GRANULAR FERTILIZERS

Relative Effectiveness of Granule Coating Agents

RIKIO KUMAGAI[1] and JOHN O. HARDESTY

Fertilizer and Agricultural Lime Section, Soil and Water Conservation Research Branch,
Agricultural Research Service,
U. S. Department of Agriculture,
Beltsville, Md.

Granular mixed fertilizers are much less subject to caking during storage than nongranular mixtures of the same formulation, but may require coatings of finely divided materials for satisfactory physical condition. The present study evaluates the effectiveness of 17 different coating agents in reducing the caking tendency of a 12-12-12 granular fertilizer. Effectiveness of coating agents was closely related to relative bulk densities. Additions of 2% of hydrated silica, synthetic calcium and magnesium silicates, and diatomaceous earth with bulk densities of 7 to 15 pounds per cubic foot reduced crushing strength of fertilizer cake 54 to 71%. Calcium carbonate, pyrophyllitic clay, and spent fuller's earth with bulk densities of 42 to 55 pounds per cubic foot effected reductions of less than 17%. The ability of coating agents to reduce or eliminate caking of granular fertilizers is dependent on the initial moisture content of the mixture, particle size and shape of the granules, and kind and amount of agent used. The data should guide the selection and use of coating agents for granular fertilizers.

GRANULATION makes possible the satisfactory use of many high-analysis mixed fertilizers that otherwise could not be used because of poor physical condition. Although granular fertilizers are much less subject to caking during storage than nongranular mixtures of the same formulation and moisture content (*1*, *4*), recent reports (*7*) have indicated the occurrence of caking in some types of granular products. The problem appears to involve the accumulation and recrystallization of soluble salts at the surface of the granule (*5*). The use of large amounts of soluble, hygroscopic salts in present-day high-analysis mixtures tends to mask the improved characteristics imparted by granulation. Attempts to improve the caking and drilling characteristics of high-analysis granular fertilizers have led some manufacturers to the use of various finely divided materials as anticaking coatings for their products. Such coating agents have been successfully used to improve storage characteristics of technical grade granular ammonium nitrate (*6*).

This paper reports the results of laboratory caking tests conducted on 12-12-12 granular mixed fertilizer with and without the addition in varying amounts of 17 selected coating agents. The work includes an evaluation of some physical characteristics of granular fertilizer, such as moisture content and particle size and shape, which determine the ultimate effectiveness or usefulness of these coating agents.

The present study is part of a joint program of research with the Tennessee Valley Authority on the production of high-analysis fertilizers of improved physical condition.

Equipment and General Procedure

A 12-12-12 fertilizer formulated as shown in Table I was prepared in 50-pound lots in a closed Allegheny-metal drum 32 inches in diameter and 12 inches in width, which was rotated at 24 r.p.m. Nitrogen solution was introduced through a hollow trunnion in the side of the drum and sprayed at a rate of 0.85 pound per minute on the rolling bed of material. Heat of reaction was supplemented by gas heat applied externally to the drum and all batches were processed at a temperature of about 170° F. The complete cycle required 15 minutes. Ammoniation time, retention time, and processing temperature were based on data obtained from preliminary investigations of optimum processing conditions for maximum yield of 10- to 20-mesh (1.65- to 0.83-mm.) granules. No water was added to the mixtures, which contained about 4% moisture derived solely from the ingredients themselves. The products were not dried and, except as otherwise noted, were screened to 10 to 20 mesh immediately after preparation and allowed to cure in closed containers. Temperature during curing was maintained at 86° F. The narrow particle-size range was selected to minimize segregation and permit better reproducibility of test results. After a selected curing period, usually 24 hours, the fertilizer was rescreened. Coating agents in amounts equivalent to 1, 2 or 3% by weight were added to 400 grams of the fertilizer and mixed for 5 minutes in a rotary jar mixer. Samples for moisture analyses were obtained immediately prior to initiation of the caking tests conducted according to the general method of Adams and Ross (*1*, *2*). All moisture determinations were made by the air-flow procedure (*3*). Cakes approximately 1 inch in thickness and 2 inches in diameter were formed under a pressure of 12 pounds per square inch in caking bombs stored for 7 days at 86° F. and 40% relative humidity. This caking

