

# Use of Ammoniating Solutions Containing Urea in Producing Granular Fertilizers

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Studies were made to compare ammoniating solutions containing urea with ammonia-ammonium nitrate solutions in the production of high-analysis granular fertilizers. The work included production of 5-20-20, 6-12-12, 8-16-16, 10-20-20, and 12-12-12 fertilizers in the TVA continuous ammoniation-granulation pilot plant. Operation with solutions containing ammonia, urea, and ammonium nitrate was about the same as with solutions containing only ammonia and ammonium nitrate. With solutions containing urea but no ammonium nitrate, more moisture usually was required for granulation, temperatures were lower, and the products contained more moisture when not dried. Granulation generally was slightly better with the urea-containing solutions. The storage properties of the products were about the same except that those made with urea solutions had harder bag set. There was no apparent loss of ammonia due to decomposition of urea during processing.

INCREASED PRODUCTION of urea in this country has promoted interest in the use of ammoniating solutions containing urea in the production of high-analysis granular fertilizers. Currently, a number of companies are marketing such solutions for this use. This paper describes tests of the use of ammoniating solutions containing urea in the TVA granulation process and compares the results with those obtained when using solutions containing only ammonia and ammonium nitrate (7).

### Materials, Equipment, and Procedures

The ammoniating solutions tested in the pilot plant were similar in composition to typical solutions available from commercial producers. The chemical compositions of these solutions are shown below:

Designation	Composition, %					Total N
	Free ammonia	Urea	Ammonium nitrate	Ammonium carbamate	Water	
X	21.7	0	65.0	0	13.3	40.6
Y	26.0	0	55.5	0	18.5	40.8
U	30.6	43.1	0	0	26.3	45.3
UC	24.1	43.3	0	15.0	17.6	45.5
UN	24.5	10.0	56.0	0	9.5	44.4

Other raw materials were ordinary and concentrated superphosphates, potassium chloride, ammonium sulfate, crys-

talline urea, sulfuric acid (66° Bé.), and phosphoric acid (78% H<sub>3</sub>PO<sub>4</sub>). Typical analyses of the solid raw materials are shown in Table I. The tests reported in this paper were made with nongranular potassium chloride.

The TVA ammoniation-granulation pilot plant used in this work has been described in detail (7).

The solid raw materials were fed through volumetric feeders. The ammoniating solutions and acids were fed through distributors submerged in the cascading bed of solids in the ammoniator. Fines produced in the crushing and screening operation were recycled to the ammoniator at a rate approximately equal to their production rate in most cases. The quantity of recycle was not considered great enough to exercise a major effect on granulation.

Each ammoniating solution was tested

in the production of the following grades of granular fertilizers: 5-20-20, 6-12-12, 8-16-16, 10-20-20, and 12-12-

12. In each test, one or more of the factors that influence granulation were varied until conditions were established that appeared to give the best granulation. When there was too much liquid phase in the ammoniator, granulation was controlled by blowing air onto the bed of solids or by substituting a solid form of nitrogen for some of the ammoniating solution. When there was too little liquid phase, additional heat and moisture were introduced by adding steam or water or by increasing the heat of reaction by the addition of sulfuric acid. Other methods could be used, possibly to advantage in practice, depending on the facilities available and materials costs. For example, steam might be substituted for some of the acid to provide heat for granulating 5-20-20. The use of granular raw materials also might be used to promote granulation in this and other grades. An increased amount of recycle might be used instead of air to control granulation of 12-12-12 and other grades that tend to overgranulate. The extent to which control is needed will often be different in large-scale plants because of differences in heat loss and other reasons.

