FERTILIZER FORMULATION

Influence of Formulation on the Physical Properties of Fertilizers

FORREST L. TURBETT and JAMES G. MacARTHUR
Research Laboratory, Spencer Chemical Co., Pittsburg, Kan.

This work was undertaken to determine to what degree caking in fertilizers could be controlled by formulation. A method for determining caking tendencies was devised. The composition of ammoniating solution and the solution phase of a 3–12–12 fertilizer were studied to determine their influence on caking. The work indicated that improvement in the condition of mixed fertilizer could be obtained by controlling ammoniation solution composition. Metathesis contributed markedly to the amount of objectional salts in solution and to crystal forms deposited from the solution phase, and, within the range normally found in mixed fertilizer, degree of ammoniation and moisture content contributed little to caking. Until drying becomes common practice in fertilizer manufacture, it appears that physical condition can be improved by selection of proper raw materials.

THE CAKING OF MIXED GOODS during the time between bagging and application is a problem, long recognized in the fertilizer industry. Various facets of the problem have been studied and worth-while information has been obtained. Adams and Ross (2) reported on the caking tendency of pure salts, Lawrence (8) discussed the factors considered most detrimental to well conditioned goods, and Rader (11) markedly increased the knowledge of the solution phase composition. Other authors have studied hygroscopicity (1, 10, 15, 16), chemical reaction (5, 6, 9, 13), and similar topics concerned with or closely related to caking of fertilizer.

Study of the reported work indicated that many factors influence caking: loss of moisture, change in temperature,

Figure 1. Apparatus for laboratory formulation of mixed fertilizer

pressure, metathesis, chemical reaction, hydration, crystal transformation, hygroscopicity, density, and particle size. Although prior investigations had indicated that crystallization from a liquid phase was the main cause of caking in fertilizers, no published information had been made available to indicate the specific effects of this crystallization.

The present work was initiated in an attempt to explain a "reversible" type of caking observed in fertilizers, wherein the material caked in the warehouse and at a later date returned to a free flowing condition. After a suitable method for evaluating caking tendencies had been devised, it became apparent that reversible caking was primarily due to temperature variations, and as this variation could not easily be controlled during storage, a study of secondary factors was undertaken. A study of ammoniating solutions was included to determine the possibility of improving the solutions now in use. Rader's work on the solution phase was also expanded to include a study of the amount and type of salts which crystallize from the solution phase of a 3–12–12 fertilizer and their effect on caking properties of the fertilizer.

Laboratory work was carried out in close cooperation with men in the field and, whenever possible, projected results were checked on a commercial scale.

Laboratory Mixing Procedure

Formulation was accomplished in the equipment shown in Figure 1. This equipment consisted of a double cone blender 12 inches in diameter, which was modified by drilling a hole through each axle. The holes were fitted with packing glands and entry tubes. The

tube shown on the left was for the solution feed sparger which extended in and across the mixer, following the curve of the side, and was equipped with 13 holes, 0.025 inch in diameter, spaced equally along the portion of the tube which would normally be submerged, and drilled on the side of the tube which faced away from the axis of the blender. The other side of the blender was equipped to obtain information such as temperature of the mix, rise in pressure during closed ammoniation, and ammonia loss during open ammoniation. Solution and/or anhydrous ammonia was weighed into small stainless steel bombs for feeding to the mixer. The other ingredients were weighed into the blender proper and agitated for 10 to 15 seconds, and the whole cycle was fixed at 1 minute. Batch size was standardized at 4 kg. Immediately after being removed from the mixer, the material was sealed in 2-gallon paint cans, and stored at 50° C. for 3 weeks. Material for determining initial caking tendencies was removed from the can after 24 hours.

Analytical Procedures

Analytical procedures of the Association of Official Agricultural Chemists (4) were used throughout the work with one exception—the determination of "free" moisture. In the work reported here, it was imperative that the free moisture be determined as closely as possible, and a great deal of study was given to establishing a suitable procedure. At the outset of the present work, the association listed the 100° C. oven drying and the benzene distillation methods as means of determining free moisture. Neither method proved satisfactory, as it was observed that cer-
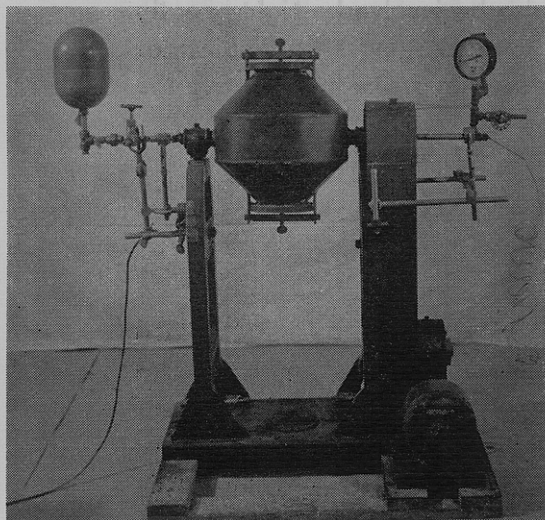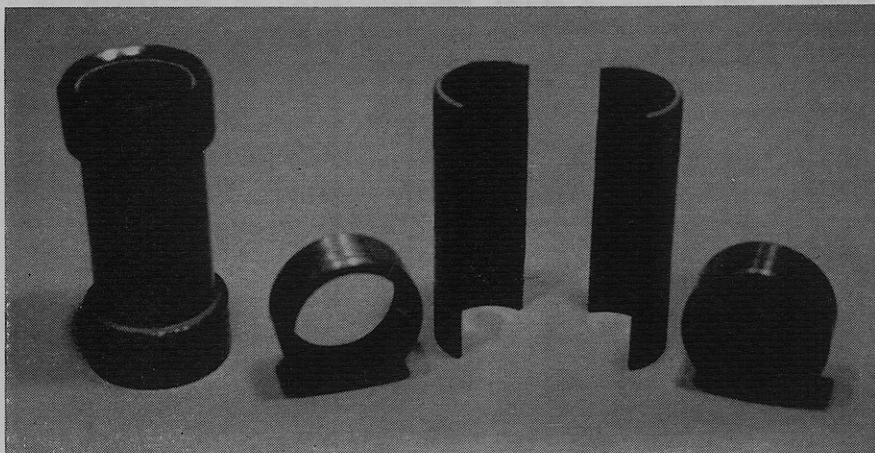
Figure 2. Cake-forming bomb assembled and disassembled

