determined with Karl-Fischer reagent (4). The vacuum desiccator method for moisture (7) was not used because equilibrium was not reached in the prescribed 16 hours, presumably because of loss of ammonia. Silverberg and Heil (6) have described the storage properties of bulk and bagged diammonium phosphate.

Losses. Losses of ammonia and phosphorous pentoxide from the crystallizer were measured by analyzing a continuous sample of the effluent from the barometric leg of the spray condenser. The rate of flow of the effluent was measured with an orifice meter. Blank determinations for nitrogen and phosphorus pentoxide were made on the cooling water to the condenser. Losses measured in this way were 2.3% of the ammonia and negligible amounts of phosphorus pentoxide. The low phosphorus pentoxide loss indicated that very little entrainment occurred in the vaporizer. The losses reported here are considered to be acceptable; however, the ammonia loss could be reduced further by lowering the operating pH or by lowering the operating temperature. More care would be necessary in using a lower pH, as monoammonium phosphate crystallizes when the pH is below about 5.8 (7). The only limitation on lowering the temperature would be the capacity of the evacuating system.

Impurities. After several weeks of operation, the mother liquor, which originally was clear and colorless, became dark and cloudy with impurities that were in the phosphoric acid. The concentration of insoluble impurities in the mother liquor varied from 0.1 to 1.0% by weight. A chemical analysis of a sample of filtered, washed, undried impurities from the mother liquor showed: 14.0% of phosphorus pentoxide, 9.3% of calcium oxide, 6.0% of silicon dioxide, 1.6% of aluminum oxide, 0.3% of ferric oxide, 1.6% of fluorine, and 57.0% of water. The insoluble impurities were discharged from the crystallizer by retention on the crystals and had no effect on operation.

Discussion

The over-all operation of the plant was exceptionally trouble-free. Close control of feed proportions was not required because diammonium phosphate crystallizes from a mother liquor that may vary widely in composition. No difficulty with freezing of material in pipelines was experienced because of the favorable temperature-solubility relationship of diammonium phosphate. Ammonia losses were controlled easily without recovery equipment. The crystals formed were strong and did not break in the centrifuge and dryer. The crystals dried quickly, and little caking occurred in the dryer. The product was free flowing and easily handled with bucket elevators, belt conveyors, vibrating conveyors, and screw conveyors. No dust or fume nuisance was created.

Acknowledgments

The authors acknowledge the contributions of L. B. Hein, formerly with TVA, who directed the first stages of the work and of M. R. Siegel who directed the work in the latter stages. T. P. Hignett, Chief of the Development Branch, gave valuable suggestions and guidance. Shift engineers were G. M. Blouin, J. L. Graham, J. S. Lewis, I. W. McCamy, and V. J. Jones. F. H. Haynie was in charge of plant design, R. E. Sentz was supervisor of plant operations, and T. C. McRight was in charge of analytical control. Julius Silverberg assisted in the preparation of this paper.

Literature Cited

(1) Association of Official Agricultural Chemists, Washington, D. C., "Official Methods of Analysis," 8th ed., p. 7, 1955.
(2) Hignett, T. P., Hicks, G. C., Jordan, J. E., *Com. Fertilizer and Plant Food Ind.* **93,** No. 4, 24–6 (1956).
(3) Houston, E. C., Yates, L. D., Haunschild, R. L., J. Agr. Food Chem. **3,** 43–8 (1955).
(4) Mitchell, John, Jr., Smith, D. M., "Aquametry", pp. 234–5, Interscience, New York, 1948.
(5) Saeman, W. C., McCamy, I. W., Houston, E. C., *Ind. Eng. Chem.* **44,** 1912–15 (1952).
(6) Silverberg, Julius, Heil, F. G., J. Agr. Food Chem. **5,** 436–41 (1957).
(7) Thompson, H. L., Miller, P., Johnson, R. M., McCamy, I. W., Hoffmeister, G., *Ind. Eng. Chem.* **42,** 2176–82 (1950).

