

Microscopic Study of the Mechanism of Caking and Its Prevention in Some Granular Fertilizers

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Microscopic studies of several types of high-analysis granular fertilizers showed that caking resulted from bonding of granules by crystals of soluble salts that formed on the surface of granules during storage. The composition of the salt depended on the formulation used in making the fertilizer. Bonding-phase salts identified were potassium nitrate, ammonium chloride, monoammonium phosphate, ammonium nitrate, and a urea-ammonium chloride complex. Drying, curing, and coating the granules with a conditioner had significant effects on the growth of bonding crystals.

GRANULAR FERTILIZERS are much less subject to caking during storage than are nongranular fertilizers of the same formulation and moisture content. However, granulation is not an infallible panacea for caking problems. Research by the U. S. Department of Agriculture and others (1, 2, 6, 17) has shown that the caking of both granular and nongranular fertilizers is influenced by such factors as size and shape of particles, moisture content, length of curing period, formulation, and amount and kind of conditioning agent used.

In TVA's experimental work on production of various granular high-analysis fertilizers (3-5, 7, 8), tests were made to evaluate the storage properties of the

products in their original condition and after they had been subjected to various combinations of drying, curing, and coating with a conditioning agent. Some of the products that caked in storage and some that stored satisfactorily were studied microscopically to determine the mechanisms of caking and the mechanisms by which the various treatments prevented or reduced caking.

The results of bag-storage tests of a number of the granular high-analysis fertilizers that were included in this study are given in Table I. Analyses of the raw materials used in their preparation are given in Table II. The products were -6 +28 mesh in size. In the storage tests, they were bagged in multi-

wall paper bags having one or two asphalt-laminated moisture barriers. They were stored in the lower four positions of 12-bag stacks in an unheated building. Bags were inspected after 3 and 6 months of storage. "Bag set" was determined by hand pressure prior to moving the bags. The bags were then removed from the stacks and were dropped four times from a height of 3 feet, once on each side and face. The percentage of +2-mesh lumps remaining after dropping the bags was taken as a measure of caking. The data show that it was possible to prevent or reduce caking of these fertilizers by one or a combination of the following treatments prior to bagging: reducing moisture con-

Table I. Results of Storage Tests and Microscopic Examinations of High-Analysis Granular Fertilizers

Formulation, Lb./Ton of Product	Product No.	Dried ?	% H ₂ O When Stored	Treatment Prior to Storage in Bags ^a	Storage Results				Bonding Phases Responsible for Lump Formation	
					3 Months		6 Months			
					Bag set	% Lumps ^b	Bag set	% Lumps ^b		
Products Made with Superphosphates and Ammonia-Ammonium Nitrate Solutions										
15-15-15										
NH ₃ -NH ₄ NO ₃ solution (X)	519	AW-1	Yes	0.8	None	Hard	26	Hard	46	
Concentrated superphosphate	291				Conditioned	Hard	0	Hard	2	
Phosphoric acid	289									
Potassium chloride	500									
Ammonium sulfate	536									
Same		AX-1	Yes	0.3	None	Medium	0	Hard	0	
12-12-12										
NH ₃ -NH ₄ NO ₃ solution (X)	499	K-16	No	1.3	None	Hard	3	Hard	6	
Ammonium sulfate	195				Conditioned	Light	0	Medium	0	
Ordinary superphosphate	571				Cured 7 days	Light	2	Light	1	
Concentrated superphosphate	272				Cured and cond.	None	0	None	0	
Potassium chloride	400									
Sulfuric acid	155									
Same		K-20-D	Yes	0.2	None	None	0	Medium	0	
10-10-10										
NH ₃ -NH ₄ NO ₃ solution (X)	509	A-20-C	No	1.6	None	Hard	10	Hard	>10	
Ordinary superphosphate	1039				Cured 7 days	Medium	0	Medium	0	
Potassium chloride	333				Cured and cond.	Light	0	Light	0	
Sulfuric acid	159									
Filler (sand)	70									
Same		A-18-D	Yes	1.1	None	Hard	2	Hard	3	

Table I. Results of Storage Tests and Microscopic Examinations of High-Analysis Granular Fertilizers (Continued)

