₃:H₃PO₄ mole ratio of 1.5. Formulations calculated on this basis and on the assumption that ordinary and concentrated superphosphates would absorb 5.8 and 3.8 pounds, respectively, per unit of phosphorus pentoxide usually gave rather low ammonia loss. In some cases somewhat higher degrees of ammoniation were used without serious ammonia loss.

Effect of State of Ammonia. A few tests were made in which anhydrous ammonia was used in the gaseous state for comparison with the use of liquid anhydrous ammonia. The formulation

was similar to that given for 5-20-20 (test JP-2, Table II). Figure 4 shows the effect of the state of ammonia and degree of ammoniation on ammonia loss.

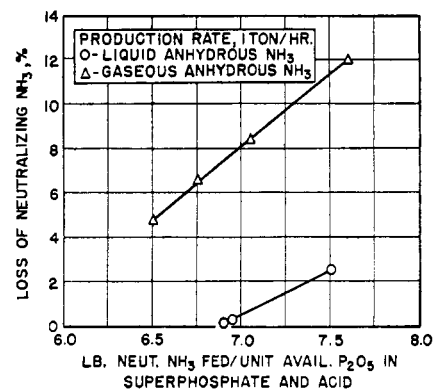


Figure 4. Effect of state of ammonia on loss of ammonia

5-20-20 granular fertilizer produced using phosphoric acid

When the degree of ammoniation was 7.0 pounds of free ammonia per unit of phosphorus pentoxide (supplied as ordinary superphosphate and phosphoric acid), there was practically no ammonia loss when liquid anhydrous ammonia was used. When gaseous ammonia was used, the loss was 8%. Thus, the use of gaseous anhydrous ammonia resulted in poorer ammonia absorption.

Effect of Production Rate. In tests with 12-12-12 in which ammonia was supplied as nitrogen solution X, the ammonia losses were low and were not affected by varying the production rate in the range of 1 to 4 tons per hour.

In tests with 5-20-20 using a formulation similar to that given in Table II for test J-19, the ammonia loss increased from 1 to 7% as the production rate was increased from 1 to 3 tons per hour when anhydrous ammonia was not premixed with water. The degree of ammoniation in these tests was 3.8 to 4.0.

When anhydrous ammonia was premixed with water, as in test J-19, the ammonia loss was lower than in similar tests in which the ammonia and water were added through separate distributors. For instance, in test J-19 in which the production rate was 2 tons per hour and the ammonia was premixed with water, the ammonia loss was only 1.4%; in a similar test in which ammonia and water were added separately, the loss was about 5%.

Effect of Kind of Superphosphate. Concentrated superphosphate made from wet-process phosphoric acid and cured in a fuel-fired dryer was purchased from a commercial producer and used in one run on 12-12-12. No difference in ammoniation or granulation efficiency was noted when this run was compared with a similar run in which concentrated

superphosphate made from electric furnace acid was used.

Special tests were made in which concentrated superphosphates made by the wet process and by the electric furnace process were ammoniated with anhydrous ammonia. No significant difference in ammonia absorption was found.

The ordinary superphosphates used in the present work were obtained from several commercial plants that used different types of equipment. The superphosphate varied somewhat in physical properties and moisture content. No differences in ammoniation characteristics or granulation efficiency were noted that could be attributed to differences in the characteristics of the superphosphates.

Mixing Efficiency and Segregation The thoroughness of mixing in the TVA-type continuous ammoniator when small quantities of material were added should be of particular interest to operators who add minor elements or pesticides to their fertilizers. The mixing efficiency of the continuous ammoniator was tested by introducing chromic oxide (Cr_2O_3) continuously at a rate of about 6 pounds per ton of product with the dry materials during the production of granular 12-12-12 fertilizer. This material was used because its color allowed visual evaluation of the degree of mixing and because it was considered to be relatively inert under the conditions in the ammoniator. Observation of grab samples taken from the granulator every 30 seconds indicated that the additive was distributed uniformly throughout the material. Chemical analyses of these samples, shown below, verified this observation.

Time Lapse since First Addition of Cr_2O_3^a , Min.	Cr_2O_3 , %
6.5	0.27
7.0	0.25
7.5	0.29
8.0	0.30
8.5	0.27

^a Retention time in ammoniator and granulator about 3 minutes.

The test showed that small proportions of finely divided materials may be expected to be distributed evenly throughout products made by the TVA process.

