Development of an Accelerated Caking Test for Urea

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A new accelerated caking test for use with urea has been developed and used in screening potential conditioning agents. The urea sample is held under pressure in a perforated cylindrical mold while temperature and relative humidity are cycled, to cause alternate absorption and loss of moisture. The degree of caking was measured by a penetrometer and was expressed as a caking index: hardness of unconditioned urea divided by the hardness of conditioned urea. Tests of $3\frac{1}{2}$ days duration were satisfactorily correlated with 1- and 3-month bag storage tests run at two different urea producing plants.

The problem of caking of fertilizers has existed since the beginning of manufacture of synthetic fertilizers. Many fertilizer components, or their reaction products with other components, are hygroscopic. Silverberg *et al.* (1958) demonstrated that caking is promoted by movement of moisture, which leads to formation of crystal bridges between particles. With the advent of high analysis fertilizers, particularly ammonium nitrate, urea, and mixtures containing these materials as components, problems of caking have multiplied.

In the investigation of factors responsible for caking, and in development of conditioners to reduce caking, a caking test for evaluation is needed.

The traditional caking test is the stacked bag test, in which the test sample, in a standard fertilizer bag, is placed at the bottom of a stack of bagged goods 15 to 20 bags high. In some tests the bagged goods are replaced by an equivalent weight. The extent of caking of the sample is evaluated after 1 to 3 months. Evaluation is usually qualitative, by inspection, or semiquantitative, by screening the material and weighing lumps, or by counting the number of times the bag must be dropped to break up the lumps.

This type of test is a "real" test, in that it shows what would happen in an actual storage situation. Although it is too cumbersome and time consuming to be used in screening potential conditioners, it is the ultimate test with which any accelerated test must be correlated.

Modified bag storage tests using smaller amounts of material have been reported (Bridger *et al.*, 1966; Iannicelli, 1966; Pierce, 1966; Rosenblatt, 1966). Although these tests reduce the amount of material needed, they do not materially reduce the length of time required for a test.

Numerous accelerated caking tests have been developed in the past 30 years. A pressure bomb test (Adams and Ross, 1941) was applied to several types of fertilizer materials in an extensive investigation of the variables influencing test results. This test has been used (Hardesty and Kumagai, 1952; Kumagai and Hardesty, 1956) in an investigation of the effectiveness of conditioners on granular mixed goods. In this test the hardness of the cake formed in the bomb, by mechanical pressure, was measured by crushing it in a hydraulic press.

Another test applied to mixed goods (Whynes and Dee, 1957) formed a cake by air pressure on a sample sealed in a rubber sleeve; caking was evaluated by crushing the sample, still in the sleeve, with a hydraulic press.

Numerous tests have been developed specifically for ammonium nitrate (Iannicelli, 1966; Varma *et al.*, 1959; Whetstone, 1949; Wilson *et al.*, 1962). Whetstone and Varma allowed ammonium nitrate to absorb water and then to dry, and measured the hardness of the cake by crushing or with a penetrometer. Wilson and Iannicelli caused caking of ammonium nitrate by repeated cycling through the 32° C transition, while maintaining the material under pressure. Both measured the hardness of the cake by crushing with a hydraulic press.

Other tests of a general nature have been described (Mischel, 1967; Parks and Granok, 1967). No test, however, has been designed specifically for evaluating caking of urea, and none of the tests described above is completely satisfactory for such use. A major disadvantage of the Adams and Ross pressure bomb test is the problem of sealing the joints of the bomb to prevent passage of water vapor. Furthermore, this test cakes urea only when the water content is relatively high.

Through use of a rubber sleeve to form cakes, the Whynes and Dee test tends to give cakes of variable dimensions, a disadvantage when the strength of the cake is to be measured by crushing.

Tests developed for ammonium nitrate, which depend on repeated cycling through the 32° C transition point to produce caking, do not work with urea, which has no such transitions.

The work described here was undertaken to develop an accelerated caking test, specifically for use with urea, the results of which could be correlated with stacked bag tests. The test which has been developed depends upon cycling the test sample, under pressure in a perforated mold, through high temperature–low humidity and low temperature–high humidity conditions, simulating day and night summer atmospheres.