Formulation, Lb./Ton of Product	Product No.	Dried ?	% H ₂ O When Stored	Treatment Prior to Storage in Bags ^a	Storage Results				Bonding Phases Responsible for Lump Formation	
					3 Months		6 Months			
					Bag set	% Lumps ^b	Bag set	% Lumps ^b		
Products Made with Superphosphates and Ammonia-Ammonium Nitrate Solutions										
10-20-20										
NH ₃ -NH ₄ NO ₃ solution (X)	504	C-26	No	1.8	None	Light	3	Hard	36	Potassium nitrate containing occluded ammonium chloride
Concentrated superphosphate	850				Conditioned	Light	0	Medium	1	
Potassium chloride	667				Cured 7 days	Medium	1	Hard	8	
Sulfuric acid	108				Cured and cond.	Light	0	Medium	0	
8-16-16										
NH ₃ -NH ₄ NO ₃ solution (Y)	403	Z-4	No	3.2	None	Hard	50	Hard	>50	
Ordinary superphosphate	1004				Conditioned	Hard	13	Hard	21	
Phosphoric acid	225				Cured 7 days	Hard	8	Hard	12	
Potassium chloride	533				Cured and cond.	Medium	0	Hard	3	
Same		Z-1	Yes	1.2	None	Medium	0	Hard	1	
Products Made with Superphosphates and Solutions Containing Urea										
12-12-12										
NH ₃ -urea solution (UC)	447	KU-1	No	3.2	None	Hard	21	Hard	23	
Ammonium sulfate	195				Conditioned	Hard	0	Hard	1	
Ordinary superphosphate	535				Cured 7 days	Hard	8	Hard	15	
Concentrated superphosphate	287				Cured and cond.	Hard	0	Hard	0	
Potassium chloride	400									
Sulfuric acid	245									
Same		KU-3	Yes	0.7	None	Hard	0	Hard	1	
10-20-20										
NH ₃ -urea solution (UC)	447	CU-2	No	4.7	None	Hard	22	Hard	28	Urea-ammonium chloride complex CO(NH ₂) ₂ .NH ₄ Cl
Concentrated superphosphate	850				Conditioned	Hard	0	Hard	1	
Potassium chloride	667				Cured 7 days	Hard	28	Hard	25	
Sulfuric acid	197				Cured and cond.	Hard	0	Hard	1	
Same		CU-6	Yes	0.4	None	Medium	0	Medium	0	
8-16-16										
NH ₃ -urea solution (UC)	358	ZU-2	Yes	4.2	None	Hard	6	Hard	13	
Ordinary superphosphate	1083				Conditioned	Hard	0	Hard	4	
Phosphoric acid	196				Cured 7 days	Hard	2	Hard	5	
Potassium chloride	533				Cured and cond.	Medium	0	Medium	0	
Same		ZU-1	Yes	1.4	None	Medium	0	Medium	0	
13-13-13										
NH ₃ -NH ₄ NO ₃ solution (Z)	508	AM-4/25	No	0.2	None	Hard	15	Hard	10	
Ammonium sulfate	332				Conditioned	Hard	0	Hard	1	
Calcium metaphosphate	427				Cured 7 days	Hard	0	Hard	0	
Potassium chloride	437				Cured and cond.	Medium	0	Medium	0	
Sulfuric acid	338									
9-18-18										
NH ₃ -NH ₄ NO ₃ solution (Z)	546	AM-2/9	No	0.9	None	Hard	22	Hard	13	Mono-ammonium phosphate
Calcium metaphosphate	590				Conditioned	Hard	7	Hard	13	
Potassium chloride	600				Cured 7 days	Medium	0	Hard	0	
Sulfuric acid	277				Cured and cond.	None	0	Medium	0	
Products Made with Superphosphates and Anhydrous Ammonia										
5-20-20										
Anhydrous ammonia	125	J-9	No	6.9	None	Hard	2	Hard	4	Chiefly mono-ammonium phosphate. Some gypsum present also
Ordinary superphosphate	262									
Concentrated superphosphate	752									
Potassium chloride	667									
Sulfuric acid	150									
Same		J-16-B	No	3.8	None	Hard	0	Hard	0	
Products Made by Nitric Acid Extraction of Phosphates										
12-12-12 (nitric phosphate)										
Anhydrous ammonia	155	NP-7	Yes	2.3	None	Hard	13			Ammonium nitrate, plus lesser amounts of potassium nitrate and ammonium chloride
Nitric acid (57%)	975				Conditioned	Hard	0			
Sulfuric acid	245				Cured 7 days	Hard	1			
Phosphate rock	707				Cured and cond.	Hard	0			
Potassium chloride	400									
Same		NP-11	Yes	0.3	None	Light	0			

Table I (Continued)

Table I. Results of Storage Tests and Microscopic Examinations of High-Analysis Granular Fertilizers (Continued)