Table I. Formula of 12-12-12 Caking Test Mixture

Materials			Plant Nutrient Units		
Kind	Nutrient content, %	Amount, Lb./Ton	N	P_2O_5	K_2O
Ordinary superphosphate	20.0 P_2O_5	600	...	6.0	...
Triple superphosphate	49.0 P_2O_5	245	...	6.0	...
Nitrogen solution	40.6 N[a]	265	5.4	...	...
Ammonium nitrate	33.5 N	277	4.6	...	...
Ammonium sulfate	20.5 N	213	2.2	...	...
Potassium chloride	60.0 K_2O	400	...	...	12.0
		2000	12.2	12.0	12.0

[a] Ammoniation rate = 4.79 lb. NH_3 per 20 lb. P_2O_5

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[1] Present address, Olin Mathieson Chemical Corp., New Haven, Conn.

pressure is approximately the same as that at the bottom of a fertilizer pile 28 feet high and having a bulk density of 62 pounds per cubic foot. Crushing strengths of the test cakes were measured by means of a hydraulic press. Tests were conducted in replicates of two or three, as shown in subsequent data.

Coating Agents

Seventeen materials available commercially in bulk quantities and having general specifications seemingly suitable for use as coating agents were selected for the tests. They included such materials as diatomaceous earth widely used for conditioning of ammonium nitrate prills, processed calcium and magnesium silicates, vermiculite, perlite, and a variety of ordinary clays and by-product materials. The relative effectiveness of these agents as coatings when added in amounts equivalent to 2% on 10- to 20-mesh 12-12-12 fertilizer cured for 1 day and containing 2.7% moisture is shown in Table II. Relative effectiveness is expressed as per cent reduction in crushing strength of fertilizer cake and may be interpreted as an index of probable improvement in bag-storage properties of the fertilizer. The data show that light, bulky materials such as hydrated silica, synthetic calcium and magnesium silicates, and diatomaceous earth with bulk densities in the range 7 to 15 pounds per cubic foot effected reductions in crushing strength of cake ranging from 54 to 71%. Phosphate by-product, kaolinitic, and montmorillonitic clays and fuller's earth with bulk densities in the range 23 to 40 pounds per cubic foot effected reductions in the range 29 to 41%. Spent fuller's earth, pyrophyllitic clay, and calcium carbonate with the highest bulk densities (42, 42, and 55 pounds per cubic foot, respectively) were the least effective of the agents tested and reduced the crushing strength of cake less than 17%. Of the agents tested, only vermiculite and perlite gave results inconsistent with their bulk densities. A previous publication (*4*) has shown that vermiculite does not readily adhere to surfaces of relatively dry fertilizer particles. Tests conducted at that time showed vermiculite of particle size comparable to that shown for sample 9 (Table II) to have only 56% of the coating power of diatomaceous earth when applied to 50- to 60-mesh (0.28- to 0.25-mm.) particles of 10-10-10 fertilizer containing 2.7% moisture. This characteristic of expanded silicates is apparently the reason for the comparative ineffectiveness of both vermiculite and perlite as coating agents for granular fertilizer.

Table II. Relative Effectiveness of Coating Agents on Caking Tendency of Granular 12-12-12 Fertilizer

Sample No.	Description of Coating Agent[a] Type	 Bulk density[b], lb./cu. ft.	 Mean particle size[c], microns	Reduction in Crushing Strength[d] of Fertilizer Cake[e], %
1	Hydrated silica	12	20	71
2	Magnesium silicate, synthetic	15	8	71
3	Calcium silicate, synthetic A	15	35	65
4	Calcium silicate, synthetic B	7	15	62
5	Diatomaceous earth	10	20	54
6	Phosphate by-product[f]	29	10	41
7	Kaolinitic clay A	26	3	40
8	Fuller's earth	24	25	39
9	Vermiculite A	13	25	35
10	Montmorillonitic clay A	23	25	35
11	Montmorillonitic clay B	31	35	31
12	Perlite	9	30	30
13	Kaolinitic clay B	40	50	29
14	Calcium carbonate[g]	55	10	17
15	Vermiculite B	18	80	15
16	Pyrophyllitic clay	42	35	13
17	Spent fuller's earth[h]	42	40	7
	L.S.D.[i], 5% level			13

[a] Added in amounts equivalent to 2% by weight of fertilizer.

[b] Laboratory measurements with 400-cc. glass cylinder under conditions permitting maximum settling of particles.

[c] Determined by examination with petrographic microscope.

[d] Crushing strength values represent means of duplicate determinations.

[e] Fertilizer (10- to 20-mesh) cured 1 day before addition of coating agent and placement in caking bombs; free moisture content, 2.7%; crushing strength of untreated cake, 72 lb./sq. inch.