Received for review September 13, 1956. Accepted March 27, 1957. Division of Fertilizer and Soil Chemistry, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

FERTILIZER STORAGE

Storage Properties of Diammonium Phosphate Alone and in Admixture with Other Fertilizer Materials

JULIUS SILVERBERG and F. G. HEIL
Tennessee Valley Authority, Wilson Dam, Ala.

Diammonium phosphate fertilizer as produced by TVA (2) in its demonstration plant is a crystalline material containing 21.0% nitrogen, 53.7% phosphorus pentoxide, and less than 0.1% moisture. It is produced from anhydrous gaseous ammonia and electric-furnace phosphoric acid in a vacuum crystallizer, and a small amount of sulfuric acid is added during crystallization to change its crystal shape from plate to almost cubical. It is relatively nonhygroscopic, having a critical humidity of about 83% at 86° F. About 85% of the product is larger than 32 mesh in size.

Because of its relatively low hygroscopicity and its very low moisture content, it was first thought that the product would not cake in storage. However, bag set and caking did occur to some degree even though the product was stored in multiwall paper bags having moisture-resistant plies; actually, light cementing of the crystals occurred. Tests were made to determine the storage properties of crystalline diammonium phosphate and to identify conditioning agents that would prevent caking.

Bag Storage of Diammonium Phosphate

The material to be tested was bagged in five- and six-ply paper bags having one- and two-asphalt laminated plies, respectively. Bags filled with 80 pounds of the material were stored for periods of up to 9 months in stacks 12 bags high. The storage area was in a large, unheated warehouse of hollow tile construction with a concrete floor. The windows of the building were open. Each test stack rested on a sand-filled dummy bag placed on a wooden platform. Three or four test stacks were used for each product. After storage periods of 1, 3, 6, and 9 months, the bags in positions 11 and 12 from the top were removed from one stack and inspected. The bags in positions 1 through 10 usually were not inspected, and in many cases dummy bags were used in these positions. At the time of inspection, the degree of bag set and the

Tests were made to determine the storage properties of diammonium phosphate fertilizer produced in TVA's demonstration-scale plant. Unconditioned product, containing 0.1% moisture, caked in 3 to 6 months in bags. Dusting the product with only 1% of calcined dolomite prevented caking for over 9 months and was more effective than dusting with 3% of kaolin or kieselguhr. Unconditioned product stored in bulk caked throughout the pile, but normal handling prior to bagging disintegrated the cake satisfactorily. Diammonium phosphate was compatible with commonly used fertilizer materials such as ammonium nitrate, ammonium sulfate, and potassium chloride. Grades of mixed fertilizers tested included 15-15-15, 18-18-18, 16-32-16, 26-26-0, and 10-30-20. Excessive segregation did not occur in dry mixtures. Granulated products containing diammonium phosphate stored as well as granulated products made from conventional materials. Formulations for liquid fertilizers containing diammonium phosphate are given.

condition of the bag were noted. The test bags were then dropped four times from a height of 3 feet, once on each face and side. The proportion of lumps larger than 2 mesh was determined by screening, and this was regarded as a measure of the degree of caking.

The diammonium phosphate used in the tests was plant product obtained on 6 different days of operation (samples A to F). Typical screen analyses of screened and unscreened products are shown in the following tabulation:

	Screen Analysis, %					
Mesh Size, Tyler	+6	−6 +10	−10 +14	−14 +20	−20 + 32	−32
Screened	0	0.1	10.3	31.2	47.0	11.4
Unscreened	0	0.1	7.3	22.2	33.4	37.0

Portions of each sample were stored both as produced and after dusting with conditioning agents. The effect of cooling untreated product prior to bagging was tested also. The results of the storage tests are shown in Table I.

No Conditioner. After 1 month, most of the unconditioned samples had a medium-hard bag set but only sample F, which had not been screened to remove fines (37% − 32 mesh), contained more than 1% of plus 2-mesh lumps. However, caking increased with further storage; half the samples were caked after 3 months and all but one were caked badly after 6 months. Cooling the material from 135° to 90° to 96° F. before bagging (samples D and E) was not effective in preventing caking during storage.