Formulation, Lb./Ton of Product	Product No.	Dried ?	% H ₂ O When Stored	Treatment Prior to Storage in Bags ^a	Storage Results				Bonding Phases Responsible for Lump Formation	
					3 Months		6 Months			
					Bag set	% Lumps ^b	Bag set	% Lumps ^b		
Products Made by Nitric Acid Extraction of Phosphates										
14-14-14 (leached-zone fertilizer)										
Anhydrous ammonia	200	Yes	3.5	None	None	0	...	0	No caking observed. During storage, granules developed hulls of potassium nitrate and ammonium chloride
Nitric acid (42%)	1460									
Sulfuric acid (50%)	920									
Leached-zone phosphate	3070									
Potassium chloride	466									
No-Nitrogen Product										
0-26-26										
Concentrated superphosphate	755	GS-8/7	No	2.5	No surface growth. Potassium chloride and monocalcium phosphate monohydrate were the two important water-soluble phases in the granules
Phosphate rock	145									
Phosphoric acid	160									
Potassium chloride	870									
No-Phosphate Product										
14-0-14										
NH ₂ -NH ₄ NO ₃ solution (X)	200	Y-2	No	0.8	No hulls in usual sense. Phases present: ammonium chloride, ammonium sulfate, potassium-ammonium nitrate
Ammonium sulfate	976									
Sulfuric acid	149									
Potassium chloride	467									
Filler (kaolin clay)	226									

^a Conditioned products were coated with 2.5% of kaolin clay or kieselguhr immediately prior to bagging. Cured products were pile-stored for 7 days immediately after production.

^b % +2-mesh lumps after dropping bag four times from 3-foot height, once on each side and face.

tent, curing in a pile for 7 days, and coating with a conditioning agent such as kaolin clay or kieselguhr.

Mechanism of Caking

Preliminary examinations of fertilizer granules were made with a stereoscopic binocular microscope at magnifications up to 90. A petrographic microscope was then used to identify crystalline phases and to make more detailed examinations of sections of the granules. Chemical microscopy was used to supplement the examinations, and x-ray diffraction analyses were obtained when required to confirm identifications.

Examinations of caked fertilizers showed that, in all cases, bonding between granules was the result of intergrowth of crystals of soluble salts that had formed on the surfaces of granules during storage. These crystals often covered the entire granule in the form of a veneer or hull. Compositions of the salts depended on the formulations used in making the fertilizers. Most of the products had numerous small cavities within the granules; these cavities apparently resulted from movement of soluble salts to the surface of the granule while the crystals were forming. The inner surfaces of these cavities often were coated with the same crystalline phases that appeared on the surface of the granule. There appeared to be sufficient moisture in the granules to

Table II. Typical Analyses of Raw Materials Used in Pilot-Plant Production of Granular Fertilizers

Solids	Total N	P ₂ O ₅		K ₂ O			
		Total	Available				
Ordinary superphosphate	20	..			
Concentrated superphosphate	48	..			
Calcium metaphosphate	62	..			
Phosphate rock	..	35			
Leached-zone phosphate	..	10			
Ammonium sulfate	20.5			
Potassium chloride	60			
Acids		H ₃ PO ₄	H ₂ SO ₄	HNO ₃			
Phosphoric acid	78			
Sulfuric acid	93	..			
Nitric acid	42			
Ammoniating Solutions		Total N	Free NH ₃	NH ₄ NO ₃	Urea	Ammonium Carbamate	H ₂ O
Type X	40.6	21.7	65.0	0	0	13.3	
Type Y	40.8	26.0	55.5	0	0	18.5	
Type Z	37.0	16.6	66.8	0	0	16.6	
Type UC	45.5	24.1	0	43.3	15.0	17.6	

propagate caking and caking was not dependent solely on moisture absorbed from external sources. This fact was demonstrated by using bags with efficient moistureproof barriers in the form of asphalt-laminated plies and, also, by using sealed cans as storage containers. The precaution of using moisture resistant bags alone, therefore, will not necessarily prevent caking.

The bonding phases found on the products that were examined are listed in Table I.

Products Made with Superphosphate and Ammonia-Ammonium Nitrate Solution. Products of this type that were studied included the following grades: 15-15-15, 12-12-12, 10-10-10, 10-20-20, and 8-16-16. The formulations for the 15-15-15 and 8-16-16 products included phosphoric acid and the formulations for the other products included sulfuric acid. Potassium chloride was the source of potash. The major crystalline compounds that constituted the bonds between granules in caked

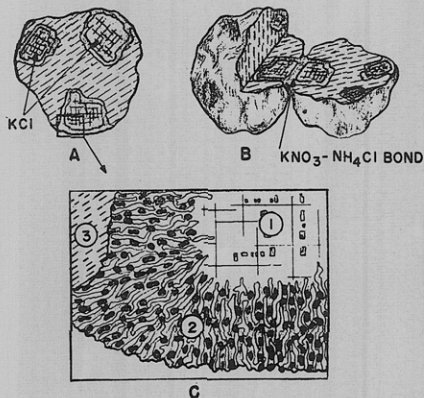


Figure 1. Observed alterations of potassium chloride

A. Cross-sectioned granule showing potassium chloride grains with hulls of alteration products
 B. Cut-away of granules bonded by potassium nitrate-ammonium chloride alteration products
 C. Enlarged section of A showing (1) unaltered potassium chloride, (2) potassium nitrate intergrown with granular ammonium chloride, and (3) main mass of granule. Elongated crystals of potassium nitrate are shown as white areas. Ammonium chloride crystals are shown in black

samples of these products were potassium nitrate and ammonium chloride.