The net rate of production was 1 ton per hour for the 6-12-12 and 10-20-20 grades, 2 tons per hour for the 5-20-20

Table I. Typical Analyses of Solid Raw Materials

Raw Material	Chemical Composition, %						Screen Analysis (Tyler), %			
	N	P <sub>2</sub> O <sub>5</sub>			H <sub>2</sub> O	K <sub>2</sub> O				
		Total	C.I.	W.S.			+6	+28	+48	-48
Ordinary superphosphate	...	20.9	0.9	18.2	6.5	...	3.1	31.7	36.9	28.3
Concentrated superphosphate	...	49.6	1.3	45.4	3.2	...	6.5	38.6	13.6	41.3
Potassium chloride	...	...	...	...	0.1	61.0	0.6	24.7	32.6	42.1
Ammonium sulfate	20.7	...	...	...	0.1	...	0.0	28.9	32.9	38.2
Urea (crystalline)	46.5	...	...	...	0.1	...	0.0	5.4	30.8	63.8

grades, and 3 tons per hour for the 8-16-16 and 12-12-12 grades. These rates were used so that the results of tests with solutions containing urea could be compared directly with the results of earlier tests made at these rates with solutions containing only ammonia and ammonium nitrate. For the same reason, most of the products were not dried artificially.

### Granulation Results

Table II shows the formulations used and the conditions required for granulation with the different ammoniating solutions. The formulations represent the actual weights of materials used and are slightly different from calculated formulations, in some cases, because of inaccuracies in feeding equipment.

**5-20-20.** The formulations for the 5-20-20 grade included ammoniating solution, ordinary and concentrated superphosphates, potassium chloride, and sulfuric acid. The acid was not required to fix the free ammonia in the ammoniating solutions but was added to increase the amount of heat released in the ammoniator and thereby promote granulation. Satisfactory granulation was obtained with each of the ammoniating solutions, but the amount of acid required varied. The amount of acid required when using solutions UN and Y was about the same—about 140 pounds per ton of product. With solutions U and UC, it was necessary to use about 165 pounds of acid, nearly the maximum that could be neutralized by the free ammonia. Also, it was necessary to add a small amount of water with solution U and to add both water and steam with solution UC.

The temperature of the material from the ammoniator, when using solution UC, was 185° F. as compared with about 205° F. when the other solutions were used. As a result, the final product cooled but not dried artificially, contained about 5% moisture as compared with about 2%. (Moisture was determined by the vacuum desiccator method.) The over-all yield of on-size material (-6 +28 mesh), including crushed oversize, was somewhat higher in the tests with solutions containing urea than in the test with ammonia-ammonium nitrate solution. The degree of ammoniation of the superphosphates in these tests was only 0.4 to 1.0 pound per unit of available phosphorus pentoxide because of the large amounts of sulfuric acid used. The loss of free ammonia, determined from samples of the ammoniator exhaust gas, was very low.

Anhydrous ammonia rather than ammoniating solution may be used to supply all of the nitrogen for 5-20-20, as described previously (2). The results obtained with anhydrous ammonia

were somewhat better than with any of the solutions, and the cost of raw materials usually would be lower.

**6-12-12.** The 6-12-12 grade was formulated from ammoniating solution, ordinary superphosphate, and potassium chloride. All of the supplemental heat and moisture needed for good granulation was supplied through the addition of steam. No acid was added and all of the free ammonia in the solutions was utilized in ammoniation of the superphosphate. The data in the table are arranged in the order of increasing steam requirement. The formulation, which contained solution Y, required the least amount of steam—150 pounds per ton of product. A small amount of water was added to compensate for the unusually low moisture content of the superphosphate used in this test. Steam requirements when using solutions UN, U, and UC were 245, 319, and 356 pounds per ton of product, respectively. In all of the tests of this grade, good granulation was obtained at a temperature of 185° to 190° F., and the moisture contents of the products from the ammoniator were about 7%. The moisture contents of the products after passing through the cooler ranged from 4.2 to 5.0%. The on-size recovery, including crushed oversize, was 83% in the tests with solutions containing urea and 78% in the test with the ammonia-ammonium nitrate solution.

The loss of free ammonia was less than 2% in the tests with solutions Y and UN in which the degree of ammoniation of the ordinary superphosphate was about 6.0 pounds per unit of available phosphorus pentoxide. In the test with solution U, the input degree of ammoniation was 6.7 because of its higher content of free ammonia. Also, in the test with solution UC, the input degree of ammoniation was high, about 7.0, because the ammonium carbamate decomposed to free ammonia and carbon dioxide in the ammoniator. Consequently, the losses of free ammonia in the tests with solutions U and UC were somewhat greater than in the tests with solutions Y and UN. The addition of sulfuric acid would have reduced the losses.