Effects of Conditioning Agents. Screen analyses and moisture contents of the conditioning agents tested are shown in Table II. The conditioners were applied by mixing them with the diammonium phosphate in a 1-ton batch mixer.

Dusting with calcined dolomite proved to be the most effective of the anticaking treatments tested. Products dusted with 1 to 3% showed no caking after 6 months and, in most tests, there was little or no bag set. Storage tests of sample D, dusted with 1 and 3% of calcined dolomite, were extended to 9 months and no caking or significant bag set was observed. Even the unscreened product (sample F), which caked in 1 month without conditioner, was free flowing after 6 months when conditioned with calcined dolomite.

Dusting diammonium phosphate with 1 or 0.5% of kaolin induced rather than prevented caking. In all tests in which these amounts of kaolin were used, caking was observed after 1 month of storage. The use of 3% of kaolin had a beneficial effect on storage properties, but in most cases it was not as effective as 1 or 3% of calcined dolomite. Apparently the absorption of moisture by kaolin, when used at the 1% level, resulted in the formation of a plastic binder; with larger proportions, the kaolin remained sufficiently dry to serve as a parting agent. In two tests, kieselguhr appeared to be no more effective than kaolin. The effect of proportion of kieselguhr was about the same as that noted in the tests with kaolin. Tests of other conditioners showed by-product phosphate (36% phosphorus pentoxide; from manufacture of sodium phosphates) and fuller's earth to be about equally as effective as kaolin or kieselguhr. By-product phosphogypsum (from manufacture of phosphoric acid) and natural gypsum induced caking rather than prevented it.

Chemical Effects of Calcined Dolomite. Beeson (*7*) reported that, in the presence of water, diammonium phosphate and uncalcined dolomite react with release of 2.33 moles of ammonia per mole of calcium carbonate–magnesium carbonate in the dolomite. The tests were carried out with 1 part of diammonium phosphate mixed with 0.86 part of dolomite in the presence of 5% moisture. Assuming that a similar reaction might occur between calcined dolomite and diammonium phosphate, calculations show that conditioning of diammonium phosphate with 3% of calcined dolomite might release up to 5% of the nitrogen from the diammonium phosphate. However, in special laboratory tests, in the bag-storage tests, and in subsequent plant experience on conditioning of diammonium phosphate of 0.1% moisture content with 3% by weight of calcined dolomite, no losses or only insignificant losses (<0.6%) of ammonia occurred. The use of 3% of calcined dolomite on the plant product did not affect the citrate solubility of the phosphorus pentoxide but decreased its water solubility by 2 to 3%.

Because of the favorable results obtained with calcined dolomite, TVA's bagged product now is being conditioned with 3% by weight of calcined dolomite unless it is requested that conditioner be omitted. The product contains about 20.3% of nitrogen and 52.1% of phosphorus pentoxide. The guaranteed analysis is 20-52-0. Studies showed that the use of 3% of calcined dolomite would be slightly more economical per unit of guaranteed plant food than 1%, which permits a 20-53-0 grade, and would give greater assurance of satisfactory storage. The use of 2% of calcined dolomite was least desirable from an economical viewpoint. Diammonium phosphate that is shipped in bulk for use in mixtures, in liquid fertilizer solutions, and in irrigation systems generally is not conditioned. The mixer is responsible for adding the conditioner needed for specific mixtures.

Use of calcined dolomite as a conditioner was found to have no undesirable effects on the Association of Official Agricultural Chemists analytical procedures for determination of nitrogen and phosphorus pentoxide. The AOAC vacuum-desiccator method for moisture determination was satisfactory for control purposes, although equilibrium is not reached in the prescribed 16-hour desiccation period, presumably because of loss of ammonia. The Karl Fischer method (*5*) gave reproducible and apparently reliable results on unconditioned diammonium phosphate, but interference by calcined dolomite prevents its use on conditioned material.