The reaction between ammonium nitrate solution and the potassium chloride crystals, which has been found to progress slowly during storage, results in an intimate intergrowth of the crystalline products, potassium nitrate and ammonium chloride. Almost always, the potassium nitrate grew as elongated units in subparallel orientation, with the ammonium chloride crystallizing as equant, granular units, which became occluded in uniform fashion within the potassium nitrate mass. This type of crystal growth and the type of bonding that it causes is illustrated in Figure 1, where the potassium nitrate is idealized as the elongated white crystals and the ammonium chloride is shown as the dark grains distributed among the potassium nitrate crystals. Potassium nitrate generally migrated farther and was more responsible for bridge-crystal formation, and only the ammonium chloride that was actually situated close to the contact zone contributed to the bond created between granules.

Granules of the 15-15-15 and 12-12-12 products had nearly continuous hulls of potassium nitrate-ammonium chloride crystals, with bonding by crystal intergrowth occurring at points of contact between granules. The 10-10-10 and 10-20-20 products had only patchy growths of the crystalline phases on the surfaces of the granules. The patches usually were near particles of potassium chloride that protruded from the surface of the granule or were just below the surface. Some crystals of ammonium nitrate and monoammonium phosphate were found on the granules of 15-15-15, 12-12-12, and 10-10-10 products.

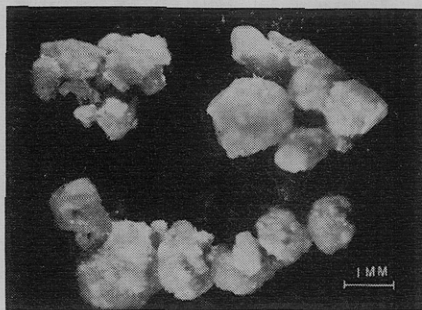


Figure 2. Caked mass of granular 12-12-12 fertilizer made from ammonium-urea solution

However, these crystals usually occurred at points other than contact points between granules and played little or no part in bonding.

In all of the products, potassium chloride showed some degree of alteration to potassium nitrate and ammonium chloride as a result of reaction with ammonium nitrate. The reaction products completely encased unaltered cores of potassium chloride; this was observed both when the particles of potassium chloride were incorporated within granules and when they remained unincorporated as a result of incomplete granulation. The degree of reaction, or alteration, apparently was dependent on the original moisture content of the granules. For example, in the 15-15-15 product that had been dried to 0.3% moisture (Table I, AX-1), the particles of potassium chloride generally showed less than 25% alteration after 6 months of storage, whereas much greater alteration was observed in the same product dried only to 0.8% moisture.

The 8-16-16 product (Z-4) was one in which there was a considerable amount of unincorporated potassium chloride. All fertilizer granules resting in contact with a potassium chloride particle became bonded to it as the potassium nitrate-ammonium chloride hull de-

veloped about the potassium chloride particle. Usually, a granule touched more than one potassium chloride particle and a bond formed at each contact point. Thus a whole network of bonds was created which caused caking. When potassium chloride particles contacted one another the bond was significantly stronger.

Products Made with Solutions Containing Urea. Examinations were made of 12-12-12, 10-20-20, and 8-16-16 fertilizers prepared with ammoniating solution Type UC (Table II), which contained ammonia, urea, and ammonium carbamate but no ammonium nitrate. These products caked severely when stored without conditioning at 3.2 to 4.7% moisture. Caking was eliminated or greatly reduced, however, when they were dried to about 1% moisture or were conditioned with about 50 pounds of kaolin clay or kieselguhr per ton of product. Curing was not very effective in improving storage. In all cases, these products developed somewhat harder bag sets than did products of the same grade and moisture content made with ammonia-ammonium nitrate solution. The granules had thick crystalline hulls of a urea-ammonium chloride complex of the composition $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_4\text{Cl}$. The inner portion of the hulls was a compact, highly intergrown crystal mass, while the exposed surfaces exhibited rather well-formed rod and needle crystals that radiated outward. The bonding between granules was due to intergrowth of the crystalline hulls at points of contact between granules. Figure 2 is a photomicrograph of a caked mass of the 12-12-12 (run KU-1) fertilizer. Figure 3 shows a typical granule of this product photographed in transmitted light at a higher magnification to reveal details of the crystalline hull of the urea-ammonium chloride complex.