**8-16-16.** In formulating the 8-16-16 grade, all 8 units of nitrogen were supplied as ammoniating solution. The solid ingredients were ordinary superphosphate and potassium chloride. Phosphoric acid was added as a supplementary source of phosphorus pentoxide and to fix free ammonia. The products from these tests were dried artificially.

The controls required for granulation varied considerably with the different solutions. When solution Y was used, it was necessary to use about 3500 cubic feet of cooling air per ton of product to prevent overagglomeration. The

formulation containing solution UN required practically no additions for control of granulation; a small amount of water was required because of the low moisture content of solution UN. When solution U was used, cooling air was required for control of granulation because a high ammoniator temperature, along with the high moisture content, would give overagglomeration. The amount of heat released in the ammoniator was less when solution UC was used, and it was necessary to add water to aid granulation. There was a relatively large amount of fines in the product from the dryer in all the tests. This was caused primarily by breakdown of granules in the dryer, particularly in the two tests with solutions U and UC in which the input moisture was high. Consequently, the on-size recovery was low when these two solutions were used.

The degree of ammoniation varied from 5.8 to 6.8 pounds per unit of available phosphorus pentoxide in these tests, depending on the type of solution used and the amount of phosphoric acid required to supplement the phosphorus pentoxide from ordinary superphosphate. The loss of free ammonia was 3% or less in all tests.

**10-20-20.** The data for the production of 10-20-20 granular fertilizer are from tests in which all of the nitrogen was supplied as solution. The other materials were concentrated superphosphate, potassium chloride, and sulfuric acid. A sufficient amount of acid was added to react with the free ammonia present in excess of about 3.8 pounds per unit of available phosphorus pentoxide. At this degree of ammoniation, the loss of free ammonia was 3.5% or less.

Air was used to control granulation. The amount of air required decreased as the amount of acid required to fix the free ammonia in the formulation decreased, except in the test with solution UC. Operation with solutions U, UN, and X required 2500, 1650, and 750 pounds of air per ton of product, respectively. With solution UC, no air was required; in fact, it was necessary to add water to promote granulation. Because of the high input moisture and the low temperature in the ammoniator, the moisture content of the product was high.

In another series of tests of 10-20-20 fertilizer, solution U was used to supply 8, 9, or 10 units of nitrogen and the remainder of the nitrogen was supplied as crystalline urea. The data from this series are tabulated below. As the amount of solution was increased, the requirement of acid increased and the amount of air required for control of granulation increased. Although the input moisture was highest when using 10 units of nitrogen from solution, the moisture content of the product was lowest because of the relatively high