tain hydrated salts which might be present in fertilizers were unstable at the temperatures involved. By substituting a water-immiscible liquid of low boiling point (n-hexane, boiling point 69°C.) for benzene in the AOAC distillation method, it was found that the results obtained agreed reasonably well with a value calculated from the total AOAC moisture of the starting superphosphate plus the known water added in the ammoniating solution. The hexane distillation method was checked against the AOAC air flow method after it became official; little difference could be found in results. The method consisted of refluxing 50 grams of the sample with 85 ml. of n-hexane (boiling point 69°C.) for exactly 2 hours and collecting the water that distilled over with

the hexane in an accurately calibrated Bidwell-Sterling distilling receiver.

Testing Method

Methods outlined in the literature for evaluating the caking properties of fertilizers were examined and in some cases tried, but none was found satisfactory. The method finally worked out incorporated certain ideas from Adams and Ross (3) and modifications which, in the authors' opinion, made the procedure simulate more nearly actual conditions that might be encountered in the field. Dead weight pressure and temperature drop were employed for the formation of standard sized cakes of the experimental products, and a sensitive crushing apparatus was used for determining the strengths of the cakes

formed. The formation pressure was estimated to be within the range of pressures encountered in the bottom layers of bags stacked in the average warehouse, and the temperature drop was selected to simulate that which might be encountered when the fertilizer was packed warm and allowed to cool in the bag. An assembled bomb and its four separate parts are shown in Figure 2. The cylinder was fabricated from 2-inch schedule 80 steel pipe and measured $1^{15}/_{16}$ inches in inside diameter and $5^1/_4$ inches in length. The bomb was coated inside and out with a single heavy coat of alkyd varnish, baked on at 180°, to prevent corrosion. The threaded collar was provided with an $1/_8$-inch offset which touched the top edge of the cylinder when fully screwed down. The threaded base was machined flat inside and out, and a special thread was cut to allow the bottom edge of the cylinder to face against the inside surface of the base when tightened.
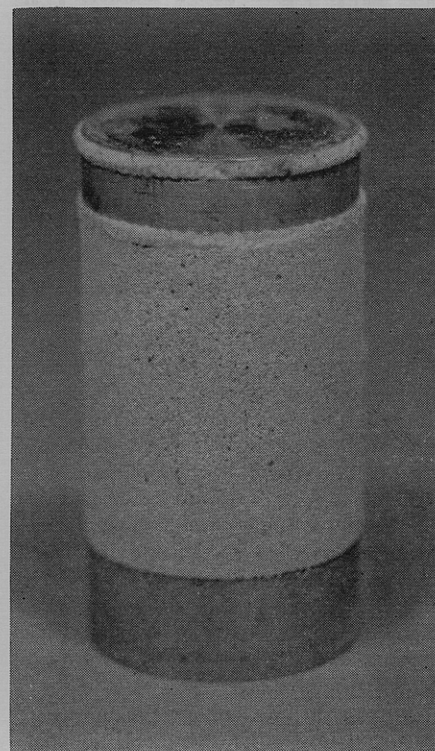
Cake-Forming Weights

Cakes of experimental mixtures were formed between two aluminum platens inside the cylinders, under a dead weight pressure of 4.24 pounds per square inch. Figure 3 shows a loaded bomb with weight in place, and also auxiliary weights for varying applied pressure. The large weight consisted of metal lead cast around one end of a 6-inch length of $1^1/_2$-inch pipe. The open end of the pipe protruded approximately $3^1/_8$ inches below the lead and was machined flat to prevent tilting when at rest upon the upper platen. The weights were cast in a steel mold measuring $3^1/_2$

Figure 3. Loaded bomb with weight in place and auxiliary foot and weights
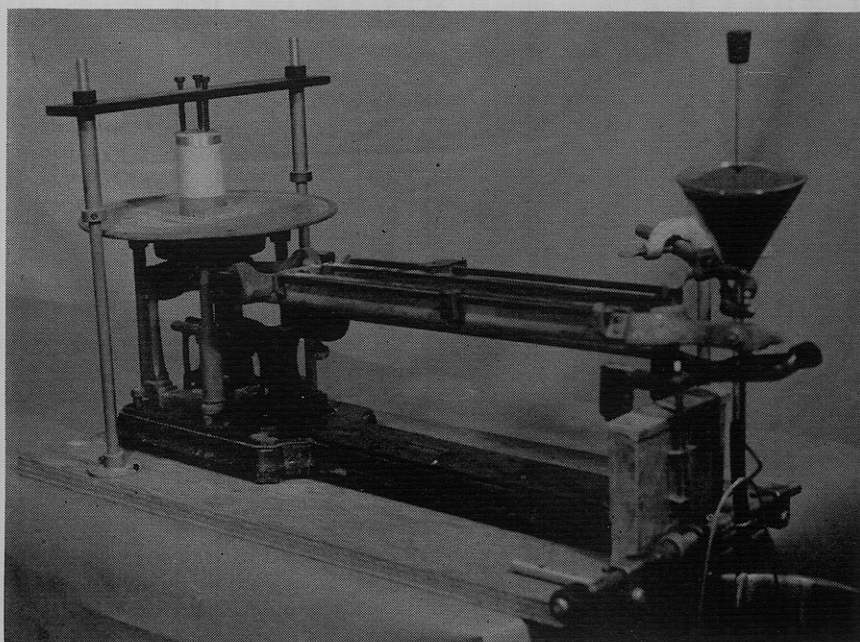