[f] Dry sludge obtained as by-product in manufacture of sodium phosphates from wet-process acid.

[g] Amorphous calcium carbonate reacted with organic compound to give hydrophobic properties.

[h] Dried residue from petroleum refineries.

[i] Least significant difference at 5% level, determined by statistical analysis of data, indicates that odds are 19 to 1 that difference of 13% between means is significant.

Figure 1 shows the effect of varying amounts of four coating agents on the caking tendency of 12-12-12 granules. Conditions for these tests were the same as those given for the tests described in Table I, except that moisture content of the fertilizer was 3.4% and the number of replications of caking tests was increased to three. In general, greatest reductions in crushing strength of 12-12-12 cake were obtained with the first 1% of coating agent added and somewhat lower reductions with each additional 1% increment. The anomalous behavior of spent fuller's earth is not readily explained. Figure 1 also shows that, under the given conditions, a 1% addition of diatomaceous earth was more effective than 3% additions of either kaolinitic clay B or spent fuller's earth and almost as effective as a 2% addition of montmorillonitic clay A. Actual amounts of specific agents required for satisfactory conditioning of granular fertilizers will vary with storage conditions as well as with physical characteristics of the mixture as determined by such factors as formulation, processing conditions, length of curing period, and moisture content (*1*, *2*, *4*, *8*).

Curing Period and Moisture Content

An ample curing period and low moisture content during storage generally have been recognized as factors favoring satisfactory physical condition of fertilizers (*1*). Table III shows the effect of curing period on relative effectiveness of selected agents added in amounts equivalent to 2% by weight of the fertilizer. Coating agents used were added to the fertilizer after the first 24 hours of the curing periods shown. No effort was made to adjust moisture contents of the cured materials and the changes in free moisture content as shown are attributed

Figure 1. Effect of varying amounts of coating agents on caking tendency of granular 12-12-12 fertilizer

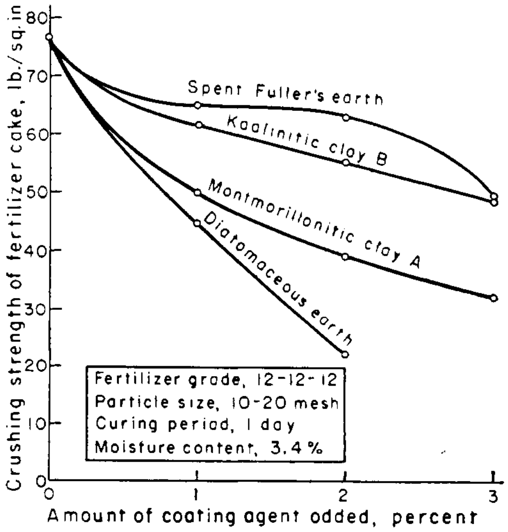

Table III. Effect of Curing Period on Caking Tendency during Storage of Coated Granular 12-12-12 Fertilizer

Description of Coating Agent (2% Addition)		Moisture Content of Fertilizer and Reduction in Crushing Strength[a] of 12-12-12 Cake			
		Cured 1 Day		Cured 8 Days	
Sample No.	Type	H_2O, %	Reduction in C.S., %	H_2O, %	Reduction in C.S., %
5	Diatomaceous earth	2.1	100	1.7	100
6	Phosphate by-product	2.1	88	1.9	93
8	Fuller's earth	2.1	81	1.9	78
12	Perlite	2.1	73	1.7	68
16	Pyrophyllitic clay	2.1	65	1.7	56
17	Spent fuller's earth	2.1	39	1.8	39

[a] Values represent means of triplicate determinations. Crushing strength of untreated cake prepared from 10- to 20-mesh granules at 1-day curing period, 74 lb./sq. inch; 8-day, 41 lb./sq. inch.

to either gain in water of crystallization during curing or losses to the atmosphere incurred during rescreening and mixing of the lots.

The data show that reductions in crushing strength of cake with use of coating agents were virtually independent of the curing period up to 8 days or of the decrease in moisture content of fertilizer from 2.1 to 1.7%. The significantly greater reductions obtained with 2% additions of the selected agents shown in Table III as compared with use of the same agents in Table II are attributed to differences in such physical characteristics of the fertilizer as particle-size distribution, moisture content, and granule density, shape, and surface characteristics which could be controlled only within rather wide limits. The relative effectiveness of the different agents, however, was not affected.