Table I. Results of Bag-Storage Tests of Diammonium Phosphate[a]

Untreated Diammonium Phosphate: Lot No.	H_2O[b], %	Conditioner Added, %	Approximate Bagging Temperature, °F.	1 Month: Bag set[c]	1 Month: Lumps,[d] %	3 Months: Bag set[c]	3 Months: Lumps,[d] %	6 Months: Bag set[c]	6 Months: Lumps,[d] %
UNCONDITIONED DIAMMONIUM PHOSPHATE									
Not Cooled Prior to Bagging									
A	0.02	None	135	L	0	M	0	H	18
B	0.02	None	135	M	1	L	0	H	0
F[e]	0.04	None	135	M	10	H	8	H	20
C	0.05	None	135	M	0	..	..	H	26
D	0.06	None	132	M	0	H	13	H	23
E	0.13	None	135	M	1	M	0	H	23
Cooled Prior to Bagging									
D	0.06	None	96	L	0	H	13	H	18
E	0.13	None	90	M	0	M	0	H	28
DUSTING AGENTS									
Calcined Dolomite									
B	0.02	3	100	O	0	L	0	H	0
F[e]	0.04	3	100	O	0	L	0	L	0
D	0.06	3	108	O	0	O	0	L	0
E	0.13	3	110	O	0	O	0	O	0
D	0.06	1	102	O	0	L	0	L	0
E	0.13	1	104	O	0	L	0	O	0
Kaolin									
A	0.02	3	100	L	0	O	0	M	0
B	0.02	3	100	L	0	L	0	L	0
F[e]	0.04	3	100	L	1	M	4	M	11
D	0.06	3	102	L	0	L	0	M	1
E	0.13	3	108	O	0	L	0	M	8
D	0.06	1	103	H	4	H	28	H	64
E	0.13	1	92	M	4	H	23	H	65
C	0.05	0.5	100	M	5	H	14	..	..
Kieselguhr									
F[e]	0.04	3	100	M	1	M	1	H	6
C	0.05	0.5	135	H	10	H	32	..	..
By-product Phosphate from Manufacture of Sodium Phosphates									
A	0.02	4	100	L	0	L	0	M	3
F[e]	0.04	4	100	L	0	M	1	M	7
Phosphogypsum									
F[e]	0.04	3	100	H	30	H	26	H	52
Natural Gypsum									
D	0.06	3	112	H	13	H	31	..	..
D	0.06	1	108	H	11	H	37	..	..
Fuller's Earth									
B	0.02	3	100	M	1	M	1	H	6

[a] All materials were stored in five- or six-ply paper bags having one or two asphalt-laminated plies.
[b] Moisture content determined by Karl Fischer method (5).
[c] Bag set before dropping: O = none, L = light, M = medium hard, and H = hard.
[d] Plus 2-mesh lumps in bags after dropping four times from 3-foot level, once on each face and side of bag.
[e] Unscreened material containing 37% minus 32-mesh particles. All other materials were screened and contained about 11% minus 32-mesh particles.

Table II. Particle Size and Moisture Contents of Conditioning Agents

Type of Material	Screen Analysis, Cumulative % through Indicated Mesh (Tyler): 100	200	325	400	10μ	Bulk Density, Lb./Cu. Ft.	Moisture, %
Kaolin	...	98	..	90	80–90	31	<4
Kieselguhr (diatomaceous earth)	...	98	94	..	76	12	<4
Calcined dolomite	95–97	90	82	..	...	38	0
By-product phosphate from manufacture of sodium phosphates	100	75	..	..	...	42	2.6
Phosphogypsum (dried)	98	93	87	..	...	44	1.2
Natural gypsum	...	100	97	..	...	49	0
Fuller's earth	(95% or more −60 +100 mesh)					33	10

Bulk Storage of Diammonium Phosphate

Unconditioned diammonium phosphate stores relatively well in bulk. A 20-foot pile of material was stored in a ventilated building for about a year. During this time, the material formed a firm cake throughout the pile, but was easily reclaimed with a power shovel. The lumps broke up readily on handling. In this respect, the properties of diammonium phosphate are similar to, but less critical than, those of potassium chloride.