The samples described above represented the total discharge from the granulator; analyses were not made to see whether the concentration of chromic oxide varied in the different size fractions of the samples. Such tests were made for potassium chloride, which is known to segregate in nongranular fertilizers. Three sizes of potassium chloride were used: 100% minus 28 (recrystallized), 77% minus 28 (flotation), and 32% minus 28 (granular).

Table IV shows the concentration of potassium oxide, reported as $\text{K}_2\text{O}:\text{P}_2\text{O}_5$ weight ratio, in the various size fractions of the granulator product (before it enters the closed crushing and screening circuit). Segregation of potassium oxide is easily noted. When the two smaller sizes of potassium chloride were used, in the production of 12-12-12 and 5-20-20 fertilizers, the concentration of potassium oxide tended to increase as the size fraction of the sample decreased. There was a greater concentration of potassium oxide in the minus 32-mesh fraction when the smallest size potassium chloride was used. Segregation was more pronounced in the 5-20-20, which contained almost twice as much potassium chloride.

When granular potassium chloride was used, in the production of the 8-16-16 fertilizer, most of the potassium oxide was concentrated in the minus 6-plus 14-mesh fraction. In the TVA process, which includes recycling of all the fines at the rate of production of fines, segregation is of little significance, as only the on-size product is removed from the system.

Fume and Flash Fires Fuming in the pilot plant ammoniator was noted in several tests at production rates of 2 and 3 tons per hour with formulations containing sulfuric acid. After several reports had been received that fuming was being encountered in plant scale installations, tests were made to determine the cause and to find methods for preventing it. It was found that the fume consisted of finely divided ammonium salts, chiefly ammonium chloride. The formation of fume seemed to be related to excessive plasticity and overagglomeration in the ammoniator and to high rates of reaction per unit volume. When excessive plasticity occurred, the bed of material in the ammoniator did not roll freely. As a result, there were poor mixing of the materials in the ammoniator and a better chance for the sulfuric acid to react with some of the potassium chloride to form

hydrogen chloride before the acid was neutralized by the ammonia. Some of this hydrogen chloride apparently reacted with ammonia above the bed of materials and appeared as fume. Another contributing factor to the formation of hydrogen chloride was the excessively high temperatures that existed in the vicinity of the acid and ammonia distributors due to poor distribution of the heat of reaction. Nitrate fume may be formed in a similar manner, and sulfate fume could result from the presence of acid mist above the bed as the result of channeling.

It was found that fuming could be avoided by preventing overagglomeration and maintaining a freely rolling bed of material. Methods for preventing overagglomeration have been discussed.

No flash fires or explosions have occurred in operation of the pilot plant. However, such phenomena have been reported a few times in commercial installations when sulfuric acid was used in formulations for high-nitrogen grades such as 10-10-10. From the limited information available, it appears that the concentration and the proportion of acid used may be the critical factors. It has been reported that flashes occurred each time 98% sulfuric acid was used at a rate of 150 pounds per ton of product but not when 93% acid was used. Others have reported flashes, preceded by excessive plasticity and mudding in the ammoniator and the evolution of brown fumes, when what they believed was 93% acid was used at a rate of 120 pounds. It is evident that excessive fuming and build-up of flammable or explosive mixtures of gases are related directly to excessive plasticity of the material in the ammoniator, and this should be avoided, especially when there is evidence of brown fumes.

Physical Properties

The storage properties of the pilot plant products were evaluated by tests

Table IV. Effect of Size of Potassium Chloride on Segregation of K_2O

Product Size Fraction; Mesh (Tyler)	Size of Potassium Chloride ^a				
	100% - 28 Mesh Recrystallized (White)		77% - 28 Mesh Flotation (red)		32% - 28 Mesh Granular
	Product Grade				
	12-12-12	5-20-20	12-12-12	5-20-20	8-16-16
	$\text{K}_2\text{O}:\text{P}_2\text{O}_5$ Weight Ratio in Different Size Fractions of Granulator Product ^b				
+6	0.98 (36) ^c	0.84 (24)	0.79 (27)	0.64 (18)	0.59 (23)
-6 +14	0.93 (39)	0.84 (41)	0.87 (41)	0.71 (37)	1.38 (50)
-14 +28	1.11 (19)	1.19 (26)	1.27 (25)	1.35 (30)	0.71 (6)
-28 +32	1.11 (1)	1.72 (2)	1.21 (4)	1.72 (7)	0.64 (12)
-32	1.21 (5)	2.78 (7)	1.01 (3)	1.48 (8)	0.45 (9)
-6 +28	0.99 (58)	0.97 (67)	1.02 (66)	1.00 (67)	1.31 (56)

^a For further breakdown in screen size, see Table I.