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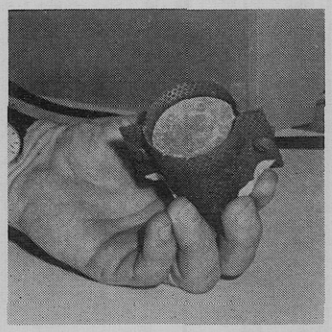

Figure 1. Test mold

EXPERIMENTAL

Materials Used. Unconditioned fertilizer urea prills (−8 + 14 mesh) and feed-grade microprilled urea (−20 + 60 mesh) were used in this work. The microprills were preferred because their small particle size accentuated the tendency to cake. Size distribution between the limits was uncontrolled. Urea from two sources was used: a Toyo Koatsu process, crystal remelt plant, and a Chemico process solution prilling plant. In general the latter contained more water and biuret.

Clay used in conditioning was Barnet kaolin, produced by United-Sierra Division of Cyprus Industries. Various other conditioners were included in screening tests.

Molds in which urea cakes were formed were split cylinder, 2 in. in diameter and 2 in. high, made of 16-gauge perforated metal with $^1/_{16}$ in. perforations on $^1/_8$ in. centers (triangular pitch). On either end of the cylinder, to retain the urea, was placed a disk of 0.004 in. polyethylene film and a disk of $^1/_{16}$ in. aluminum sheet 1-$^7/_8$ in. in diameter (Figure 1).

The test rack, in which the molds were placed for application of pressure, comprised an inverted "T" made of $^3/_8$ in. aluminum plate. The test molds rested on the base formed by the cross bar of the inverted "T," while on either side of the vertical perpendicular plate were bolted three air cylinders (Alkon Products, Wayne, N.J., Series D Model 24, 6″ stroke). Each test rack could therefore accept six molds.