Table III. Typical Analyses of Raw Materials Used in Dry-Mix Fertilizers Containing Diammonium Phosphate

	Chemical Composition, %				Screen Analysis (Tyler Mesh), %					
Raw Material	N	Available P_2O_5	K_2O	H_2O	+6	−6 +10	−10 +14	−14 +20	−20 +32	−32
Diammonium phosphate	21.0	53.7	...	<0.1	0	0.1	10.3	31.2	47.0	11.4
Ammonium nitrate										
Prilled	32.5	...	...	<0.1	...	67.2	15.4	15.6	1.1	0.7
Crystalline	33.5	...	...	<0.1	0	0	0.5	20.6	64.3	14.6
Ammonium sulfate										
Granular	20.9	...	...	<0.1	0	1.6	8.9	22.9	43.9	22.7
Nongranular	20.7	...	...	0.1	0	0	0.3	3.1	34.7	61.9
Potassium chloride										
Granular	...	...	60.2	0.1	0	16.8	28.8	16.7	18.9	18.8
Nongranular	...	...	61.0	0.3	0	0.3	1.3	9.1	48.8	40.5
Calcium metaphosphate	...	62	...	0.1	0	(−10, +20, 15%)		(−20, +32, 32%)		53

Diammonium phosphate absorbs moisture during very humid weather and gives up moisture during periods of low humidity. During bulk storage in the ventilated building, the moisture content of the outer 1-inch layer of the pile of unconditioned diammonium phosphate fluctuated from less than 0.1% to about 1.2%, depending on atmospheric humidity. At a depth of 6 inches, however, the maximum moisture content was about 0.25%, and samples taken deeper in the pile showed practically no increase in moisture.

Dry Mixtures and Granulated Products

The high plant-food content of diammonium phosphate permits the production of higher analysis mixtures than can be made with conventional fertilizer materials. Because of the advantages inherent in producing and distributing high-analysis fertilizers, tests were made of several grades of dry mixtures based on diammonium phosphate and of granulated products in which diammonium phosphate was used as a source of phosphorus pentoxide.

Dry Mixtures. The dry mixtures were prepared by blending the fertilizer materials and conditioning agent in a 1-ton mixer. The mixtures then were bagged and stored in stacks 12 bags high as described. The fertilizer materials, in addition to diammonium phosphate (DAP), were ammonium nitrate (AN), ammonium sulfate (AS), potassium chloride (KCl), and calcium metaphosphate (CMP). Chemical and screen analyses of these materials are given in Table III. The bag-storage test procedure was the same as described for diammonium phosphate fertilizer. The results of the tests are shown in Table IV.

Diammonium Phosphate, Ammonium Sulfate, and Potassium Chloride

An unconditioned 15-15-15 mixture, prepared from diammonium phosphate, ammonium sulfate, and potassium chloride, had a hard bag set and contained 5% of plus 2-mesh lumps after only 1 month of storage and over 17% of lumps after 6 months (lumps after drop test). However, the same mixture conditioned by dusting with 3% of kaolin, kieselguhr, or calcined dolomite had a light to medium bag set and no lumps after dropping at 6 months. The use of granular potassium chloride resulted in decreased bag set.

Conditioning mixtures of diammonium phosphate and potassium chloride (10-27-27) and diammonium phosphate and ammonium sulfate (20-20-0) with 3% of kaolin, kieselguhr, or calcined dolomite also was effective in preventing caking during 6 months of storage. The 10-27-27 mixture, made with either granular or nongranular potassium chloride, had only a light bag set. The use of granular ammonium sulfate in the 20-20-0 mixture reduced bag set from hard to light.

Diammonium Phosphate, Ammonium Nitrate, and Potassium Chloride

Diammonium phosphate, ammonium nitrate, and potassium chloride were used in different proportions to produce 18-18-18 and 16-32-16 mixtures. The ammonium nitrate was in the form of commercial-grade prills or crystals (33.5% of nitrogen). Mixtures prepared without the addition of a conditioning agent caked excessively, and no difference was noted from the use of prilled or crystalline ammonium nitrate. Conditioning with 3% of kaolin was not effective in eliminating caking except when granular potassium chloride was used in the 16-32-16 mixture. Generally satisfactory storage resulted when the mixtures were conditioned with 3% of kieselguhr or with 10% of kaolin which lowered the grades to 17-17-17 and 15-30-15. Calcined dolomite was unsatisfactory as a conditioning agent for mixtures containing ammonium nitrate because it reacted with the ammonium nitrate to liberate ammonia and formed a very hygroscopic and wet product.