^b Sample from granulator; before crushing and screening.

^c Values in parentheses show weight per cent of size fraction.

made with 80- to 100-pound bags in stacks 12 bags high. The products were stored in five-ply paper bags having one asphalt-laminated ply. The bagging temperature did not exceed 120° F. The tests were carried out in a large, unheated building, the windows of which were kept open to simulate open warehouse storage. The building had a concrete floor, but the stacks of fertilizer were placed on a wooden platform. The usual procedure was to place bags of the fertilizer to be tested in positions 4, 8, and 12 from the top of the stack. The other positions were filled with dummy bags, each containing 100 pounds of sand.

Inspections usually were made after 1 and 3 months of storage. Some tests were extended to 6, 9, and 12 months, but there seldom was much change in bag set or caking after 3 months. After each interval, the fertilizer in one stack was removed and inspected. Observations were made before the material was moved, to determine the degree of bag set that had occurred. The bags were dropped four times from a height of 3 feet, once on each face and side, to simulate handling probably encountered from warehouse storage to field, and were then cut open and inspected. The condition of the fertilizer, size and loca-

tion of lumps, if any, evidence of penetration of moisture through the bag, and condition of the bag were observed. After the test material had been quartered, half of it was used to determine the proportion of plus 2-mesh lumps present and the hardness of the lumps. The other half was tested for drillability with a John Blue No. 30 auger-type distributor.

The results of bag-storage tests of a number of the granular (-6 +28 mesh) products are given in Table V. The tests included studies of the effects of drying, short periods of curing, and the use of a conditioner (parting agent).

The data in practically all cases show a definite benefit for curing, even as little as 1 day, and for dusting with kaolin. High-nitrogen products such as 10-10-10, 12-12-12, and 10-20-20, which contained 1 to 2% moisture without artificial drying, had a hard bag set after 3 months if stored without being cured or dusted, and contained 3 to 6% by weight of lumps larger than 2 mesh after the drop test. Dusting of these products with 2.5% by weight of kaolin practically eliminated bag set and entirely eliminated the presence of lumps after the bags were dropped.

The 8-16-16 grade produced without artificial drying contained about 3%

moisture and caked badly. Curing for 7 days reduced caking to the extent that, after the drop test, there were only 4% of lumps. Curing and dusting the product eliminated the presence of lumps. The 8-16-16 that was stored after being dried to 1.2% moisture had a medium bag set and was free of lumps after dropping.

Bag-storage tests were made with 6-12-12 and 5-20-20 grades that contained 5 and 7% moisture, respectively. The 6-12-12 stored satisfactorily without curing or dusting. It had a medium bag set after 3 months, but was entirely free of lumps after the drop test. Curing for 7 days decreased bag set to only a light crust. The 5-20-20 with about 7% moisture (not cured, not dusted) caked somewhat in storage. However, another sample, containing 5.9% moisture and cured for 2 days, showed only a very light bag set after 3 months of storage. Curing and dusting of these products probably would have eliminated caking entirely.

In the production of the very low-nitrogen grades (3-12-12 and 4-16-16), the amount of moisture required for granulation of the charge materials was high (14 to 16%) and the temperature in the ammoniator was low (108° to 144° F.). There was little evaporation of moisture during processing and the products from the granulator were rather wet. Some of these products were dried to 6 to 7% moisture, which was believed to be low enough to ensure satisfactory storage. The data show that these low-nitrogen products had a medium bag set, which was reduced to only a light crust by conditioning with kaolin, and contained no lumps after dropping.

The 15-15-0 fertilizer as produced without artificial drying contained about 2.5% moisture and caked excessively. Curing for 7 days decreased caking to 4%, and the lumps were very weak. Dusting decreased bag set and eliminated caking. Drying practically eliminated bag set.

Drillability tests were made on the dusted and undusted products after the bags had been dropped according to the procedure described above. As would be expected, materials containing no lumps drilled satisfactorily; all the material passed through the drill at a uniform rate. Moreover, lumps present in any of the products tested, with the exception of the 8-16-16 product, were so weak that they disintegrated in the machine and did not interfere with drilling. The lumps present in the uncured 8-16-16 were rather hard; although some of them broke down in the drill, about 5% did not pass through the opening. Curing and dusting rendered this material satisfactory.