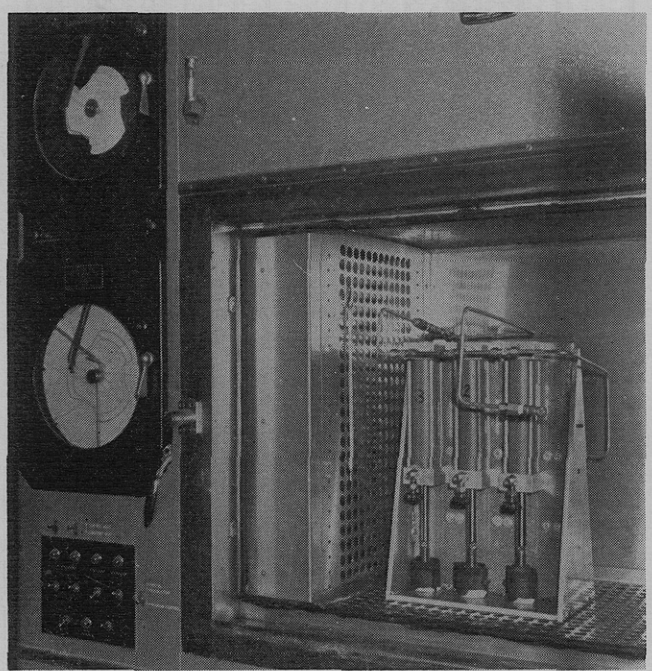

Figure 2. Test rack with molds in climate-lab®

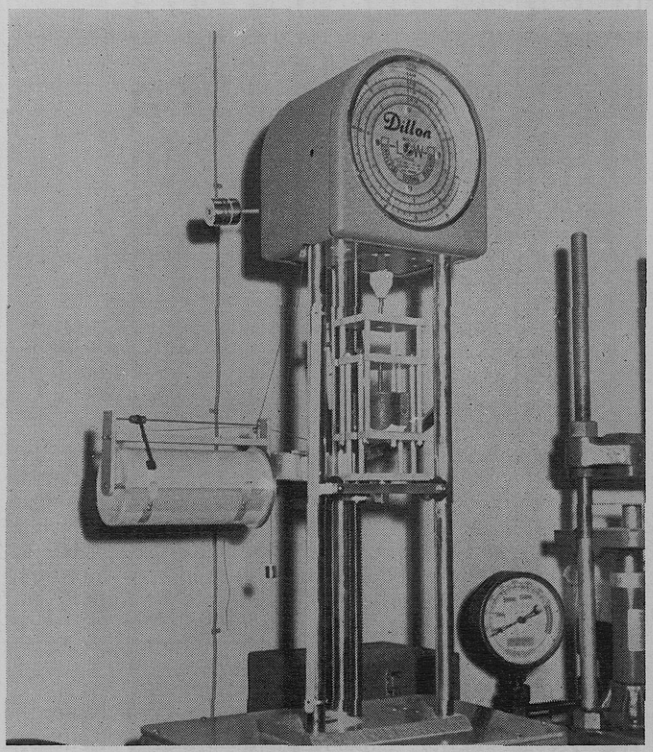

Figure 3. Caked sample in compression tester

Low pressure air was supplied to the cylinders through a Moore Nullmatic regulator (Model 41-30). Pressure was measured by a test gauge (Figure 2).

The test racks were set inside an American Instrument Climate-Lab, Model 4-5500. Cams for the cycle timer of this instrument were cut to give the desired time-temperature-relative humidity.

Hardness of the urea cakes was measured with a Dillon Multi Low Range Tester, with a compression cage. The upper platen of the cage was drilled and tapped to accept a $^1/_4$-20 NC stainless steel machine screw, the end of which was turned to a 60° cone (Figure 3).

Solid conditioners were applied to urea experimentally with a Patterson-Kelly laboratory model Twin-Shell blender. Liquids were applied by spraying with a DeVilbiss atomizer onto a rolling bed of urea prills, in a pill-coater or similar device (Figure 4).

PROCEDURES

Formation of Cakes. The bottom of the test mold was covered with a piece of paper, held on with masking tape. An aluminum disk and then a polyethylene disk were put in the bottom of the mold, 50 g of urea prills were added, and finally another polyethylene and an aluminum disk were placed on top of the urea. The assembly was placed in the

Figure 4. Spraying conditioner on urea

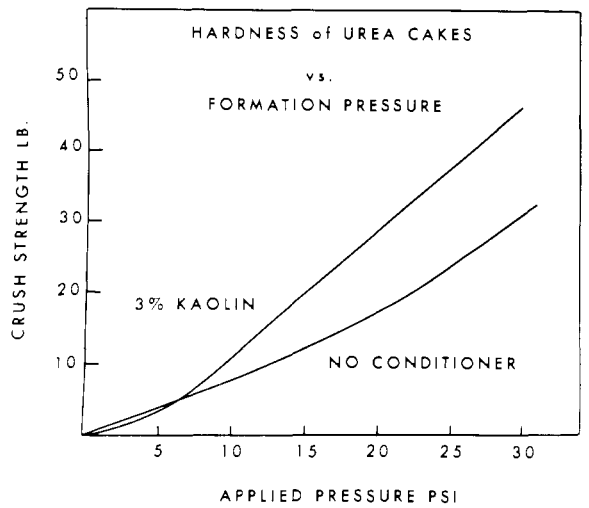

Figure 5. Effect of pressure on cake hardness

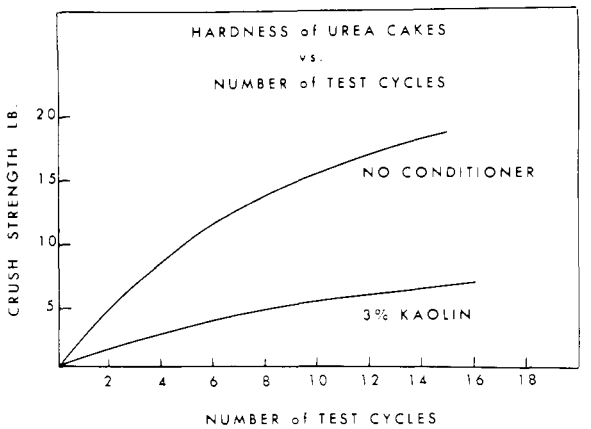

Figure 6. Effect of test duration at low pressure

test rack directly under the air cylinder. The test rack was placed in the Climate-Lab, and the desired air pressure applied under the desired conditions of temperature and humidity.