Figure 4. Formed cake ready for crushing
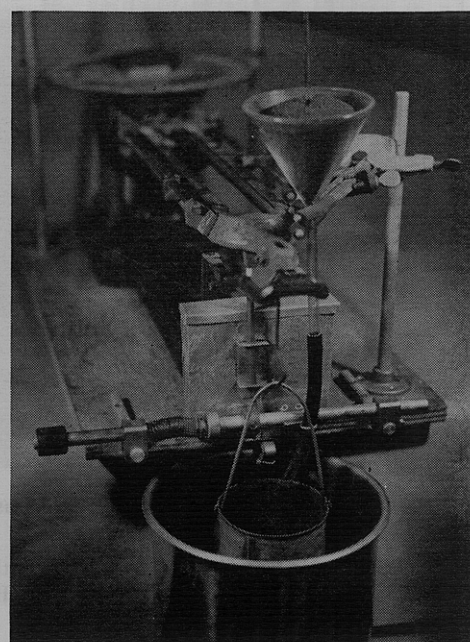
Figure 5. Crushing apparatus with cake in position

Figure 6. Mechanism for shot cutoff

inches in diameter at the top and tapering to $3^3/_8$ inches at the bottom. The exact weight of the assembly was $12^1/_2$ pounds.

Cake-Forming Platens The platens were machined from aluminum rod and both flat surfaces were coated with baked alkyd varnish. Figure 4 shows a cake of fertilizer as removed from the bomb, with both platens in place. The lower platen measured $1/_{64}$ inch less in diameter than the inside diameter of the bomb and was $3/_4$ inch thick. This platen served as a convenient finger hold in transferring the cakes to the crushing apparatus. The upper platen had a diameter $1/_{32}$ inch less than the bomb diameter and was $5/_8$ inch thick. Two small wiping rings of ordinary cotton pipe cleaners were carefully fitted into small grooves cut at the edges of the upper platen to provide a smooth sliding surface and prevent the platen from becoming wedged with particles of fertilizer when the forming weight was applied.

Cake-Crushing Apparatus The test cake was crushed by means of pressure exerted by fine (1-mm.) lead shot flowing through a 5-mm. orifice at a rate of approximately 220 grams per second, into a receiver hung on the end of the beam of a modified 20-kg. Troenmer balance. Figure 5 shows a side view of the crushing apparatus with a cake in position for crushing. The cake was centered in a chuck on the balance pan directly beneath the rigid steel crusher bar, which was provided with three adjustable contact points, made from $1/_4$-inch machine bolts. The cake, with platens in place, was brought to balance using the sliding weights on the balance beam. The balance pan was depressed, and the con-

tact points were screwed down to light contact with the top platen. The lead shot was then allowed to flow into the receiving can by removing the glass rod from the funnel.

Automatic Shot Cutoff A close-up view of the automatic shot cutoff, in cocked position, is shown in Figure 6. The rubber hose leading from the funnel to the receiver was attached to a movable horizontal rod which was activated by a strong compression spring. The rod was held in the cocked position against a

trigger which came in contact with a collar fixed to the rod. The trigger was activated by a small vertical shaft running through guides upward to a point below the end of the balance beam. At the instant of crushing, the beam fell, and struck the shaft which released the trigger and the shot delivery tube was jerked from the can in a fraction of a second.

Testing Procedure One hundred and fifteen grams of the material was placed in an assembled bomb having the lower platen in place. The top surface of the material was lev-
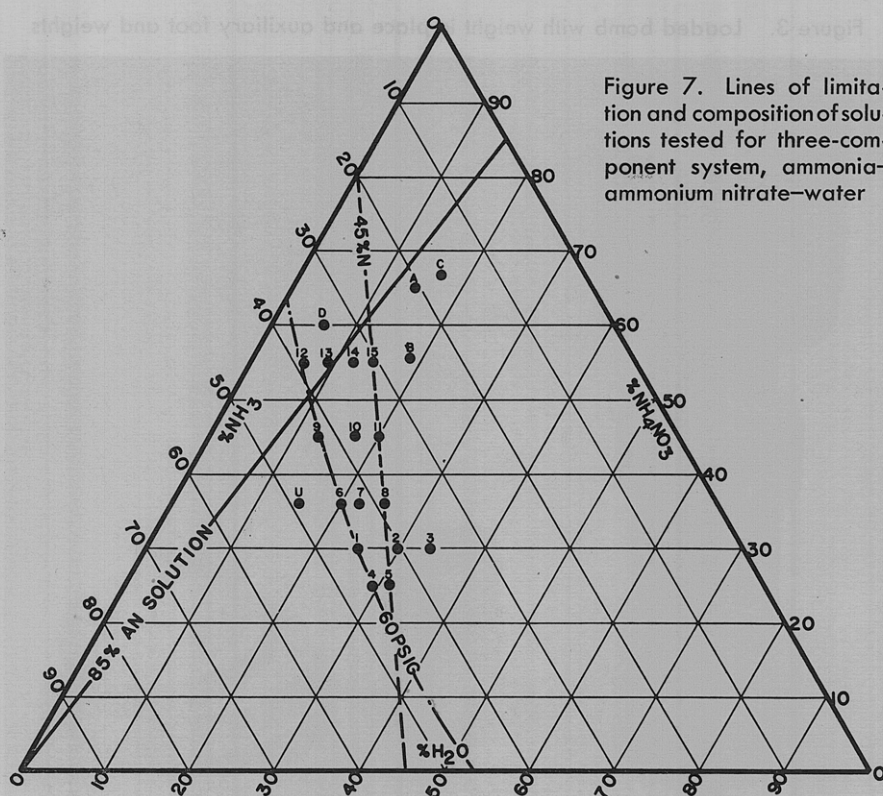

