THE EFFECT OF LOW CONCENTRATIONS OF ORGANIC MATERIALS ON THE PROPERTIES OF AMMONIUM NITRATE

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Armour Industrial Chemical Co. retained Arthur D. Little, Inc., to investigate the properties of ammonium nitrate coated with the organic anti-caking agents developed by Armour. It has been found that these are effective anti-caking agents with concentrations at least an order of magnitude lower than previously used organic materials.

We studied two properties of ammonium nitrate that we felt might be affected by a surface coating of small amounts of organic material: explosive sensitivity and thermal stability. In order to evaluate these properties over a range of concentration, we prepared and evaluated samples containing up to 20 times the recommended concentration of anti-caking agent.

Sample preparation

Test samples of ammonium nitrate were batch-coated at elevated temperatures with the anti-caking agents. A soft, porous ammonium nitrate prill taken from the product stream of the Crystal City, Missouri, plant of Armour Agricultural Chemical Co. in 300-pound lots was used for our tests. The prills used were at a temperature of 150° to 170° F and held about 5% fines and 0.5% to 1.0% H_2O.

The prills were coated in a 1-ton cement mixer by spraying with a measured amount of the anti-caking agent as the sample was mixed. The total mixing time was 10 minutes.

The three coating agents used in these tests were Armoflo 65, 66, and 21, with melting points of 41° F, 86° F, and 115° F respectively. They are soluble in oil, insoluble in water, and cationic in nature.

Explosive sensitivity

Pure ammonium nitrate can be exploded; therefore, to determine the effects of organic coatings, it is necessary to measure differences in explosive sensitivity. For transportation according to I.C.C. regulations, an explosive is defined as a material which is initiated by a No. 8 cap. For our purposes, this sensitivity test is unsatisfactory, since a No. 8 cap will not initiate AN prills and low concentrations of organic coating.

The study of initiation sensitivity in systems of a scale where steady state detonation is possible would be meaningful. However, such tests would be awkward and expensive since the minimum diameter for unconfined detonation is about 12 inches with pure AN prills.

Primacord wrap test

In our work on the development of a safe and inexpensive mining explosive, a simple but accurate sensitivity test was developed for ammonium nitrate-fuel mixtures.[1] Even a small quantity of high explosive in contact with ammonium nitrate will initiate a detonation which will propagate for a short distance, the distance depending on the strength of the initiation and the sensitivity of the sample.

Conversely, the level of initiation required to make a detonation propagate a fixed distance can be used as a measure of explosive sensitivity.

Our test configuration is shown in Figure 1. A 1-pint paper ice-cream container is filled with sample material. The variable-strength initiating charge is wrapped around the top of the container and fired. Since it is not possible to determine whether the unstable detonation propagated over a fixed distance sim-

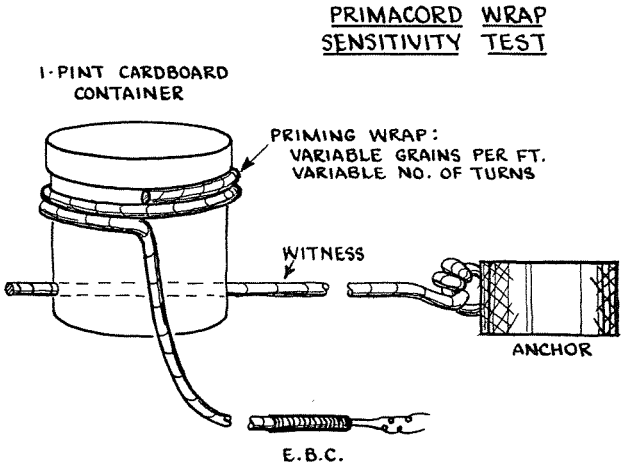

Figure 1. Test configuration for Primacord wrap test.

ply by observing the noise and flash from the test, the detonation of an indicator explosive threaded through the base of the sample is used as an indication of propagation for a given fixed distance.

We use Primacord for both initiation of the sample and detection of propagation. Primacord consists of a core of PETN with a protective plastic jacket, resembling plastic clothesline. It is available with a range of core loadings between 30 and 400 grains per foot. The Primacord initiation strength is varied by changing the loading and number of turns used. We express our results in terms of grains of Primacord per foot of circumference, that is, the product of the number of turns and the core loadings in grains per foot.

We determine a 50% detonation level for each sample, that is, the initiation that will detonate the indicator Primacord 50% of the time. The 50% detonation level is measured in work on explosive sensitivity because it gives, with the least number of tests, a number characteristic of a sample.