Optical data on the urea-ammonium

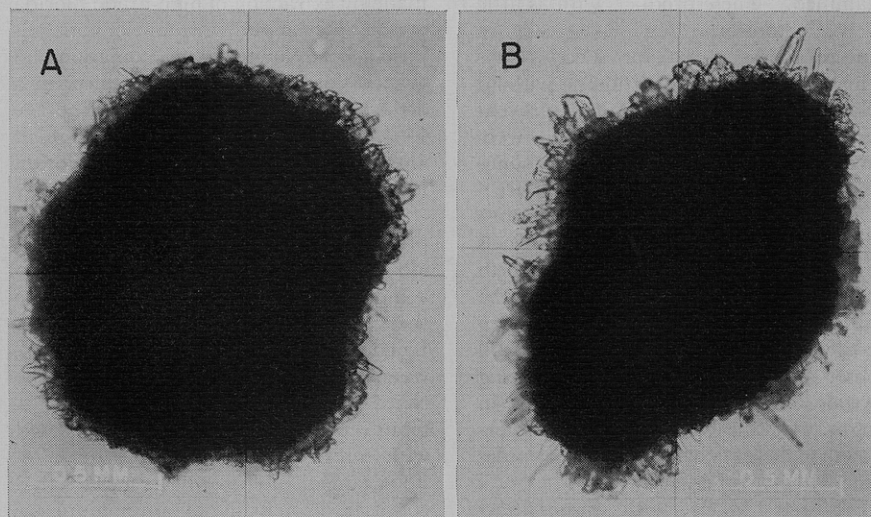


Figure 3. Granules of 12-12-12 fertilizer showing typical crystalline hulls of urea-ammonium chloride complex after storage for 3 months in bags

A. Uncured B. Cured 7 days prior to bagging

chloride complex were not found in the literature. This complex was identified only after it was synthesized in the laboratory, using a method described by Thorpe (10), and after its optical properties were determined. The properties of the synthesized material were the same as those of the crystalline phase on the granules of fertilizer. Microchemical and x-ray studies confirmed the identification. The urea-ammonium chloride complex crystallized as monoclinic rods and prisms that were biaxial (+) with an optical axial angle, $2V$, of about 40° . The refractive indices were $N_\alpha = 1.536$, $N_\beta = 1.545$, $N_\gamma = 1.610$, with N_β nearly parallel to the axis of elongation and the optical-axial plane normal thereto. The urea-calcium sulfate complex $[\text{CO}(\text{NH}_2)_2 \cdot \text{CaSO}_4]$ (12) was not detected.

Products made with solution containing ammonia and urea, but no ammonium carbamate, also developed hulls of urea-ammonium chloride complex which were responsible for caking. However, products made with solution containing ammonia, ammonium nitrate, and about 10% of urea did not have the usual urea-ammonium chloride hull when inspected after prolonged storage. In some cases, no urea or adduct could be detected; analysis indicated that all the urea probably had hydrolyzed. In other cases, the hulls comprised rounded crystals of ammonium chloride and irregularly shaped crystals of potassium nitrate and some urea-ammonium chloride complex intimately associated with the ammonium chloride and potassium nitrate.

Products Made with Calcium Metaphosphate and Ammonia-Ammonium Nitrate Solution. Crystals of monoammonium phosphate constituted the bonds between granules of fertilizers made from ammonia-ammonium nitrate solution, calcium metaphosphate, potassium chloride, and sulfuric acid; 13-13-13 and 9-18-18 products were examined. These products with as little as 0.2% moisture, tended to cake in storage unless cured for several days prior to bagging. Conditioning without prior curing usually did not prevent caking. The caked granules were covered with surface growths of monoammonium phosphate crystals. Figure 4 is a photomicrograph taken with transmitted light (left) and crossed-Nicols (right) that shows this surface growth on the 9-18-18 product. Much of the hull consisted of a dense array of bristling needle crystals that radiated from a still denser mass of crystals. The projecting crystals averaged 30 to 35 microns in length. Caking was the result of intergrowth of these crystals where the granules touched each other.

Products Made with Superphosphates and Anhydrous Ammonia. Monoammonium phosphate also was the major constituent of the caking bonds

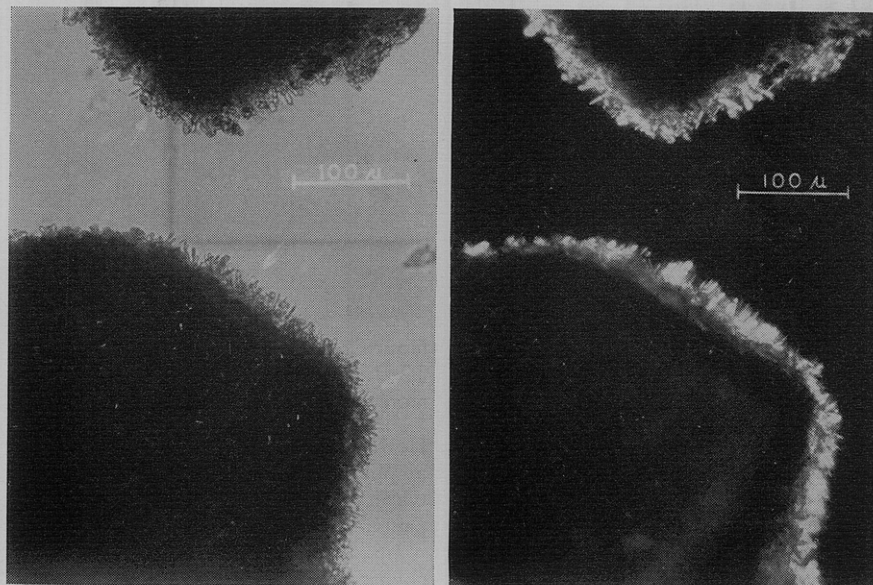


Figure 4. Crystalline hulls of monoammonium phosphate on granules of 9-18-18 fertilizer made from calcium metaphosphate