Figure 7. Lines of limitation and composition of solutions tested for three-component system, ammonia–ammonium nitrate–water

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Table II. Formulation of Mixed Goods Used to Check Laboratory and Field Results

Material, Lb.	54½° Bé. Superphosphate				57° Bé. Superphosphate			
	8-8-8	8-8-8	5-10-5	5-10-5	8-8-8	8-8-8	5-10-5	5-10-5
Ammoniating soln. A	..	122	..	152	..	122	..	152
Ammoniating soln. U	92	..	114	..	100	..	122	..
Sulfate of ammonia	549	535	202	189	528	535	182	189
Weak superphosphate	857	827	1041	1041	..	..	..	..
Strong superphosphate	..	..	..	..	867	836	1053	1053
60% muriate	273	273	173	173	273	273	173	173
Kemidol oxide	20	20	20	20	20	20	20	20
Limestone	209	223	450	425	212	214	450	413

	Field Mfg.		Laboratory Mfg.	
Superphosphate	57° Bé. super	54½° Bé. super	57° Bé. super	54½° Bé. super
Moisture, %	7.74	8.07	5.78	5.99
Total P₂O₅, %	20.15	20.44	21.36	21.35
Cit Ins P₂O₅, %	0.07	0.06	0.56	0.77
Water-sol. P₂O₅, %	19.18	19.39	19.14	19.02
Fluorine, %	1.77	1.59	1.69	1.81
Free acid (H₂SO₄), %	3.95	2.74	1.18	1.09

Analysis of raw materials. Ammonium sulfate, 20.85% N
Potassium chloride, 59.70% K₂O

eled and the upper platen gently inserted. The bomb was then placed inside an air-tight constant temperature oven maintained at 40° C. and the forming weight was applied. In order to retard loss or gain of moisture, the relative humidity of the atmosphere inside the oven was maintained at a point near the critical relative humidity of the fertilizer undergoing test by placing a large exposed mass of the same material inside the oven. After 24 hours, the bomb was transferred to a cold conditioning chamber maintained at 6° C. and also having controlled relative humidity, where it was allowed to remain an additional 24 hours. The bomb was then opened and the cake crushed immediately. All tests were conducted in replicates of five, and no test was considered if more than one cake was damaged in handling. The average crushing strength of four or five bombs, in pounds per square inch, was used as an expression of the relative caking tendency of the fertilizer.

The cake forming conditions established were such that crushing strengths of cakes formed from the poorest grade of fertilizer fell below the maximum capacity of the Troenmer balance. Duplication among replicates was good in fertilizers having high caking strength and decreased as the caking strength dropped. The test was of little value for fertilizers having caking tendency under 1 pound per square inch; however, materials caking below 4 pounds per square inch were well enough conditioned to cause little, if any, trouble in the field and, therefore, it was not felt necessary to refine the procedure further.

Experimental

Observations made during the initial work on the standardization of testing procedures indicated that the two most important contributing factors to the condition of the finished fertilizer were the composition of the ammoniating solution and the properties of the superphosphate from which the fertilizers were made.

Because of the great amount of work already reported on superphosphate, it was felt the initial study should be concerned with ammoniating solution. To overcome the effects of variations in the superphosphate it was necessary to complete any one phase of the study within a relatively short time and to use only one specific superphosphate for that phase. The superphosphate was obtained from a nearby manufacturer and was compounded from Florida rock and 55.5° Bé. sulfuric acid using an acid to rock ratio of 0.56. The minimum curing time was 5 weeks.

The initial step in the investigation was to block out an area on the graph of the three-component system ammonia–ammonium nitrate–water, considered most likely to contain solutions that could feasibly be used commercially (Figure 7). Boundaries for the selected area were:

A. All solutions should have a total nitrogen content of more than 45%. This boundary is designated in Figure 7 as 45% N. All mixtures to the left of this line contain more than 45% nitrogen.

B. The vapor pressure of the ammonia–ammonium nitrate–water system should be lower than 60 pounds per square inch when measured at 40° C. This boundary is projected on Figure 7 and designated as 60 pounds per square inch. All solutions to the right of this line fulfill this qualification.

C. The ammonium nitrate–water ratio

Table I. Effect of Solution Composition on Caking Tendency of a 3-12-12 Fertilizer

	Solution Data					Mixed Goods Data			
Solution No.	NH₄NO₃, %	NH₃, %	H₂O, %	Total N, %	Approx. VP at 40° C., lb./sq. inch gage	Amm. rate, wt. % all soln. 3-12-12 goods	NH₄NO₃ in finished goods, %	Free moisture, wt. %	Av. caking tendency, lb./sq. inch, 3 and 5 weeks' cure
1	30.0	44.5	25.5	47.2	62	4.7	1.9	5.95	3.3
2	30.0	40.5	29.5	43.9	44	4.6	2.1	6.34	4.3
3	30.0	36.8	33.2	40.8	36	4.5	2.2	6.77	4.2
4	25.0	45.8	29.2	46.5	69	4.9	1.6	6.21	3.1
5	25.0	43.9	31.1	44.9	50	4.9	1.7	6.41	3.1
6	36.0	44.3	19.7	49.1	62	4.5	2.2	5.53	3.3
7	36.0	42.0	22.0	47.2	57	4.5	2.3	5.73	3.7
8	36.0	39.0	25.0	44.7	48	4.4	2.4	6.01	2.7
9	45.0	42.3	12.7	50.6	69	4.2	2.7	5.08	2.9
10	45.0	38.0	17.0	47.1	45	4.0	2.9	5.42	4.0
11	45.0	35.0	20.0	44.6	40	3.9 •	3.0	5.68	5.8
12	55.0	39.0	6.0	51.4	63	3.8	3.2	4.68	4.3
13	55.0	36.0	9.0	48.9	46	3.7	3.4	4.88	4.0
14	55.0	33.0	12.0	46.4	46	3.6	3.6	5.13	4.1
15	55.0	30.8	14.2	44.6	32	3.5	3.7	5.29	4.9
U	36.0	49.0	15.0	53.0	97	4.6	2.0	5.18	3.7
A	65.0	21.7	13.3	40.6	11	2.7	4.8	5.32	8.0
B	55.5	26.0	18.5	40.9	15	3.2	4.1	5.69	6.5
C	66.8	16.6	16.6	37.1	3	2.2	5.4	5.67	9.0
D	60.0	34.0	6.0	49.0	50	3.5	3.7	4.70	4.7