Particle Size of Fertilizer

Most granular fertilizers on the market today contain a large proportion of material in the particle-size range of 5 mesh (4.0 mm.) to 35 mesh (0.4 mm.). A previous study (*4*) showed that the caking tendency of fertilizer during storage increased with decrease in particle size. In an extension of that study the relative caking tendencies of 12-12-12 mixtures containing varying proportions of 10- to 20-mesh and 20- to 35-mesh granules cured for 1 week and adjusted to a moisture content of 3.7% were determined (Table IV). Also shown are effects of 2% additions of diatomaceous earth on the various mixtures. Results indicate that gradual replacement of 10- to 20-mesh granules with 20- to 35-mesh granules produced a maximum increase in crushing strength of 35% (from 65 to 88 pounds per square inch) at a particle-size distribution of 25% 10- to 20-mesh and 75% 20- to 35-mesh particles. This phenomenon is not readily explained. Cakes prepared from 100% 20- to 35-mesh granules had crushing strengths 12 pounds per square inch or 18% higher than those from 100% 10- to 20-mesh granules. Crushing strengths of cakes prepared with 2% additions of diatomaceous earth exhibited only slight and nonsignificant increases with increasing proportions of the 20- to 35-mesh granules and indicated that the effect of the coating agent was substantially independent of relative proportions of the two size fractions.

Granule Shape

The foregoing data have indicated that effectiveness of a coating agent is dependent on the amount used and its particle size, density, and adhesiveness as well as on the particle size and moisture content of the fertilizer. Because density and shape as well as particle size of fertilizer determine the surface area which can be covered by a given amount of coating agent, tests were conducted to determine the effect of granule shape on caking tendency of granular fertilizer. Hard, dense discrete granules of well cured 8-16-16 fertilizer were used for the tests. The fertilizer had been formulated with ordinary and triple superphosphates, ammonium sulfate, nitrogen solution, potassium nitrate, potassium chloride, and a small amount of calcined kieserite. Size fractions of 8 to 10 mesh (2.4 to 1.65 mm.) and 10 to 20 mesh were obtained by preliminary screening. A second set of the same size fractions was obtained by screen fractionation of fragments obtained by crushing the oversize (2.4- to 4.0-mm. granules) from the original lot. The adjacent screen-size fractions were selected because it was desired to minimize possible variations in granule density. Each of the four batches was adjusted to 5.5% moisture and stored in closed containers for 48 hours to permit equilibration of the moisture. Crushing strengths of cakes prepared from the materials with and without 1 and 2% additions of diatomaceous earth (Table V) indicate that those coatings applied to regular-shaped granules reduced the crushing strength of cake substantially more than the same amounts used with irregular-shaped granules of the same sieve size. These data show that variable results with use of coating agents often obtained under commercial conditions may be due to alterations in physical characteristics of the fertilizer granules as a result of changes in processing techniques.

Table IV. Effect of Particle-Size Distribution on Caking Tendency of Coated and Uncoated Granular 12-12-12-Fertilizer

Particle-Size Distribution, % of Total		Crushing Strength[a] of 12-12-12 Cake[b], Lb./Sq. Inch	
10–20 mesh	20–35 mesh	Without coating agent	Containing diatomaceous earth (2% addition)
100	0	65	0
75	25	73	0
50	50	79	3
25	75	88	6
0	100	77	4

[a] Crushing strength values represent means of triplicate determinations.

[b] Fertilizer cured for 1 week before test; adjusted moisture content, 3.7%.

Table V. Effect of Granule Shape on Caking Tendency of Coated and Uncoated Granular 8-16-16 Fertilizer

Description of 8-16-16 Fertilizer[a]		Crushing Strength[b] of Cakes Containing Diatomaceous Earth, Lb./Sq. Inch, Added in Amounts of		
Particle-size range, Tyler mesh	Bulk density, lb./cu. ft.	None	1%	2%
Uncrushed Granules				
8–10	62	59	7	0
10–20	55	68	12	3
Crushed Granules				
8–10	62	56	30	14
10–20	54	53	35	22

[a] Adjusted moisture content, 5.5%.

[b] Values represent means of triplicate determinations.