Table II. Pilot-Plant Data for Production of Granular Fertilizers

Grade	5-20-20						6-12-12						8-16-16						10-20-20						12-12-12					
	UN	Y	U	UC	Y	U	UN	U	UC	Y	U	UC	UN	U	UC	Y	U	UC	UN	X	UC	X	UC	UN	UN	X	UC	X	UC	UN
Type of solution	242	252	208	218	329	298	285	291	291	405	384	369	450	457	499	431	431	387	431	431	431	431	431	431	431	431	431	431	431	431
Units N from solution	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Formulation, lb./ton	260	260	321	351	1265	1214	1266	1232	992	982	1072	1066	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ammoniating solution	741	741	705	672	0	0	0	0	0	241	221	195	817	820	854	815	815	300	300	300	300	300	300	300	300	300	300	300	300	300
Ammonium sulfate	657	669	653	607	414	407	412	406	515	535	533	504	652	655	620	622	622	417	417	417	417	417	417	417	417	417	417	417	417	417
Urea	137	143	168	165	0	0	0	0	0	0	0	0	189	113	93	151	126	132	132	132	132	132	132	132	132	132	132	132	132	132
Ordinary superphosphate	0	0	0	0	0	93	102	94	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Concentrated superphosphate	2037	2065	2055	2013	2008	2012	2065	2023	2153	2122	2169	2111	2108	2045	2066	2019	2045	2061	2061	2061	2061	2061	2061	2061	2061	2061	2061	2061	2061	2061
Potassium chloride	208	397	183	174	431	513	365	489	402	407	0	0	315	285	392	253	465	537	537	537	537	537	537	537	537	537	537	537	537	537
Sulfuric acid (66° Bc.)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Filler (sand)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total	204	206	205	185	187	190	185	190	192	192	186	172	201	198	197	172	199	201	201	201	201	201	201	201	201	201	201	201	201	201
Recycle	3.4	4.4	5.0	12.9	11.5	13.6	17.9	17.6	6.6	6.8	9.6	10.2	7.2	3.6	3.6	7.9	4.5	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Water	3.5	4.4	4.1	8.1	7.3	6.8	7.0	7.0	4.6	5.2	6.1	8.4	4.5	2.7	2.9	5.8	2.4	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Steam	1.6	1.7	1.9	5.1	4.2	5.0	4.7	5.0	0.9	1.5	1.8	4.1	2.8	1.6	1.1	4.6	1.5	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Air, cu. ft./ton	0.8	1.0	0.4	0.7	6.1	6.0	6.7	7.0	3.0	3.0	2.1	1.3	3.9	3.9	3.9	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
Ammoniator temperature, ° F.	0.3	0.1	0.0	0.1	1.2	1.8	4.0	11.7	3.0	2.1	1.3	1.0	2.1	1.6	2.8	2.0	1.4	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Moisture content, %	38	31	21	40	35	23	23	37	39	41	22	20	28	38	30	33	26	25	25	25	25	25	25	25	25	25	25	25	25	25
Input	60	56	70	59	52	67	66	55	41	47	37	45	70	61	69	58	69	70	70	70	70	70	70	70	70	70	70	70	70	70
Ammoniator product	2	13	9	1	13	10	11	8	20	12	41	35	2	1	1	9	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Final product (cooled)	88	80	86	89	78	84	84	83	70	78	53	60	91	89	91	83	88	89	89	89	89	89	89	89	89	89	89	89	89	89
Input degree of ammoniation, lb. NH <sub>3</sub> /unit available P <sub>2</sub> O <sub>5</sub>	5.2	5.0	4.9	4.8	6.9	6.3	5.9	6.4	8.0	8.3	8.2	8.3	9.8	10.3	10.4	9.9	11.6	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9
Loss of free ammonia, %	21.2	20.7	20.0	19.4	13.1	12.8	12.7	12.2	16.6	16.6	17.0	16.9	19.6	19.5	19.1	20.7	12.6	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3	12.3
Granulation, %	18.5	21.3	21.6	20.7	12.3	10.0	12.9	13.0	17.3	15.4	15.1	14.0	20.3	20.6	19.6	19.1	12.0	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2	12.2
Oversize (+6 mesh)																														
On-size (-6 +28 mesh)																														
Undersize (-28 mesh)																														
On-size recovery after crushing oversize, %																														
Product analysis, %																														
Total N																														
Available P <sub>2</sub> O <sub>5</sub>																														
AOAC K <sub>2</sub> O																														

air rate used and the large amount of heat released in the ammoniator, both of which increased the amount of water evaporated.

Units N from solution U	8	9	10
Sulfuric acid (66° Bc.), lb./ton	99	144	189
Air, cu. ft./ton	0	900	2500
Ammoniator temperature, ° F.	185	192	201
Moisture content, %			
Input	5.4	6.7	7.2
Ammoniator product	4.7	4.8	4.5
Final product (cooled)	3.4	3.5	2.8
On-size recovery after crushing oversize, %	92	90	91

12-12-12. The 12-12-12 grade was formulated from ammoniating solution, ammonium sulfate or crystalline urea, ordinary and concentrated superphosphates, potassium chloride, and sulfuric acid.

Ten units of nitrogen from solution was the maximum that could be used without excessive overagglomeration. Good granulation was obtained when 10 units of nitrogen were supplied as solution UC and 2 units were supplied as ammonium sulfate, and a moderate amount of cooling air, 3100 cubic feet per ton product, was used. When solution X was used to supply 10 units of nitrogen, 5200 cubic feet of air were required. Only 9 units of nitrogen could be supplied as solution UN without causing excessive agglomeration; the requirement of air was 2000 cubic feet per ton of product. When an attempt was made to supply 9.5 units of nitrogen as solution UN, excessive agglomeration could not be prevented even though a large amount of air was used.