A mixture of equal proportions of diammonium phosphate and ammonium nitrate to give a 26-26-0 grade stored satisfactorily when conditioned with 3% of kaolin.

Diammonium Phosphate, Calcium Metaphosphate, and Potassium Chloride

Mixtures of diammonium phosphate, calcium metaphosphate, and potassium chloride in proportions to give a 11-33-22 grade, when stored in sample bottles without applied pressure, caked lightly in a short period of time; the mixture with nongranular potash was caked harder than the one with granular potash. The addition of limestone or sand prevented caking to some degree. The addition of kaolin also was beneficial. However, calcined dolomite thoroughly coated and dried the constituents of the mixture and made it relatively fluid. Bag-storage tests are being made of 10-30-20 mixtures containing 960 pounds of diammonium phosphate, 150 pounds of calcium metaphosphate, 670 pounds of granular or nongranular potassium chloride, 160 pounds of sand or granular limestone filler, and 60 pounds (3%) of kaolin or calcined dolomite conditioner. At the 1-month inspection, all the mixtures showed only a very light bag set or crust that was easily broken with finger pressure; there were no lumps after the bags were dropped.

Chemical Compatibility and Segregation

The diammonium phosphate was found to be compatible with the various materials used in the mixtures, and tests did not show excessive segregation in bagging or in drilling. The mixtures for the segregation tests were made with TVA diammonium phosphate and crystalline ammonium nitrate and granular and nongranular sulfate and potassium chloride. All mixtures were prepared by placing weighed batches of the desired raw materials in a 1-ton rotary mixer and mixing for 30 minutes. After mixing, the material was bagged (80 pounds per bag). As many as 17 bags of each mixture were prepared and each mixture represented a single batch operation. Analyses were made of samples taken from near the top and bottom of the bags and of thief samples. Table V shows the average analysis for each

Table IV. Results of Bag-Storage Tests of Fertilizer Mixtures Containing Diammonium Phosphate[a]

Formulation, % by Wt.[b]									Condition after Storage for 6 Months	
Diammonium Phosphate	Calcium Meta-phosphate	Ammonium nitrate		Ammonium sulfate		Potassium chloride		Conditioner, 3%	Bag set[c]	+2-mesh lumps[d], %
		Prills	Crystals	Gran.	Non-gran.	Gran.	Non-gran.			
DIAMMONIUM PHOSPHATE, AMMONIUM SULFATE, POTASSIUM CHLORIDE										
15-15-15 Grade										
29	...	..	..	..	45	...	26	None	H	>17
29	...	..	..	..	45	...	26	Kaolin	M	0
29	...	..	..	..	45	26	...	Kaolin	L	0
29	...	..	..	45	..	...	26	Kaolin	H	0
29	...	..	..	45	..	26	...	Kaolin	M	0
29	...	..	..	..	45	...	26	Kieselguhr	M	0
29	...	..	..	45	..	26	...	Calcined dolomite	L	0
29	...	..	..	..	45	26	...	Calcined dolomite	L	0
10-27-27 Grade										
53	...	..	..	..	..	...	47	None	H	11
53	...	..	..	..	..	...	47	Kaolin	L	0
53	...	..	..	..	..	47	...	Kaolin	L	0
53	...	..	..	..	..	...	47	Kieselguhr	L	0
20-20-0 Grade										
39	...	..	..	..	61	...	...	None	H	>34
39	...	..	..	..	61	...	...	Kaolin	H	2
39	...	..	..	61	..	...	...	Kaolin	L	0
39	...	..	..	61	..	...	...	Kieselguhr	L	0
39	...	..	..	..	61	...	...	Calcined dolomite	H	0
DIAMMONIUM PHOSPHATE, AMMOMIUM NITRATE, POTASSIUM CHLORIDE										
18-18-18 Grade										
35	...	34	..	..	..	...	31	None	H	8
35	...	..	34	..	..	...	31	Kaolin	H	6
35	...	..	34	..	..	...	31	Kaolin[e]	H	1
35	...	..	34	..	..	...	31	Kieselguhr	H	1
35	...	..	34	..	..	31	...	Kieselguhr	M	0
35	...	..	34	..	..	...	31	Calcined dolomite (Not stored; strong odor of NH_3 and very hygroscopic)		
16-32-16 Grade										
61	...	11	..	..	..	...	28	None	H	19
61	...	..	11	..	..	...	28	Kaolin	H	11
61	...	..	11	..	..	28	...	Kaolin	H	0
61	...	..	11	..	..	...	28	Kaolin[f]	M	0
61	...	..	11	..	..	28	...	Kieselguhr	H	2
61	...	..	11	..	..	...	28	Kieselguhr	H	2
26-26-0 Grade										
50	...	..	50	..	..	...	...	Kaolin	M	0
DIAMMONIUM PHOSPHATE, CALCIUM METAPHOSPHATE, POTASSIUM CHLORIDE										
10-30-20 Grade[g]									After 1 month	
48	7.5	..	..	..	..	33.5	...	Kaolin	L	0
48	7.5	..	..	..	..	...	33.5	Kaolin	L	0
48	7.5	..	..	..	..	...	33.5	Calcined dolomite	L	0