should be such that the solution could be manufactured from an 85% ammonium nitrate solution without concentration— i.e., there should be not more than 85 parts of ammonium nitrate for every 15 parts of water in the finished mixture. This boundary is designated in Figure 7 by the line labeled 85% AN solution. All mixtures below this line fulfill this qualification.

The ratios of total nitrogen and ammonium nitrate to water were calculated and vapor pressures were obtained from the charts of Sanders and Young (14).

None of the solutions now manufactured fell within the area outlined; however, the commercial solutions were tested along with 13 solutions from within the area and three other solutions selected from outside the area. (Solution 2 fell outside the specified area because of an error in formulation; however, its proximity to the 45% N line led to its being considered as one of the bounded solutions.) The reasons for testing solutions from outside the specified area were varied. Solution 3 was chosen as a solution having the same nitrogen content as commercial solution B, but lower ammonium nitrate content per unit of nitrogen. Solution 12 was used to determine the effect of increasing the ratio of ammonia to ammonium nitrate on commercial solution D.

Solution U had the same ratio of ammonia to ammonium nitrate as solution 2 but a much lower water content.

Results

The results of the tests are shown in Table I, which also shows the solution composition and pertinent data regarding 3–12–12 mixtures. The vapor pressures of the solutions shown in column 6 were determined only approximately; however, they were of the same order of magnitude as those calculated from the work of Sanders and Young and were assumed to be relatively correct.

The caking tendencies shown in the last column represent an average of two determinations made after 3 and 5 weeks of curing. Substantial increase in water (column 9) did not necessarily increase caking, and where the ammonium nitrate content of the finished goods was below 3%, the caking tendencies were consistently low. The solutions now offered for sale, with few exceptions, showed poorer conditioning properties than those selected from the area. The obvious disadvantage of the solutions within the area is higher vapor pressure of the solution.

With reference to the solutions selected from outside the area, solution 3 showed marked improvement in caking tendency over solution B, solution 12 showed little change from solution D, and solutions U and 2 had comparable caking tendencies. As both of the latter solutions showed marked improvement over present commercial solutions, because of its high nitrogen content, and despite its

Table III. Comparative Caking Tendencies of Field and Laboratory Manufactured Fertilizer

(Pounds per square inch)

Grade	Soln.	54½° Bé. Acid			57° Bé. Acid		
		2-week cure	4-week cure	6-week cure	2-week cure	4-week cure	6-week cure
		Field Tests					
8–8–8	U	5.4	4.9	3.65	4.3	4.2	1.0
8–8–8	A	7.0	5.4	6.75	7.3	5.2	2.7
5–10–5	U	2.9	2.6	2.04	1.9	1.2	1.1
5–10–5	A	6.8	2.9	3.58	5.2	3.8	3.4
		Laboratory Tests					
8–8–8	U	9.5	6.9	6.2	6.2	3.5	1.6
8–8–8	A	11.3	7.3	7.1	8.8	5.8	4.8
5–10–5	U	8.1	3.7	4.4	5.0	3.3	2.9
5–10–5	A	7.1	5.0	4.5	4.7	3.8	2.7

Table IV. Formulation and Analysis of 3–12–12 Fertilizer Used for Solution Phase Studies

Formulation	Grams	Analysis	%
Ammoniating solution B (40.8% N)	153	Total P_2O_5	14.0
Superphosphate (19½% APA)	1268	Cit.-insol. P_2O_5	1.5
Potassium chloride (60% K_2O)	408	H_2O-sol. P_2O_5	3.9
Coarse dolomite	211	Total N	2.9
		K_2O	11.9
		Moisture (free)[a]	5.6

[[a] Determined by n-hexane entrainment.

high vapor pressure, solution U was selected as the material for field testing.

Field Tests

The initial field tests using solution U were conducted on 3–12–12 material and showed definite improvement over similar materials made with a B solution (Table II). However, the most comprehensive tests were made using two other formulations and superphosphate made with two different strengths of acids. The ammoniating solutions compared in these tests were U and A. The formulations were 8–8–8 with 2.5 units of nitrogen from solution and 5–10–5 with 2.7 units of nitrogen from solution, the balance of the nitrogen being furnished by the addition of ammonium sulfate. Superphosphate raw materials were made from 54.5° and 57° Bé. acid. Superphosphate was manufactured and formulated in the laboratory and caking tendencies were determined upon the laboratory-manufactured material as well as those manufactured in the field.

Field material was cured in 60-ton piles. The material went into the pile at approximately 140° F. and had dropped to approximately 90° F. by the end of the 6-week curing period. Laboratory material was cured in sealed cans at a constant temperature of 122° F. The field material was bagged in 5-ton lots at 2-week intervals. Results of all the tests are shown in Table III.

The caking tendencies of field-made mixes were consistently below those made in the laboratory. The materials made

with 57° Bé. acid were consistently lower in caking than those made from 54.5° Bé. acid. The 8–8–8 materials made with solution U were substantially lower than those made with solution A. The 5–10–5 showed little improvement when made with solution U in the laboratory.