Limited tests were made to determine whether breakdown in size of granules

Table V. Results of Bag-Storage Tests^a

(Duration, 3 months)

Grade	Test Series	Artificially Dried	Days Cured ^b	Moisture Content, % H ₂ O	Condition after 3 Months			
					Bag Set ^c		% +2-Mesh Lumps after Drop ^d	
					Undusted	Dusted ^e	Undusted	Dusted ^e
10-10-10 ^f	A	No	0	1.9	3	2	5	0
			1	...	3	1	6	0
			7	1.8	2	1	4	0
12-12-12	K	No	0	1.5	3	1	3	0
			1	1.5	3	0	0	0
			7	1.4	1	0	0	0
10-20-20	C	No	1	1.8	1	1	3	0
			7	1.2	2	1	<1	0
6-12-12	H	No	0	5.2	2	0	0	0
			7	4.3	1	0	0	0
5-20-20	J JP JP	No	0	6.9	3	..	2	..
			0	6.9	3	..	6	..
			2	5.9	1	..	<1	..
8-16-16 ^f	Z	No	0	3.2	3	3	39	4
			1	2.8	3	2	16	1
			7	2.9	2	2	4	0
			0	1.2	2	1	0	0
15-15-0	WB	No	0	2.6	3	1	12	0
			7	2.1	3	2	4	0
			0	0.6	1	0	0	0
3-12-12	X	Yes	0	7.0	2	1	0	0
4-16-16	O	Yes	0	5.6	2	1	<1	0

^a All materials stored in five-ply paper bags having one asphalt-laminated ply.

^b Cured in steam-heated bin at 110° F.

^c Bag set before dropping. 0 = none, 1 = light crust, 2 = medium hard crust, 3 = hard crust.

^d After dropping four times from 3-foot level, once on each face and side of bag.

^e Dusted with 2.5% by weight of kaolin.

^f Only 1 month of storage.

Table VI. Reversion of P₂O₅ to Citrate-Insoluble Form during Storage of Granular Fertilizer at Elevated Temperatures

Grade Test Series ^a	10-	12-	15-15-15		8-16-16		10-	15-15-0	0-	5-20-20			3-	6-	4-
	10-10 A	12-12 K	AW	D	Z	ZA ^b	20-20 C	WA and WB	20-20 Q	J	J	JP	12-12 X	12-12 H	16-16 O
Degree of ammoniation ^c	5.3	4.4	5.7	3.5	6.1	6.5	3.6	3.8	0	3.6	3.9	7.7	3.3	6.5	6.8
Input moisture, %	2.3	1.3	0.9	1.1	1.2	1.1	2.2	1.8	5.0	0.4	6.0	6.2	6.5	7.4	5.9
Loss of P ₂ O ₅ availability during storage, %															
At 100° F.															
30-day storage	0.3	0.1	0.0	0.0	0.1	0.0	0.0	...	0.8	...	1.1	0.0	0.2	3.2	1.9
60-day storage	0.3	0.1	0.0	0.0	0.1	0.0	0.0	...	0.5	...	1.9	0.9	1.0	4.7	3.1
90-day storage	1.1	0.1	...	0.0	0.0	0.0	0.0	...	0.4	...	2.5	6.0	0.3	6.3	3.1
At 130° F.															
30-day storage	0.3	0.2	0.0	0.0	0.1	0.0	0.0	0.2	0.4	0.5	1.3	1.5	1.6	4.5	6.2
60-day storage	1.1	0.1	0.0	0.0	0.8	0.0	0.0	0.2	0.5	0.5	2.8	4.7	2.4	7.1	7.5
90-day storage	1.1	0.2	...	0.6	0.0	0.0	0.7	0.2	0.0	0.8	2.9	6.0	1.8	9.6	6.9
At 180° F.															
30-day storage	0.3	0.1	0.0	0.1	0.1	0.0	0.2	0.3	0.4	0.5	4.5	2.9	5.1	8.6	8.1
60-day storage	2.0	0.2	0.6	0.0	0.1	0.0	0.0	0.4	0.0	0.5	4.9	6.6	5.2	9.5	10.0
90-day storage	2.0	0.1	...	0.6	0.7	0.0	0.7	0.6	0.4	0.8	4.9	4.8	3.9	10.3	9.3

^a Formulation for grade is shown in Tables II and III under test number having same letters as test series.

^b Same formulation as Z series except wet-process phosphoric acid was used in ZA series.