[a] All mixtures were stored in five- and six-ply paper bags having one and two asphalt-laminated plies, respectively.
[b] Before conditioning.
[c] Bag set before dropping: O = none, L = light, M = medium hard, and H = hard.
[d] Plus 2-mesh lumps in bags after dropping four times from 3-foot level; once on each free and side of bag.
[e] Grade was 17-17-17 after addition of 10% conditioner.
[f] Grade was 15-30-15 after addition of 10% conditioner.
[g] Includes 8% granular limestone as filler and 3% conditioner.

batch and the arithmetic average of deviations from the average analysis.

The drilling tests were made with a John Blue No. 30 screw-type fertilizer distributor. The distributor hopper was vibrated with a V-9 Syntron vibrator and was "bumped" every 30 seconds during the drilling period. Samples of the material delivered were taken for a period of 2 to 4 seconds, 30 seconds after drilling was started and at intervals of 3 minutes thereafter. The analyses of these samples were compared with the average analysis of the batch. The mean deviation of these analyses was

Table V. Tests of Segregation of Dry Mixtures Containing Diammonium Phosphate

Grade[a]	Average Batch Analysis, % N	P_2O_5	K_2O	Bag Analysis, Mean Deviation from Batch, ± % N	% P_2O_5	% K_2O	Segregation in Drilling Test, Mean Deviation from Analysis of Batch, ± % N	% P_2O_5
18-18-18[b]	18.2	19.0	18.3	0.3	0.8	0.2	0.3	0.8
16-32-16[c]	16.4	33.6	16.3	0.6	0.4	0.7	0.6	0.4
16-32-16[d]	16.1	33.1	...	0.3	0.9	...	0.5	0.2
15-15-15[e]	15.2	15.2	15.4	0.2	0.3	0.1	0.2	0.3
15-15-15[f]	15.4	15.8	...	0.0	0.2	...	0.0	0.4
11-28-28[g]	11.2	29.2	27.9	0.1	0.4	0.2	0.1	0.4
20-20-0[h]	20.4	20.4	...	0.0	0.4	...	0.0	0.4

[a] For screen sizes of materials used in mixtures see Table III.
Materials and proportions by weight:
[b] DAP 35, crystalline AN 34, granular KCl 31; plus 3% kaolin.
[c] DAP 61, crystalline AN 11, granular KCl 28; plus 3% kaolin.
[d] DAP 61, crystalline AN 11, nongranular KCl 28; plus 3% kaolin.
[e] DAP 29, granular AS 45, granular KCl 26; plus 3% kaolin.
[f] DAP 29, nongranular AS 45; nongranular KCl 26; plus 3% kaolin.
[g] DAP 53, granular KCl 47; no conditioner.
[h] DAP 39, granular AS 61; plus 3% kaolin.

generally less than the deviation of analyses of the individual bags filled from the mixer. The segregation that might be expected to occur in a fertilizer distributor is not significant.