The discrepancy between field and laboratory work was accredited to differences in superphosphate manufacture; however, as the laboratory mixture was almost always consistently higher or at least equal to commercially prepared goods, as far as caking tendency was concerned, the discrepancy was in the right direction for allowing prediction of field results in the laboratory.

Crystallization from Solution Phase of a 3–12–12 Fertilizer

The solution phase was considered to to be of primary importance in the caking of fertilizers; and, in order to gain additional understanding of the mechanism of caking, some knowledge had to be gained regarding its composition and the type and character of materials which would be obtained when solids were allowed to crystallize from solution. Fortunately, Rader (12) had outlined a procedure for obtaining samples of solution phase and had listed (11) composition and properties for the solution phase of several fertilizers. However, a 3–12–12 grade was not included in his listing. A sample of solution phase was displaced from a 3–12–12 which had been formulated with 3 units of nitrogen from

solution, allowed to cure for 6 weeks, and brought to temperature equilibrium at 35° C. The analysis and formulation of the fertilizer are shown in Table IV.

The only variations made in the Rader technique applied to this work were: substitution of methanol for ethanol as the "ram" solution and making no effort to adjust free moisture content. In order to obtain enough solution phase to study the crystals formed upon cooling, it was necessary to composite collection from several displacements. Results given below are based on analysis of approximately 125 grams of solution collected from 13 kg. of fertilizer.

The composited solution was cooled by stages to 25°, 15°, and 6°. At each temperature the crystals formed were removed by filtration, sucked dry on a fritted crucible, dried overnight at 40°, and weighed. The final filtrate and various crystal fractions were analyzed (Table V, A).

Types of Crystals Deposited By Solution Phase

A study of the crystal forms of the various salts that might possibly crystallize from the saturated solution phase of fertilizers, revealed that the ammonium and calcium phosphates and potassium chloride had crystal forms which would have only minor knitting effect when mixed with inert material— that is, these salts all crystallized in equidimensional cubic or rhombohedral forms, or as triclinic plates. On the other hand, potassium nitrate formed long trigonal crystals; ammonium chloride, dendritic crystals; and ammonium nitrate, either elongated monoclinic or orthorhombic crystals. The three last-named salts would tend to increase knitting of nonsoluble porous particles, through formation of crystal bridges with fewer fracture lines.

Table VI. Effect of Varying Ammoniation Rate, Water Content, and ANE Factor on Caking of X-12-12 Fertilizer

Solution No.	Solution Analysis				Calcd. Analysis of Finished Goods			Caking Tendency, Lb./Sq. Inch	
	NH_4NO_3, %	NH_3, %	H_2O, %	N, %	NH_4NO_3, %	Amm. rate, wt. %	H_2O, %	Initial	3 weeks
1-N	24.3	43.8	31.9	44.6	1.0	3.0	5.8	5.7	8.8
2-N	39.1	35.3	25.6	42.8	2.0	3.0	5.8	7.0	8.0
3-N	49.1	29.5	21.4	41.5	3.0	3.0	5.8	8.4	9.9
4-N	56.3	25.3	18.4	40.6	4.0	3.0	5.8	10.3	10.9
5-N	61.6	22.2	16.2	39.9	5.0	3.0	5.8	13.6	12.7
6-N	65.9	19.8	14.3	39.4	6.0	3.0	5.8	17.2	15.0
1-W	65.5	29.5	5.0	47.2	4.0	3.0	4.8	11.5	12.5
2-W	56.3	25.3	18.4	40.6	4.0	3.0	5.8	10.3	11.0
3-W	49.3	22.2	28.5	35.5	4.0	3.0	6.8	11.9	11.3
4-W	43.9	19.8	36.3	31.7	4.0	3.0	7.8	11.4	10.2
5-W	39.6	17.8	42.6	28.5	4.0	3.0	8.8	11.1	10.3
6-W	36.0	16.2	47.8	25.9	4.0	3.0	9.8	9.4	10.2
1-A	61.4	18.5	20.1	36.7	4.0	2.0	5.8	12.5	11.1
2-A	56.3	25.3	18.4	40.6	4.0	3.0	5.8	10.5	10.5
3-A	51.9	31.1	17.0	43.8	4.0	4.0	5.8	12.4	9.7
4-A	48.1	36.1	15.8	46.6	4.0	5.0	5.8	14.0	11.0

Microscopic study of crystals taken from the solution phase showed the characteristic dendrite form of ammonium chloride and long barlike crystals assumed to be potassium nitrate. The actual composition of the individual crystals obtained was not determined; they could have been pure salts, solid solutions of the ammonium and potassium salts, or mixtures of all three. In any event, the shape of the crystals appeared to be such that their formation would have a detrimental effect upon the fertilizer.

Variation in Solution Phase During Cooling

Actual chemical analysis of the solution phase was not obtained for the various temperatures of crystallization. However, from the weights and analysis of the 6° filtrate and the 6°, 15°, and 25° crystals shown in Table V, A, it was possible to calculate the analysis of the solution phase at the various temperatures. Results of the calculations are shown in Table V, B, where it is seen that the main loss of material from solution was contributed by the ammonia and nitrate nitrogen, potassium oxide, and chloride ions. Further calculations indicated the effect of cooling upon the ion content of the 35° solution phase. The results of these calculations are shown in Table V, C, and allow speculations as to the types of salts which crystallize from solution upon cooling.