The data of Table II also show the effect of using solid urea in the production of 12-12-12 granular fertilizer. When 4 units of solid urea and 8 units of solution U or UC were used, a large amount of cooling air, about 5600 cubic feet per ton product, was required to prevent serious overagglomeration. When 4 units of nitrogen were supplied as ammonium sulfate and 8 units as solution UC, no cooling air was required. This difference was due, presumably, to the greater solubility of urea.

The formulations for the 12-12-12 tests were calculated to provide 5.8 pounds of free ammonia per unit of available phosphorus pentoxide in the ordinary superphosphate and 3.8 pounds per unit in the concentrated superphosphate. Although inaccuracies in feeding of materials resulted in higher ratios of free ammonia to phosphorus pentoxide than desired in some tests, losses of ammonia were less than 4.5%.

Discussion of Results. Operation with solution UN, which contained ammonia, ammonium nitrate, and urea, was similar to or slightly better than with the nonurea solution when producing granular fertilizers containing up to

10 units of nitrogen. There was no significant difference in the controls required for granulation, and granulation efficiency was better in some cases when the urea-containing solution was used. A smaller portion of the nitrogen could be obtained from solution when the 12-12-12 grade was formulated with solution UN, however. This may have been caused by greater solubility exhibited by mixtures of urea and ammonium nitrate than by either component alone.

Formulations with solution U, which contained urea and ammonia, required more heat or moisture to promote granulation in the low-nitrogen grades than did formulations with solutions which contained ammonium nitrate. In most cases, the moisture contents of the undried products made with solution U were higher because of the greater amount of water in this solution. Granulation was equal to or better than that obtained with the ammonium nitrate-ammonia solutions in most cases.

The use of solution UC, which contained ammonium carbamate, usually resulted in a lower temperature in the ammoniator than was obtained when using the other solutions. This presumably was due to the heat absorbed by the decomposition of the carbamate. Consequently, it was more difficult to promote granulation of the low-nitrogen grades with this solution. More supplementary heat and moisture were required and the moisture content of the product usually was higher. This characteristic may be of some advantage in the production of high-nitrogen grades in which overgranulation is a problem.

There was no evidence that the amount of ammonia lost was influenced by the type of solutions used. The loss of phosphorus pentoxide availability, which was less than 1.5% in most of the tests, also was not affected by the type of solution.

### Hydrolysis of Urea

Urea hydrolyzes at elevated temperatures to form carbon dioxide and free ammonia. Jensen (3) reported that urea in mixed fertilizers stored at 110° F. hydrolyzes at a rate of about 5% per month. As considerably higher temperatures are attained in the continuous ammoniator and, in some cases, exist in storage piles, tests were made to determine to what extent hydrolysis of urea would occur during processing and storage. The amount of urea hydrolyzed was estimated by material balance methods. In analyzing the products, the determination of ammoniacal nitrogen in the presence of urea was made by a method described by Yee and Davis (4). The difference between the ammoniacal and the total nitrogen

content was assumed to be urea nitrogen. This method was not applicable to products made from solution UN, which contained nitrate nitrogen.

The results of these tests indicated that no appreciable amount of urea was hydrolyzed during processing, as the indicated hydrolysis ranged from -3 to +3.5% which was considered to be within the accuracy of the analytical procedure used.

The effect of storage on hydrolysis of urea was determined on two 12-12-12 products formulated with 8 units of nitrogen from solution containing urea and 4 units from solid urea. One product contained 1% moisture and the other contained 3% moisture. Samples were placed in closed jars and stored for 12, 30, 60, and 90 days in ovens maintained at 100°, 130°, and 180° F.

The effect of storage time and temperature on hydrolysis of urea is shown in Figure 1. About one third of the urea was hydrolyzed during 60 to 90 days of storage at 180° F. At 130° F., which probably is closer to the storage tempera-