Granulated Products. Tests were made in the TVA ammoniation-granulation pilot plant (*3*) to study the use of diammonium phosphate in the production of granular, high-analysis fertilizers (*4*). The use of diammonium phosphate offers the advantages of (1) higher analysis products than can be made with conventional raw materials, (2) increased water solubility of the products, (3) better control of granulation for grades in which the heat of reaction otherwise is in excess of that desired, and (4) possible lower costs in some cases, which may result from the high plant-food content of diammonium phosphate and from lower moisture contents of the products with resultant decrease in drying costs or elimination of the drying step.

The products tested included the following grades: 13-39-0, 12-24-12, 8-24-24, 15-30-0, 16-20-0, and 20-20-0. Very good granulation was obtained. The granules were strong and hard, and the diammonium phosphate was satisfactorily incorporated in the granules.

Bag-storage tests indicated that the physical properties of the granular fertilizers containing diammonium phosphate were about the same as those of other granular, high-analysis fertilizers. There was little or no caking when the products were cured for a few days before bagging and when the moisture content was below 3%. Some of the products did not cake even when the moisture content was higher than 3%, if coated with a conditioner. The grades that contained potash were more apt to cake than those that did not when the moisture content was comparable. Potash-containing grades probably should be dried to less than 2% moisture to ensure good storage properties.

Liquid Fertilizer Solutions

Diammonium phosphate can be used in the preparation of liquid fertilizer solutions. Formulations for several grades of solutions are given in Table VI. These formulations are based on the use of completely soluble diammonium phosphate such as is produced from ammonia and relatively pure phosphoric acid. Tests made in the laboratory indicate that salting out of crystals will not occur if the solutions are kept at the temperature shown in the table.

Acknowledgment

The authors are indebted to Frank P. Achorn and Homer G. Graham, Jr., for significant contributions to this work. Jamie B. Wells and Paul T. Kimbrough carried out the testing of the products. George Hoffmeister assisted in the preparation of the manuscript.

Literature Cited

(1) Beeson, Kenneth C., *Ind. Eng. Chem.* **29**, 705–9 (1937).
(2) Getsinger, J. G., Houston, E. C., Achorn, F. P., J. Agr. Food Chem. **5**, 433–6 (1957).
(3) Hein, L. B., Hicks, G. C., Silverberg, Julius, Seatz, L. F., *Ibid.*, **4**, 318–30 (1956).
(4) Hignett, T. P., Hicks, G. C., Jordan, J. E., *Com. Fertilizer and Plant Food Ind.* **93**, No. 4, 24–6 (1956).
(5) Mitchell, John, Jr., Smith, Donald Milton, "Aquametry," pp. 234–5. Interscience, New York (1948).

Received for review September 13, 1956. Accepted December 10, 1956. Division of Fertilizer and Soil Chemistry, 130th Meeting, ACS, Atlantic City, N. J., September 1956.

Table VI. Formulations for Liquid Fertilizers Containing Diammonium Phosphate

Plant-food ratio	1:1:1		1:2:1		1:2:2		1:1:0	
Grade	6-6-6	7-7-7	5-10-5	6-12-6	4-8-8	5-10-10	12-12-0	13-13-0
Formulation, lb./ton								
Diammonium phosphate (21% N, 53% P_2O_5)	227	266	377	455	302	377	454	491
Urea (46.5% N)	140	162	10	12	18	24	292	316
Ammonium sulfate (21% N)	38	44	83	98	41	53	50	50
Potassium chloride (62% K_2O)	194	228	161	194	258	323	...	...
Water	1401	1300	1369	1241	1381	1223	1204	1143
Total	2000	2000	2000	2000	2000	2000	2000	2000
Approximate salting out temperature, °F.	Below 30	38	Below 30	46	Below 30	77	Below 30	59