Types of Salts Crystallizing From Solution

Assuming ammonium nitrate as the crystallized material, and using nitrate nitrogen as a basis for calculation, the 35° solution phase would contain 27.2% ammonium nitrate, or its equivalent. At 6°, the original solution would have lost 12.4% of ammonium nitrate, indicating that 45% of the ammonium nitrate in solution would have been removed by crystalliza-

Table V. Partial Crystallization from Solution Phase of a 3-12-12 Fertilizer

A. Analysis of Fractions

	Filtrate	Crystals	Crystals	Crystals
Temp., ° C.	6	6	15	25
Wt. % of original solution	78.5	5.5	6.3	9.7
NH_3 nitrogen, %	5.78	8.86	7.98	7.37
NO_3 nitrogen, %	3.31	9.28	9.35	10.86
K_2O, %	7.99	26.91	30.57	33.14
Na_2O, %	1.71	1.43	...	...
Cl, %	11.51	19.67	18.86	17.74
P_2O_5, %	2.45	6.56	0.42	0.37
SO_3, %	2.00	...	...	...

B. Calculated Analyses of Solution Phase at 35°, 25°, and 15° C.

	35	25	15	6[a]
Temp., ° C.				
NH_3 nitrogen, %	6.25	6.13	5.99	5.78
NO_3 nitrogen, %	4.76	4.10	3.70	3.31
K_2O, %	12.89	10.71	9.23	7.99
Na_2O, %	1.42	1.57	1.69	1.71
Cl, %	13.03	12.52	12.05	11.51
P_2O_5, %	2.35	2.56	2.71	2.45
SO_3, %	1.57	1.74	1.87	2.00

C.[b] Calculated Materials Still in Solution After Cooling Solution Phase to Indicated Temperature

% of original soln. phase ppt.	0.0	9.7	16.0	21.5
NH_3 nitrogen, %	6.25	5.53	5.03	4.54
NO_3 nitrogen, %	4.76	3.70	3.11	2.60
K_2O, %	12.89	9.67	7.75	6.27
Na_2O, %	1.42	1.42	1.42	1.34
Cl, %	13.03	11.30	10.12	9.04
P_2O_5, %	2.35	2.31	2.28	1.92
SO_3, %	1.57	1.57	1.57	1.57

[a] Actual analysis.
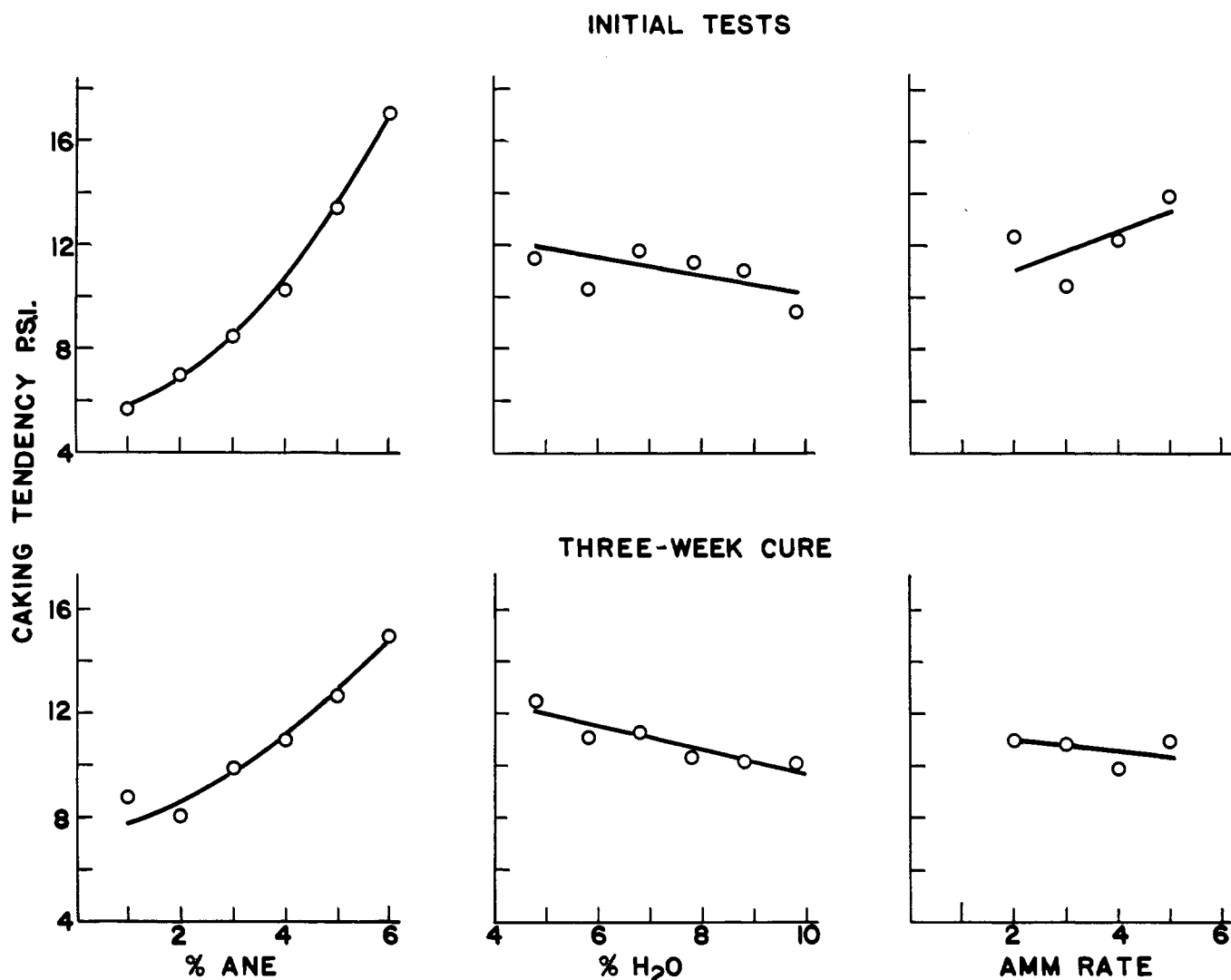[b] Basis, 100 parts of solution phase from 35° extraction.