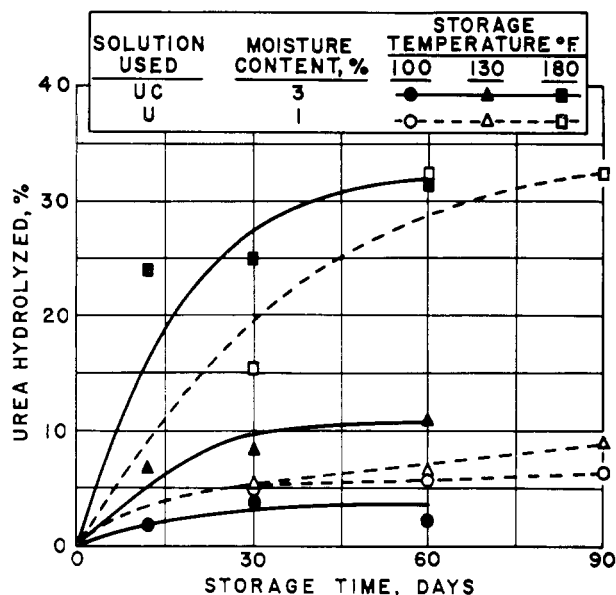


Figure 1. Effect of storage time and temperature on hydrolysis of urea in 12-12-12 fertilizer

ture found in practice, about 10% or less of the urea hydrolyzed. At these temperatures the rate of hydrolysis was greater in the samples having higher moisture content. At 100° F., about 5% or less was hydrolyzed in 60 days.

No actual loss of ammonia occurred during the storage tests. The free ammonia resulting from the hydrolysis of urea was fixed through further ammoniation of the superphosphate in the samples. As shown in the following tabulation, there was a marked increase in the degree of ammoniation and a decrease in the water-soluble phosphorus pentoxide with increase in storage temperature. The citrate solubility of the phosphorus pentoxide in the product that contained 1% moisture was not affected on storage at 130° F. and decreased from 98 to 95% on storage at 180° F. However, the citrate solubility of the phosphorus pentoxide in the product containing 3% moisture decreased from 95 to 93% on storage at 130° F. and to 85% on storage at 180° F.

	Original Sample	After 60 Days Storage at:		
		100° F.	130° F.	180° F.
INITIAL MOISTURE, 1%				
Degree of ammoniation, lb. NH <sub>3</sub> /unit P <sub>2</sub> O <sub>5</sub>	4.0	4.7	4.9	8.5
Water-soluble P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	55	41	38	10
Citrate-soluble P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	98	98	98	95
INITIAL MOISTURE, 3%				
Degree of ammoniation, lb. NH <sub>3</sub> /unit P <sub>2</sub> O <sub>5</sub>	4.1	4.5	5.9	8.8
Water-soluble P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	47	40	25	5
Citrate-soluble P <sub>2</sub> O <sub>5</sub> , % of total P <sub>2</sub> O <sub>5</sub>	95	95	93	85

**Table III. Results of Bag-Storage Tests**

Source of Nitrogen Type of solution		Artificially Dried?	Moisture Content as Made, %	3-Month Storage Results							
				Not Cured				Cured 7 Days			
				Not Conditioned		Conditioned <sup>a</sup>		Not Conditioned		Conditioned <sup>a</sup>	
Other	Bag set	% lumps <sup>b</sup>	Bag set	% lumps <sup>b</sup>	Bag set	% lumps <sup>b</sup>	Bag set	% lumps <sup>b</sup>			
5-20-20 Grade											
UN	None	No	1.8	Medium	0	Medium	0	Medium	0	Light	0
Y	None	No	1.8	Medium	0	Medium	0	Medium	0	Light	0
U	None	No	2.1	Hard	0	Hard	0	Medium	0	Medium	0
UC	None	No	5.7	Hard	0	Hard	0	Hard	0	Medium	0
6-12-12 Grade											
U	None	No	3.0	...	..	...	..	Hard	1	Medium	0
U	None	No	4.3	Hard	1	Hard	0	Hard	6	Hard	0
UN	None	No	4.7	...	..	...	..	Hard	0	Light	0
UC	None	No	5.2	Hard	1	Hard	0	Hard	1	Hard	0
Y	None	No	5.2	Medium	0	None	0	Light	0	None	0
8-16-16 Grade											
UN	None	Yes	1.2	Hard	0	Medium	0	Medium	0	Light	0
Y	None	Yes	1.2	Medium	0	...	..	Medium	0	...	..
U	None	Yes	1.4	Medium	0	...	..	...	..	...	..
UC	None	Yes	4.2	Hard	6	Hard	0	Hard	2	Medium	0
10-20-20 Grade											
UC	None	Yes	0.4	Medium	0	Light	0	Light	0	Light	0
UN	None	No	1.8	Hard	8	Medium	0	Medium	0	Light	0
X	None	No	1.8	Light	3	Light	0	Medium	1	Light	0
UN	None	No	2.1	Hard	3	Medium	0	Hard	0	Medium	0
X	None	No	2.8	Hard	19	Light	0	Hard	10	Light	0
U	Urea-2 units	No	3.5	Hard	18	Hard	1	Hard	21	Hard	0
U	Urea-1 unit	No	3.6	Hard	15	Hard	0	Hard	6	Light	0
UC	None	No	4.7	Hard	22	Hard	0	Hard	28	Hard	0
12-12-12 Grade											
UC	A/S <sup>c</sup> -2 units	Yes	0.7	Hard	0	Medium	0	Medium	0	Light	0
X	A/S <sup>c</sup> -2 units	No	1.3	Hard	3	Light	0	Light	0	None	0
UN	A/S <sup>c</sup> -3 units	No	1.7	Hard	7	Hard	0	Hard	1	Medium	0
U	Urea-4 units	No	2.4	Hard	21	Hard	13	Hard	13	Medium	0
UC	A/S <sup>c</sup> -4 units	No	3.2	Hard	21	Hard	0	Hard	8	Hard	0
UC	Urea-4 units	No	3.3	Hard	19	Hard	6	Hard	13	Medium	0