In the final development of the test, 12 samples were tested simultaneously. The position of the samples in the test rack was chosen at random. In general each set of samples was tested three times (further replication did not improve precision) and the average value of cake hardness was calculated. In a series of tests the average standard deviation was ±10–20%, satisfactory for our purposes.

Measurement of Cake Hardness. In early work, cake hardness was measured by makeshift methods because no equipment for more precise measurement was available. Meaningful data were obtained only with purchase of a Dillon Multi Low Range Test machine, with which to measure compressive strength.

Initially cake hardness was measured by applying force to the flat ends of cylindrical cakes, removed from the molds. The cake faces were not adequately parallel to prevent random shear, and results were erratic. Pressure was then applied to the sides of the cylindrical cakes. These cakes broke cleanly along the plane through the axis of the cylinder, parallel to the applied force. While results were somewhat less erratic, the number of prill-prill bonds broken was too small and not adequately random.

The test finally adopted was a variation of the penetrometer test. A $^1/_4$-20 stainless steel machine screw, with a 60° conical end, was installed in the compression cage of the tester, to bear upon the top of the cake.

The test cake, still in its mold, was placed in the cage and the force needed to rupture the cake was measured. The cake ruptured downward, from the point of the spike, in roughly a 60° cone. Most of the prill-prill bonds within this cone of material were broken.

DISCUSSION

Based on trials of a number of previously reported caking tests, we expected to be able to accelerate caking of urea by holding it under high pressure at high temperature. We held fertilizer prills, in our test molds, under varying pressures and temperatures for 18 hr, at relative humidity equal to the critical for urea at the temperature. After 18 hr we reduced the relative humidity to 25% for 2 hr, then released the pressure and desiccated the test sample at room temperature for 2 hr. After a few screening tests with unconditioned prills, we settled on 130° F −55% RH, and 22.9 psi as the holding conditions. When these conditions were tried for fertilizer prills conditioned with kaolin, however, the cake formed were harder than those from unconditioned urea. Figure 5 shows a plot of cake hardness *vs.* pressure for unconditioned and kaolin-conditioned fertilizer prills.

Since elevated pressure did not simulate real performance, we decided to try a cycle of temperature and humidity to simulate diurnal variation, using a low pressure about equivalent to a 15-bag stack. Figure 6 shows the results obtained under 3 psi with a cycle of 4 hr at 104° F −53% RH and 2 hr at 68° F −81% RH. Figure 7 shows the wet and dry bulb temperature chart for a 24-hr period.

Based on the results shown in Figure 6, we standardized on a holding time of 11 $^1/_2$ cycles; that is, we started and ended the test at high temperature–low humidity conditions. The test thus took 3 $^1/_2$ days. A series of tests run on unconditioned and conditioned fertilizer grade urea prills showed the standard deviation of the test to be about 20% of the absolute value of cake hardness. Similar tests run on microprills likewise indicated the standard deviation to be about 20%.

To validate the test we set up stacked-bag tests at two producing plants: one at Niagara Falls, Canada, and the second near New Orleans, La. Individual batches of experimentally conditioned urea microprills were made at each site, using freshly-produced prills. Bags were stacked 15 high, with the test bags at the bottom. The condition of the samples was evaluated by plant personnel after 1 month and after 3 months by carefully slitting the bags, screening the contents on a $^1/_2$-in. screen, and reporting the percentage of the material caked. Attempts were also made to evaluate the hardness of the lumped urea.

At the time the batches were made, a portion of each was shipped to Princeton and evaluated by the accelerated test. Samples of unconditioned urea were tested at the same time. Cake hardness for the unconditioned urea from the two plants was not the same numerically. It is possible that this variation is caused by different particle-size distribution, or by difference in initial water or biuret content. To put conditioner tests on the same basis, results of the test were calculated as a caking index by dividing the hardness of the unconditioned urea cake by the hardness of the conditioned cake.