Summary

Laboratory caking tests were conducted on granular 12-12-12 fertilizer with and without the addition in varying amounts of 17 different coating agents. With the exception of such materials as vermiculite and perlite, which do not readily adhere to surfaces of fertilizer particles, effectiveness of coating agents was closely related to relative bulk densities. Additions of 2% of hydrated silica, synthetic calcium and magnesium silicates, and diatomaceous earth with bulk densities in the range of 7 to 15 pounds per cubic foot effected reductions in crushing strength of fertilizer cake in the range 54

to 71%. Under the same conditions, kaolinitic and montmorillonitic clays, fuller's earth, and phosphate by-product with bulk densities in the range 23 to 40 pounds per cubic foot effected reductions in the range 29 to 41%. Calcium carbonate, pyrophyllitic clay, and spent fuller's earth with bulk densities in the range 42 to 55 pounds per cubic foot, effected reductions of less than 17%. A 1% addition of diatomaceous earth with bulk density of 10 pounds per cubic foot was more effective than 3% additions of either kaolinitic clay or spent fuller's earth with bulk densities of 40 and 55 pounds per cubic foot, respectively.

Caking tendency of uncoated granular 12-12-12 fertilizer decreased with extension of the curing period from 1 to 8 days. Percentage reductions in crushing strength of cake attributable to presence of coating agents were largely independent of the curing time. Reducing the particle-size range of fertilizer from 10–20 mesh to 20–35 mesh increased the caking tendency of fertilizer 18% but did not significantly alter the effect of 2% additions of diatomaceous earth. Caking tests conducted with regular-shaped and crushed irregular-shaped granules of 8-16-16 fertilizer indicated that coating agents were substantially more effective in reducing the caking tendency of fertilizer when used with the regular-shaped granules. In general, the study showed that a number of finely divided materials of low bulk density currently marketed may be used as coating agents to effect significant reductions in caking tendency of granular fertilizers.

Acknowledgment

The authors wish to thank the producers who furnished samples of their materials for these tests and to express their appreciation to John B. Breen for general laboratory assistance and to G. W. Wieczorek for particle-size evaluations of coating agents.

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Received for review September 9, 1955. Accepted November 5, 1955. Division of Fertilizer and Soil Chemistry, 128th Meeting, ACS, Minneapolis, Minn., September 1955.

UREA-FORMALDEHYDE FERTILIZERS

Solubility Relationships and Nitrification Characteristics of Urea-Form

K. G. CLARK, J. Y. YEE,
V. L. GADDY, and F. O. LUNDSTROM

Fertilizer and Agricultural Lime
Section, Soil and Water Conservation
Research Branch,
Agricultural Research Service,
U. S. Department of Agriculture,
Beltsville, Md.

Solubility relationships and nitrification characteristics are reported for urea-formaldehyde reaction products ranging from 0.75 to 1.4 in mole ratio of urea to formaldehyde. Although possible suitability of such materials for fertilizer use is indicated by U/F > 1, increases in this ratio are not necessarily directly related to improved solubility and nitrification characteristics. The primary components of the neutral permanganate activity, the solubility pattern, and the activity index recently adopted by the Association of Official Agricultural Chemists, were found to be highly correlated with the degree of nitrification observed in a 3-week incubation period. Increase in nitrification between 3- and 15-week incubation periods was more highly correlated with the secondary components of the solubility pattern and activity index than with that of the permanganate procedure. In consequence, the solubility pattern procedure and the recently adopted activity index, AI $\geqq$ 40, are considered more reliable than neutral permanganate activity in characterizing the suitability of urea-formaldehyde materials for fertilizer use.

THE GENERIC TERM "UREA-FORM" has been applied to urea-formaldehyde fertilizer materials. Such products have been described as mixtures of polymethyleneureas (*5*, *6*) which exhibit urea-formaldehyde mole ratios greater than 1, U/F > 1, nitrogen contents in excess of 37%, low solubilities in water and organic solvents, and lower rates of nitrification in soil media than the more soluble forms of chemical nitrogen fertilizers. The present paper reports the composition and solubility and nitrification characteristics of a wide variety of urea-formaldehyde reaction products in relation to their suitability for fertilizer use.

Urea-Formaldehyde Mole Ratio

The fact that urea and formaldehyde react to form products with U/F > 1 requires at least some of the urea residues to be present as branched- or straight-chain methylene linkage-type polymers in which $2 \geqq \mathrm{U/F} = \frac{n+1}{n} \geqq 1$, as shown in Figure 1. For large values of n, U/F $\doteq$ 1, whereas for $n = 1$, U/F = 2 and the product is soluble methylenediurea.

Any degree of cross linkage between the urea residues in the polymer results in a decrease in the U/F mole ratio to the range $1/2 \leqq \mathrm{U/F} = \frac{m+1}{2m} = \frac{m+n+2}{2m+n+1} \leqq 1$. The highly cross-