^c Pounds of neutralizing ammonia retained per unit of available P₂O₅ in superphosphate and acid.

occurred during storage. Although sufficient quantities of materials were not available for building large storage piles as might be practiced in industry, it was thought that worth-while information could be obtained under conditions available in the pilot plant. In these tests, 12-12-12 and 5-20-20 granular fertilizers were stored in open, unheated bins in the pilot plant building for 1 month in quantities of from 3 to 7.5 tons; the depths of the piles ranged from 3 to 8 feet. At the end of the storage period the materials were caked slightly throughout the pile. They were removed from the pile by manual digging. Screen analyses of the materials before and after storage showed only slight differences, which were ascribed to the inability to obtain truly representative samples.

In another test, the effect of changes in temperature on the strength of granules was studied by subjecting a sample of 12-12-12 (formulated as in run K-20, Table II) to changes in temperature from 40° to 135° F. The samples were held under a pressure of 12 pounds per square inch and were alternately cooled or heated for 2-day periods for 2 weeks. After this time, the cakes formed were carefully disintegrated. Screen analyses of the material before and after the test indicated that no breakdown of the granules had occurred.

Reversion of Phosphorus Pentoxide during Storage

A number of the products made in the pilot plant were tested to determine the effects of length of time and temperature of storage on reversion of phosphorus pentoxide to a citrate-insoluble form. As sufficient quantities of materials were

not available for building large piles that would retain their temperatures for extended periods, laboratory scale tests were made under conditions simulating pile storage. Fresh product was sealed in glass jars and kept in ovens for 1, 2, and 3 months at 100°, 130°, and 180° F. The citrate solubilities of the samples before and after storage were compared.

The results of the tests are shown in Table VI. All the products of low moisture content (<2.5%: 10-10-10, 12-12-12, 15-15-15, 8-16-16, 10-20-20, 15-15-0) and the 0-20-20 grade (no nitrogen, 5% water) showed relatively little reversion of phosphorus pentoxide to a citrate-insoluble form even after storage for 90 days at 180° F. Appreciable reversion of phosphorus pentoxide occurred in products containing about 6% or more moisture and increased with length of storage, temperature of storage, and degree of ammoniation. The detrimental effect on phosphorus pentoxide availability of storing ammoniated fertilizer materials of high moisture content has been reported (7-5). The effect of moisture on reversion is shown by the 5-20-20 grade, which was stored undried at about 6% moisture and after drying to 0.4% moisture.

The availability of the phosphorus pentoxide in the high moisture material decreased about 5% after storage for 90 days at 180° F., whereas the decrease in availability of the other material was only 0.8%. The effect of degree of ammoniation on reversion of phosphorus pentoxide in products stored at high moisture content can be seen from the data for the 3-12-12 and 6-12-12 fertilizers. Both products contained about 6% moisture, but the degrees of ammoniation were 3.3 and 6.5 pounds of neutralizing ammonia, respectively, per unit of

available phosphorus pentoxide. The loss of phosphorus pentoxide availability in the 6-12-12 was about 10% after storage for 90 days at 180° F. as compared with about 4% for the 3-12-12 product.

Effects of Water Solubility and Particle Size on Crop Response

Greenhouse tests were made with materials of 1:2:2 ratio to determine the effects of water solubility and particle size on crop response. Because the water solubilities in current tests in the ammoniation-granulation pilot plant ranged only from 25 to 60%, two additional materials of 0 and 100% water solubilities were prepared.

The materials, having four degrees of water solubility of the phosphorus each in three particle size groups, were tested on two soils. Sudan grass was the test crop. Two cuttings of Sudan grass were obtained, the first when the growth was about 8 inches high and the second at the early heading stage. The Clarksville soil was unlimed and had a pH of about 5.5, while the Hartsells soil was limed to a pH of 6.0. Sufficient supplemental nitrogen and potassium oxide were added to be equivalent to that supplied by the 80-pound rate of phosphorus pentoxide from the several materials. Materials were incorporated into the soil at rates of 20, 40, and 80 pounds of phosphorus pentoxide per acre. As the same trends in yields were obtained at all three rates, the data in Table VII show the average yields obtained from the three phosphorus pentoxide rates.