<sup>a</sup> Dusted with 2.5% kaolin. Similar results obtained with kieselguhr.

<sup>b</sup> Plus 1/2-inch lumps after dropping bag four times from 3-foot level—once on each face and side.

<sup>c</sup> A/S = ammonium sulfate.

**Physical Properties**

**Bag Storage.** The bag-storage properties of the pilot-plant products were tested by storing them in five-ply paper bags having one asphalt-laminated ply. The bagged products were placed in the lower four positions of stacks 12 bags high in an unheated building. The tests included study of the effects of curing before bagging and the use of kaolin and kieselguhr as conditioners. After storage for 3 months, some bags were inspected for bag set. Other bags were dropped four times from a height of 3 feet, once on each face and side, and then examined to determine the proportion of 1/2-inch lumps present after dropping. The results of the bag-storage tests are given in Table III. Results with kieselguhr were the same as with kaolin and, therefore, are not included. The tests are arranged in the table according to moisture contents of the fertilizers. Results on some nonurea products are included for comparison.

Uncured, unconditioned 5-20-20 and 6-12-12 product containing urea showed little or no lumps after the drop test when bagged at moisture contents up

to the maximum tested, which was about 5%. However, bag sets were hard in almost all cases. A combination of 7-day curing plus conditioning with 2.5% of kaolin prior to bagging reduced bag sets in most of these products to light or medium. Products of 8-16-16 grade containing 1.4% or less moisture that were stored without curing or conditioning contained no lumps after the drop test. Cured, conditioned product of 4% moisture content also was free of lumps. Bag sets of the uncured, unconditioned products were medium to hard; curing and conditioning reduced bag set somewhat.

The 10-20-20 and 12-12-12 grades, when stored without curing or conditioning, showed lumps after the drop test except when the moisture content was below about 1%. When products of these grades were cured and conditioned prior to bagging, there were no lumps in any of the products. Bag sets of the cured, dusted products were light or medium when moisture content was below about 3%.

When products that contained urea were conditioned without prior curing, the reduction in lump formation was

almost as great as when the products were both cured and conditioned. However, bag sets were not reduced in most cases by dusting alone. In tests of curing without dusting, there was little improvement in storage properties. Microscopic examination of samples of the granular fertilizers containing urea showed that the caking was due to extensive growth of crystals of urea-ammonium chloride complex on the surface of the granules during storage. These crystals, which had the composition CO(NH<sub>2</sub>)<sub>2</sub>.NH<sub>4</sub>Cl, formed bridges between granules. The use of kaolin conditioner on the granules was found to modify the nature of this crystal growth and weaken the bonds between granules. It was noted that growth of the surface crystals was still active after 3 months of storage, which probably explains why 7-day curing of these products was not very effective in reducing caking.