Table I shows the caking index for five conditioner systems,

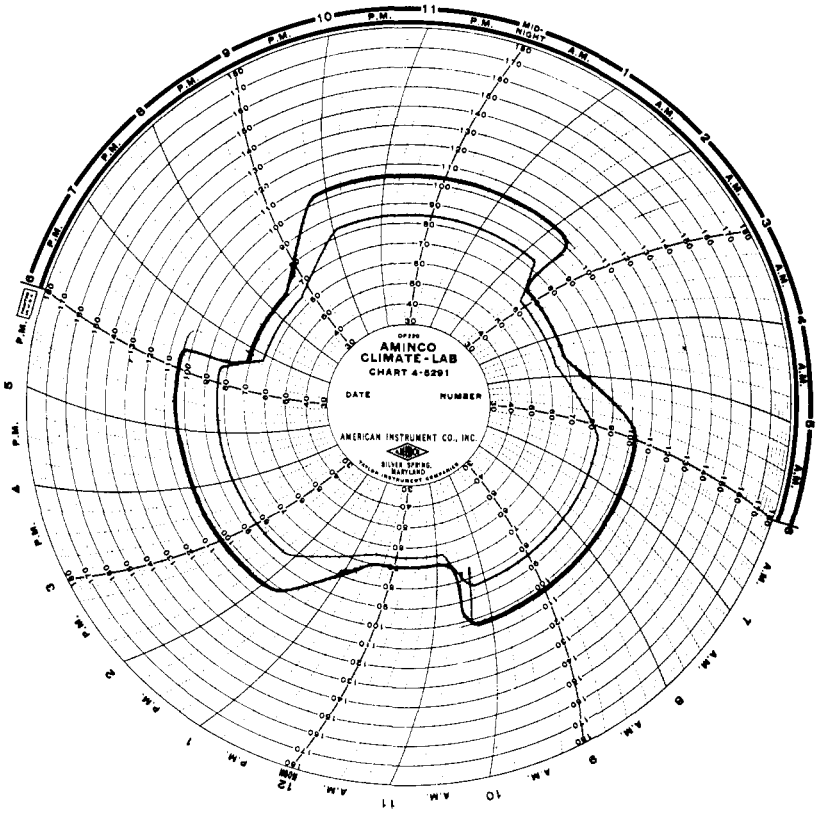

Figure 7. Chart from climate-lab®

Table I. Comparison of Accelerated Test with Bag Storage Test

Conditioner System	% Lumps 3 Mo[a]		Caking Index	
	Plant A	Plant B	Plant A	Plant B
1	6	16	36	12.5
2	15	7	22	10.2
3	100	100	1	1
4	36	39	18	15
5	36	79	2.1	0.8

[a] All lumps reported medium hardness by both plants, except for System 1, Plant A.

as prepared at the two plants. For comparison the percentage of lumps after 3-months storage is also shown. Although agreement between indices for the two plants is not perfect, the index in general follows the percent lumps. Data are plotted in Figure 8.

The scatter of data in Figure 8 is due, at least to some extent, to the fact that screening of urea from a bag storage test to determine percentage of lumps gives only semiquantitative results: the better the conditioner, the softer the lumps and the more likely they are to be broken in screening.

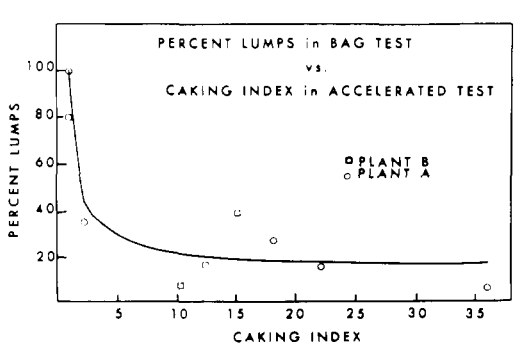

Figure 8. Correlation of lumps with caking index

Mirroring, as they do, the differences in preparation at two widely separated plants, by different personnel, on different substrates; storage under widely different climatic conditions; and evaluation by different operators, we feel that the data are adequate verification of the test. In practice, materials showing poor performance in the accelerated test have likewise shown poor performance in the stacked-bag test. However, good performers in the accelerated test do not always perform well in the bag test.

This test is now in use for routine screening of proposed conditioner systems for urea.

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