Results indicate that, for the first crop on both soils, a definite trend in yield was in favor of the material of fine particle size for the low-water-soluble prod-

Table VII. Effects of Water-Soluble P₂O₅ Content and Particle Size on Yield of Sudan Grass on Two Soils

(Yields, in grams dry weight/pot, are averages of 20, 40, and 80 lb. of P₂O₅/acre rates)

Product Size Fraction	Clarksville		Hartsells	
	First crop	Second crop	First crop	Second crop
7-14-14 (6% Water Solubility of P ₂ O ₅)				
-6 +14	2.14	9.56	2.57	8.98
-14 +35	2.22	10.18	3.12	9.61
-35	3.12	10.10	4.06	8.42
6-12-12 (25% Water Solubility of P ₂ O ₅)				
-6 +14	2.24	9.12	2.79	8.12
-14 +35	2.41	10.44	2.94	8.15
-35	2.13	11.05	3.04	7.90
10-20-20 (60% Water Solubility of P ₂ O ₅)				
-6 +14	2.51	10.23	3.64	8.16
-14 +35	2.14	10.35	3.26	8.40
-35	2.20	10.11	3.18	6.96
11-22-22 (100% Water Solubility of P ₂ O ₅)				
-6 +14	3.01	9.92	4.51	8.69
-14 +35	1.96	10.92	3.43	8.00
-35	1.90	10.84	2.89	7.01
No phosphate	0.70	5.8	1.60	5.6

uct and, conversely, in favor of the material of large particle size for the high-water-soluble product. No significant differences were obtained among different particle sizes for products with intermediate water solubility.

These trends were much less pronounced on the second crop. On the Clarksville soil the coarse particle size yielded less in three of four cases. On the Hartsells soil the fine particle size yielded less in three of four cases. These data would indicate that the Hartsells soil has a more pronounced ability to render soluble phosphates unavailable to plants than the Clarksville soil.

It can be concluded that, generally, best results will be obtained from low-water-soluble products that are finely ground and from high-water-soluble materials that are coarser. Particle size does not seem to have a particularly important effect on the efficiency of fertilizers having intermediate water solubility.

Field tests are being made by a number of state experiment stations with the same materials to determine the effects of particle size and phosphorus pentoxide water solubility on crop response.

Summary

The TVA-type ammoniator proved to be excellent for use in the production of granular fertilizers. Combining the ammoniation and granulation steps permitted economies in equipment. Economies of formulation were based on use of increased proportions of the lower cost nitrogen sources, ammonia and nitrogen solutions. Economies in operation were based on granulating at low moisture content and utilizing the heat of the

ammoniation reactions to dry the products.

The underlying principle upon which the TVA process is based is the introduction of the ammoniating medium and acid, when needed, under the rolling bed of materials in the continuous ammoniator and regulating the proportion of liquid phase to that required for the desired degree of granulation.

The methods used to obtain and control granulation in the pilot plant were changing the formulation, varying the amount of cooled fines recycled to the ammoniator, blowing a controlled amount of air on the bed of material in the ammoniator, spraying water or injecting steam onto the material in the ammoniator, and varying the particle size of the solid raw materials.

Several formulations were studied in which sulfuric or phosphoric acid was added to permit the use of larger proportions of ammonia or nitrogen solution. Use of the acids also increased the heat of reaction, which promoted granulation at lower moisture contents. In some formulations, steam or water was added to promote granulation. Typical grades studied were 10-10-10, 12-12-12, 15-15-15, 10-20-20, 8-16-16, 6-12-12, 5-20-20, and 15-15-0. For most of these grades artificial drying did not appear necessary.

High nitrogen grades such as 10-10-10, 12-12-12, 10-20-20, and 15-15-0 were produced without artificial drying at moisture contents less than 2%. When bagged after 7 days of curing, these grades did not cake in 3 months' storage in 12-bag stacks. Some bag set occurred when no coating agent was added; when 2.5% kaolin was added, little or no bag set occurred.

Grades of lower nitrogen content such as 6-12-12 and 5-20-20, produced at moisture contents of 2 to 5% without artificial drying, were satisfactory in bag-storage tests when cured and dusted.

The effects of artificial drying on the storage properties were studied; products that were well dried remained free flowing in bag-storage tests without curing or dusting. Some formulations required artificial drying to ensure satisfactory physical properties.

Reversion of phosphorus pentoxide to a citrate-insoluble form during storage was negligible in granular fertilizers containing less than 2% moisture; significant reversion occurred in products of 6% or more moisture and increased with length of time and temperature of storage.

Greenhouse and field tests showed no appreciable difference in fertilizer efficiency between coarse granular and fine materials when the water solubility of the phosphorus was in the range of 25 to 60%.

About 50 commercial installations of the TVA-type continuous ammoniator are in operation. A large portion of them are being used successfully to produce a granular fertilizer.

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