The storage properties of the products formulated with solutions containing urea appear to be about the same as those of nonurea products of equal grade and moisture content, except that bag sets, generally, were harder. No dif-

ferences in storage properties were noted that could be attributed to differences between the several types of solutions that contained urea.

**Particle Strength.** The particle strengths of the pilot-plant products were compared by a procedure that involved the use of a small ball mill. The mill was a cylinder, 10 inches in diameter by 12 inches long, equipped with flights. About 1 quart of the product and 100  $\frac{5}{16}$ -inch steel balls were placed in the mill, which was rotated for 5 minutes at about 60 r.p.m. The decrease in the proportion of +28-mesh material during milling was used as a measure of the strength of the particles.

There was no appreciable difference in the strength of products made with

the different solutions except for the 5-20-20 grade. This product made with solution UC was somewhat weaker than the others probably because of the larger amount of moisture required for granulation. The particle strengths of the high-nitrogen grades generally were greater than those of the low-nitrogen grades.

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## **CALCIUM METAPHOSPHATE IN FERTILIZERS**

### **Utilization of Calcium Metaphosphate in Production of Granular Fertilizers**

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A process was developed to increase the utility of calcium metaphosphate by increasing its water solubility and granulating it with other fertilizer components. The process consists of partially hydrolyzing calcium metaphosphate in the presence of a mineral acid and ammoniating the hydrolyzate in the TVA continuous ammoniator. In pilot-plant studies, a wide variety of grades of granular fertilizers was produced using calcium metaphosphate to supply all or part of the phosphate. The products had moderately high water solubility, unusually low moisture content, and very good physical properties.

**F**ERTILIZER-GRADE CALCIUM METAPHOSPHATE  $[\text{Ca}(\text{PO}_3)_2]$  is a vitreous material produced by the reaction of phosphate rock with phosphorus pentoxide at an elevated temperature (8, 10). Expressed on an oxide basis, the product of this reaction contains about 65% phosphorus pentoxide, 25% calcium oxide, 7% silicon dioxide, and minor amounts of aluminum, iron, and fluorine. Substantially all of the phosphate is in a citrate-soluble form, but the material dissolves very slowly in water at room temperature and little water-soluble phosphate is detected by the standard method of the Association of Official Agricultural Chemists (AOAC).

The Tennessee Valley Authority (TVA) has produced calcium metaphosphate fertilizer for test-demonstration purposes for a number of years and at present is the sole producer. As part of this test-demonstration program, agronomic studies have been made on demonstration farms in every section of the country by land grant colleges, the U. S. Department of Agriculture, and

organizations of farmers. These tests have shown calcium metaphosphate to be equal to superphosphate as a source of phosphorus for most crops on acid and neutral soils (5). The acceptance and widespread use of calcium metaphosphate have been limited, however, because of its slow solubility in water and because it cannot be used as a carrier of low-cost ammonia.

Because of the high phosphate content of calcium metaphosphate, which leads to low handling and shipping costs, TVA and others (7) have sought methods for increasing its water solubility and for using it in the manufacture of high-analysis granular fertilizers. The initial work by TVA was based on the knowledge that calcium metaphosphate can be hydrolyzed rapidly in the presence of mineral acids and thus rendered readily water soluble (2, 3, 6). Hydrolysis is used in this paper to mean any reaction of calcium metaphosphate with water or acid that converts the phosphate into a readily water-soluble form. A series of reactions takes place with formation of

complex compounds intermediate between metaphosphate and orthophosphate. Bench-scale tests showed that the hydrolyzate could be ammoniated with commercially available nitrogen solutions and potassium chloride could be added to produce fertilizers of various N:  $\text{P}_2\text{O}_5$ : $\text{K}_2\text{O}$  ratios.

In searching for engineering equipment for carrying out such a process, tests were made in the TVA pilot-plant continuous ammoniator (4, 9). The advantage of this approach was that this type of equipment was already in use in many fertilizer plants. As adapted for use in the continuous ammoniator, the process consists of hydrolyzing part of the calcium metaphosphate in the presence of acid in the first half of the ammoniator and ammoniating the hydrolyzate with nitrogen solution in the second half. When desired, potassium chloride is added in the ammoniator. The ammoniated material is then cooled and screened to separate the product-sized fraction. The oversized fraction is crushed and recycled to the ammonia-