in a granular 5-20-20 fertilizer made from anhydrous ammonia, ordinary and concentrated superphosphates, potassium chloride, and sulfuric acid. This product stored satisfactorily at about 4% moisture without curing or conditioning but caked when the moisture content was 6.9%. Curing and conditioning were not tested. The monoammonium phosphate bonds between granules were chiefly intergrown hulls of rodlike crystals that had formed on granules. Some plate crystals of gypsum were present also. The main mass of the hulls consisted of a dense array of projecting crystals while the inner region of the hull was a more compact, intergrown mass of much smaller crystals.

Products Made by Nitric Acid Extraction of Phosphates. Two products made by processes involving nitric acid extraction of phosphates are listed in Table I. The 12-12-12 product was made by extraction of high-grade Florida pebble phosphate with nitric and sulfuric acids followed by ammoniation and granulation of the extraction slurry in a TVA ammoniator-granulator. The 14-14-14 product was made from a high alumina phosphate known as Florida leached-zone phosphate.

Nitric phosphates such as the 12-12-12 product produced from high-grade Florida phosphate usually required drying to a moisture content of below 1% before they stored well without conditioning. Uncured, unconditioned product (2.3% water) caked severely in storage. The caked granules were inspected after 1 month of storage; they were coated with hulls, about 50 microns thick, of fine-grained, intergrown crystallites that consisted principally of ammonium nitrate with lesser amounts of potassium nitrate and ammonium chloride. Bonds between granules were simple inter-

growths of the ammonium nitrate crystals at points of contact.

The 14-14-14 leached-zone nitric phosphate, which contained a high proportion of aluminum derived from the leached-zone ore, had unusually good storage properties (9) even at relatively high moisture contents. This product stored well in bags at a moisture content of 3.5%. A similar product containing about 12% moisture remained free flowing in a bottle over a long period of time. The granules, after storage, had well-defined crystalline hulls with smooth, lustrous crystalline surfaces. Figure 5 is a photomicrograph that shows cross sections of the hulls on granules that contained 3.5% moisture. The crystalline phases in the hull were chiefly potassium nitrate and ammonium chloride with some ammonium nitrate present also. The interior of the granules was a fine-grained pulverant mass that consisted primarily of a colloidal, hydrated aluminum phosphate. This mass contained numerous microscopic cavities that apparently resulted from migration of soluble materials to the surface of the granules. Practically no particles of unreacted potassium chloride were found in the granules except for a few, near the surface, that were occluded in the hulls. However, there was no bonding between hulls on adjacent granules, which is in contrast to the behavior of other products in which hulls of the same soluble salts formed.

The following observations may explain this unexpected behavior. The colloidal, hydrated aluminum phosphate acts to immobilize moisture and salt solution by capillary action to such a degree that even in the product containing 12% moisture, granule surfaces remained dry, whereas their interiors



Figure 5. Granules of 14-14-14 leached-zone fertilizer cleaved to show hulls of potassium nitrate and ammonium chloride that developed during storage

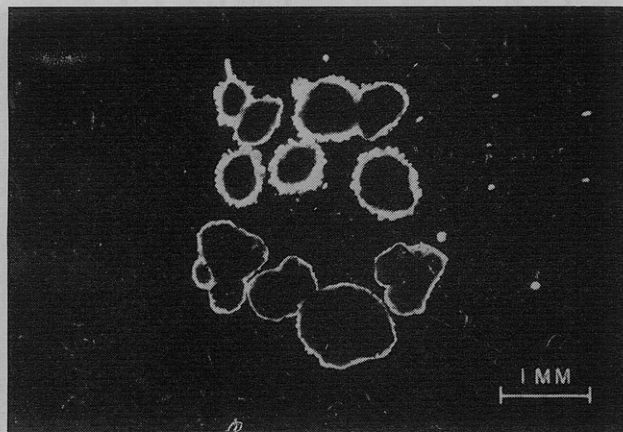


Figure 6. Difference in hull thickness of undried (top) and dried (bottom) 12-12-12 granular fertilizer made with ammonia-urea solution

were noticeably wetted by solution. Also, the hulls showed a banded structure caused by cyclic crystallization. As crystallization of salts from solution occurs beneath the previously deposited shells of salts, moisture probably is drawn back into the granule interior, and the process repeated. Each incremental addition to hull thickness would tend to reduce escape of moisture to the granule surface. By these processes, the moisture level external to the granule appeared to be maintained at so low a level as to prevent intergrowth of hulls at contact points.