Figure 8. Effect of varying component concentration on caking tendency of mixed fertilizer

tion. Using ammonia nitrogen for the same calculation, the original solution would contain 35.7% ammonium nitrate, and would have lost 9.8% of its weight, or 36.0% of the ammonium nitrate in solution would have been removed by crystallization. The difference between the two calculations indicated that a substance containing nitrate nitrogen, other than ammonia nitrate, was crystallized. Janecke (7) pointed out that ammonium nitrate and potassium chloride would not coexist in solution, but would double decompose to form ammonium chloride and potassium nitrate, and the addition of potassium nitrate to a saturated solution of ammonium chloride actually increased the solubility of ammonium chloride.

Janecke also indicated that solid phase in equilibrium with this solution would consist of mixed crystals of potassium nitrate and ammonium chloride. In the case of 3–12–12 fertilizer, this solution would undoubtedly be in equilibrium with potassium chloride, and possibly with a potassium chloride–ammonium chloride solid solution. In any event, if it is assumed that metathesis took

place, calculation of weight losses from the solution phase, using the ammonia nitrogen as a basis for ammonium chloride and nitrate nitrogen for potassium nitrate, showed that cooling the solution from 35° to 6° would deposit 15.6% of the solution weight as potassium nitrate and 6.5% as ammonium chloride for a total loss of 22.1%. This value agreed fairly well with the 21.5% shown in Table V, C, and gave good ion balance.

Other ions would increase the calculated value to approximately 23%. Although ammonium nitrate, as such, did not appear to be present in the solution phase, it seemed definitely to be contributory to the types and amount of salts that were in solution and would, therefore, be a controlling factor in the caking of mixed goods containing high potash. This further substantiated the results obtained previously (Table I) and led to the establishment of a term known as the ammonium nitrate equivalent (ANE) of a mixed goods.

The term ANE was arbitrarily defined as "the apparent weight per cent of ammonium nitrate in a finished fertilizer."

The effective ammonium nitrate equivalent of fertilizer, from the standpoint of reversible caking, would be that portion which was in the solution phase. The 3–12–12 used in these experiments had an ammonium nitrate equivalent of 4.2% and, based on the nitrate nitrogen, all of the ammonium nitrate equivalent was in solution at 35° C. At 6°, however, the effective ammonium nitrate equivalent was only 0.9%.

Ion summation of the 35° solution phase showed the solids content to be 59%, whereas actual drying at 40° gave a value of 62%. If, to round off figures, it is assumed that solids content is 60% and that the fertilizer contained 6% free moisture, then the solution phase would consist of approximately 15% the total weight of the fertilizer and would deposit 3.2% of the fertilizer weight upon cooling at 6°. This same grade of fertilizer, having an ammonium nitrate equivalent factor of 1%, would undoubtedly have less solution phase, deposit fewer, if any, objectionable type crystals and have much lower caking tendency.

Effect of Variations In Ammonium Nitrate Equivalent, Free Water, And Ammoniation Rate The validity of the above theory was checked by a series of experiments wherein fertilizers were manufactured with varying ammonium nitrate equivalent contents, while the phosphorus and potash were held constant at 12 and 12. To clarify the problem further, free water and ammoniation rate were likewise varied in separate series. Results of these tests are shown in Table VI and plotted in Figure 8.

Each group of tests contained a common mix (4-N, 2-W, 2-A), and it was interesting to note the good checks in caking tendencies among these similar mixes. Although there was some variation from the anticipated curve (Table I), after 3 weeks' curing the trend plainly indicated ammonium nitrate equivalent to be a substantial contributor to caking, water content to be almost negligible with a slight downward trend, and ammoniation rate to be detrimental initially with no marked effect after 3 weeks' cure. The last noted phenomenon is in line with other work which indicated greater disturbance of the water of hydration of calcium phosphates with increased ammoniation rate.

These conclusions are valid only so long as no change is made in the physical characteristics or normal water content of the superphosphate, as these appear to be important factors in the caking of mixed goods.

Summary

The experimental information indicated that caking in high potash fertilizer could be controlled to some degree by control of the ammonium nitrate equivalent. Increasing the ratio of ammonia to ammonium nitrate in ammoniating solutions improved the conditioning effect. Above a certain moisture content, "free" water did not contribute to caking, and the effect of ammoniation rate was transitory. Metathesis played an important part in caking.

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SWEET POTATOES

Physiological and Biochemical Effects of Maleic Hydrazide on Pre- and Postharvest Behavior

BOYCE D. EZELL and MARGUERITE S. WILCOX

Biological Sciences Branch, Agricultural Marketing Service, U. S. Department of Agriculture, Beltsville, Md.

This work is a part of a general study on the storage behavior of sweet potatoes, carried on during several seasons. Preharvest foliar sprays of maleic hydrazide have been used with other root crops to reduce sprouting and prolong the commercial storage life. This work was to determine the effect of similar sprays on the pre- and postharvest behavior of sweet potatoes. Preharvest foliar sprays had little if any visible effect on the foliage and no significant effect on the accumulation of carotenoid pigments in the roots during the interval between treatment and harvest. However, the treatment caused surface pitting of the harvested roots and seriously interfered with the normal synthesis of provitamin A (carotene) and other carotenoid pigments during storage.

USE OF PREHARVEST FOLIAR SPRAYS of maleic hydrazide to inhibit sprout formation and prolong the storage life of several bulb, tuber, and root crops has been reported (*4, 8, 9*).

Intact onion plants sprayed 2 weeks before harvest with 2500 p.p.m. of maleic hydrazide showed no sprouting after 1 month at 35° F. plus 4 months at 55° F. (*9*). Flavor, color, and odor were apparently not affected. The treated bulbs remained dormant for 8 weeks when planted in the greenhouse while nontreated bulbs grew normally and produced large vegetative tops.