No-Nitrogen and No-Phosphate Products. Other products studied included a 0-26-26 product (no nitrogen) made from concentrated superphosphate, phosphate rock, phosphoric acid, and potassium chloride and a 14-0-14 product (no phosphate) made from ammonia-ammonium nitrate solution, potassium chloride, ammonium sulfate, and sulfuric acid. These products had been stored without prior curing or conditioning. The 0-26-26 product contained about 2.5% moisture at bagging and was not caked badly after 9 months of storage. Inspection revealed no surface growth on the granules. Potassium chloride and monocalcium phosphate monohydrate were the two important water-soluble phases present in the granules. The 14-0-14 product was bagged at less than 1% moisture; it was caked severely after 3 months of storage. Crystalline phases present were ammonium chloride, ammonium sulfate, and a potassium-stabilized, form III ammonium nitrate.

Effect of Moisture

Examinations were made to determine the effect of the initial moisture content of granular fertilizers on the growth of the crystalline compounds responsible for caking. The products studied were the 15-15-15 and 12-12-12 grades made with superphosphates and ammonia-ammonium nitrate solution and

the 12-12-12 grade made with ammonia-urea-ammonium carbamate solution. The extent of crystalline hull formation on granules was less in the products of low moisture content. The hulls were not only thinner, but were denser and did not display prominent projecting crystal growths. Also, the potassium chloride particles in the granules of lower moisture content showed much less alteration.

Figure 6, a photomicrograph, taken with crossed Nicol prisms, shows the differences in hull thicknesses on the low and high moisture 12-12-12 products formulated with urea solution (products KU-1 and KU-3). The surface hulls appear as bright halos surrounding the denser granule body. After only 3 months of storage without prior curing or treatment with a conditioning agent, the product of high moisture content was badly caked whereas that of low moisture content was not caked. The granules of high moisture content were covered with much thicker hulls of urea-ammonium chloride complex than were the granules of low moisture content. The thicker hulls consisted mainly of stout rod and needle crystals oriented roughly normal to the granule surfaces; the thickness of the hulls was about 100 microns. The hulls on the granules of low moisture content averaged only about 25 microns in thickness, and the crystals forming these hulls were intergrown masses of randomly oriented, small crystallites.

Effect of Curing

Pile curing for 7 days prior to bagging helped to reduce or prevented caking of the granular products in subsequent storage. These products caked in the pile during the curing period, but the lumps were broken up before the cured materials were bagged. When the lumps were broken, there was considerable fracture of granules, which attested to the strength of the bonds that had formed. Microscopic comparisons of cured and un-

cured products were made after 3 and 6 months of storage. Usually there were little or no differences in the extent of formation of crystalline hulls on the cured and uncured products, even though there were differences in degrees of caking. When there were differences, the hulls on the cured products were more highly developed. Curing probably served to accelerate the hull formation processes as a result of the retention of heat and moisture in the pile. In products that responded well to curing, there apparently was not sufficient additional development of crystals after curing to cause caking.

Figure 7 shows a comparison of cured and uncured 9-18-18 made from ammonia-ammonium nitrate solution, calcium metaphosphate, potassium chloride, and sulfuric acid. Curing induced the same hull formation of mono-ammonium phosphate that developed on uncured product during several months of storage. Hull formation apparently was completed during curing.

Figure 3 is another comparison of cured and uncured 12-12-12 material made from ammonia-urea solution, ammonium sulfate, superphosphate, potassium chloride, and sulfuric acid. Again, the same uniform hull formation was observed. However, with this product, both cured and uncured material showed continued growth of the hulls during storage, and curing resulted in only slight improvement in storage properties.

Effect of Conditioning

All the products listed in Table I showed improved storage properties when they were conditioned by dusting with 2.5% by weight of kaolin clay or kieselguhr in a rotary tumbler prior to bagging. Kieselguhr usually gave slightly better results than kaolin, but kaolin was satisfactory for most products and was used because of its lower price. The kaolin was in the form of a dust;

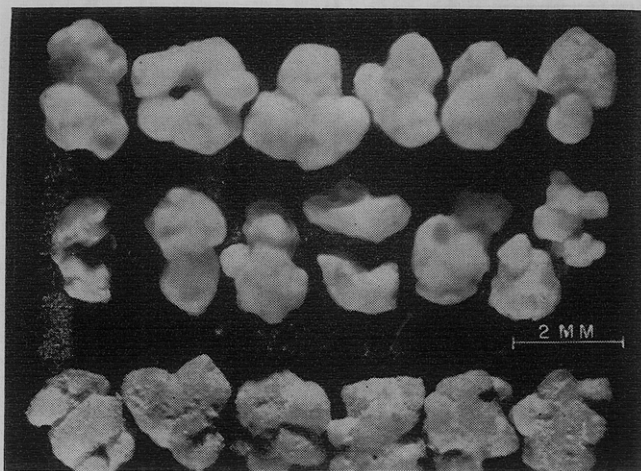


Figure 7. Granular 9-18-18 fertilizer made from ammonia-ammonium nitrate solution, calcium metaphosphate, potassium chloride, and sulfuric acid

Top, uncured; middle, cured; and bottom, cured and conditioned

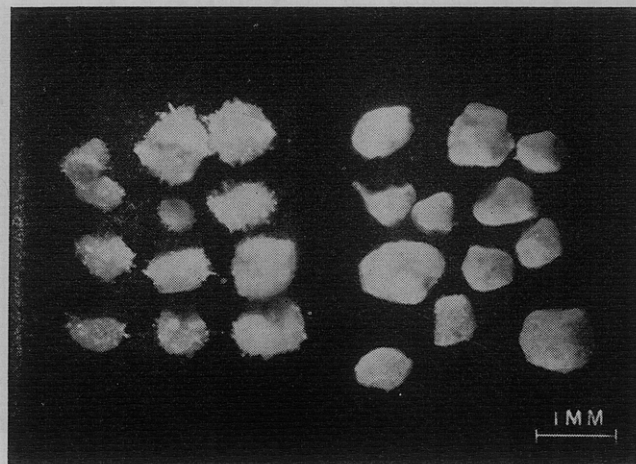


Figure 8. Granular 12-12-12 fertilizer made from ammonia-urea solution

Left, cured-unconditioned and right, cured-conditioned

90% of the particles were smaller than 10 microns, the bulk density was 31 pounds per cubic foot, and the moisture content was less than 1%. The kieselguhr was 76% -10-micron particles, the bulk density was 12 pounds per cubic foot, and the moisture content was about 4%.

Microscopic examinations of conditioned granules after bag storage showed that most of the products were coated uniformly with the conditioning agent and that the functions of the conditioner in preventing caking were about the same in all cases. The presence of the conditioner did not prevent the formation of crystalline hulls on the granules; however, in most cases, the hulls formed beneath the coating of conditioner and seldom did the crystals project beyond the layer of conditioner. The conditioner appeared to have aided in extending the crystallizing phase over the surface of the granules, thus preventing localized growth of crystals at contact points between granules. Another very obvious result of conditioning was that crystals comprising the surface hulls were much finer grained, more intergrown, and more densely packed than were those that comprised the hulls on unconditioned products. These effects are believed due to a seeding action of foreign nuclei supplied by the conditioner. A third function of the conditioner was as a separator between granules, which discouraged intergrowth of crystalline hulls during and after their formation.

The effect of conditioner in modifying the nature of the crystalline hulls on granules is illustrated in Figure 8, which compares conditioned and unconditioned 12-12-12 products containing urea. The conditioner was 2.5% by weight of kaolin. Both products were pile-cured for 7 days prior to bagging. Conditioning was done just prior to bagging. The unconditioned product, after 9 months of storage, showed an average hull thick-

ness of 100 to 150 microns with individual crystals frequently being as long as 350 microns. The crystal growth generally was oriented normal to the surface of the granule. In contrast, the conditioned granules, after the same period of storage, showed an average hull thickness of only about 50 microns with very few crystal projections exceeding 50 microns. The crystals were very fine grained and were oriented randomly within the hull, with the result that it was smoother and more compact. Here the conditioner aided in developing uniform, more compact, fine-grained crystalline growths, and possibly in removing moisture by adsorption so that dissolution and recrystallization processes took place at a much slower rate, as evidenced by the sharp difference in the extent of hull formation.

The crystalline hulls on conditioned products that caked in storage had developed upward into the layers of conditioner to varying degrees and, as a result, conditioner had become occluded in the hulls. In some products, relatively large proportions of the conditioner generally had been occluded in the surface hulls, and in some places no surface conditioner remained. In other cases, the unoccluded conditioner appeared to have been agglomerated into sparsely distributed lumps, probably by a flocculating action of salt solutions permeating the layer of conditioner. When these processes occurred, they contributed to the destruction of the separation function of conditioner and were responsible, to a large degree, for caking.

Unincorporated potassium chloride particles that were present in some products because of poor granulation also became well coated with conditioner. Nevertheless, these particles still showed reaction below the layer of conditioner similar to that noted in the unconditioned products. However, the

coating of conditioner was not destroyed, and no caking bonds resulted. Coating with a conditioner, therefore, appeared to counteract the effects of poor incorporation of potassium chloride. A conditioner, therefore, does not necessarily prevent movement of reactive solutions between granules, but it does serve to modify the crystalline growths that result.

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