An experimental technique known as the "up-and-down test"[2] is commonly used to determine the 50% detonation level. With this test a level of initiation is selected and is followed by a stronger level of initiation if the first test failed, or a weaker level if it succeeded. The procedure is continued until an examination of the test results indicates that a 50% detonation point has been determined with sufficient precision. The evaluation of results is simplified by the use of normal probability graph paper. Both the 50% detonation point and its standard deviation can be read from the best straight line through the plotted points.

Table I gives a relative scale of the sensitivity of various materials in the Primacord wrap test. The values below 50 grains per foot were measured indirectly by placing a shock-absorbing barrier between the Primacord wrap and the sample and measuring its attenuating factor with a previously tested sample.

TABLE I. RELATIVE MATERIAL SENSITIVITIES IN THE PRIMACORD WRAP TEST

Material	Grains per foot of circumference
AN Prills	500
AN Fines	300
AN Prills + 6% Oil	200
AN Prills + 2% Oil	100
Crushed AN Prills + 6% Oil	70
50% Sensitive to No. 8 Cap	50
Hammermilled AN Prills + 6% Oil	40
Crushed AN Prills + 2% Oil	35
Hammermilled, Specially Fueled, AN	20
60% Ammonia Dynamite	4

Results

Figure 2 summarizes the results of our experiments.

During the course of our test program we noted a lack of uniformity in both the physical appearance and explosive sensitivity of our samples. The effects observed could be related to the presence of fines and to a non-uniform distribution of anti-caking agent. As would be expected, the lack of uniformity increased with the melting point of the agent and with the amount added.

We blended some samples in a "V" cone blender but found that the prills were broken up by this treatment. We also screened a number of samples to remove fines before testing.

Another effective anti-caking material is the combination of an Armoflo and clay. In this application clay acts both as a desensitizing and anti-caking agent.

Curve 1 gives the results of a 1:20 mixture of Armoflo 65 and clay. Both samples (1/2 pound per ton Armoflo 65, 10 pounds per ton clay; and 1 pound per ton Armoflo 65, 20 pounds per ton clay) were blended and screened (+20 mesh) before testing. The uncoated sample was prepared in a similar fashion.

Curve 2 shows the effect of different application rates of Armoflo 21 in samples that were blended and screened before testing.

Curve 3 shows results obtained with samples of Armoflo 21 that were tested without screening.

Curve 4 shows the effect of different application rates of both Armoflo 65 and 66 on sensitivity.

Discussion of results

The particle size of an ammonium nitrate sample appears to have a strong effect on its measurable explosive sensitivity. Our tests, performed on uncoated prills, gave 50% detonation levels of 500, 450, 350, and 300 grains per foot for screened prills, unscreened prills, hammermilled prills, and fines, respectively.

The effect of organic coatings on the 0.05% does not seem to be significant since the effects observed are on the same scale as those caused by particle size change in uncoated nitrate.

Armoflo 21 appears to have a different and smaller effect on explosive sensitivity than the lower-melting Armoflos.

The application of Armoflo 21 at a rate of 0.03% will produce an anti-caking performance equivalent to that of a 0.05% application rate of the more liquid Armoflos. The effect on explosive sensitivity caused by use at this application rate is hardly detectable with the Primacord wrap test.

Absorbent and inert material such as clay on the surface of prills reduces the effect of organic material on explosive sensitivities while improving anti-caking action. Curve 1 of Figure 2 shows the sensitivity of the combination of Armoflo 65 and clay.

Although it does not appear to be significant in terms of shipping and handling, the presence of fines distributed in a sample of prills increases its explosive sensitivity. This can be seen by comparison of Curves 2 and 3 of Figure 2.

Self-heating

During the investigation following the Texas City explosion, Arthur D. Little, Inc., developed a test to determine the effect of organic materials on the thermal stability of ammonium nitrate.[3] This test simulates the condition in the center of a large pile of ammonium nitrate.

A flask containing about 30 pounds of sample is placed in the center of a well-insulated container. The sample is heated electrically with a coil of resistance wire wound on the outside of the flask. Thermocouples at the surface and center of the sample measure the temperature differential across the sample and can detect a temperature rise at the center, and thus self-heating. Gases collected outside the container through a glass tube sealed into the top of the flask indicate decomposition. Thus, the onset of significant decomposition is shown in two ways—by the evolution of gases and by a temperature differential in the sample.

We tested the following samples: uncoated prills and prills with 5 and 10 pounds per ton of Armoflo 21.

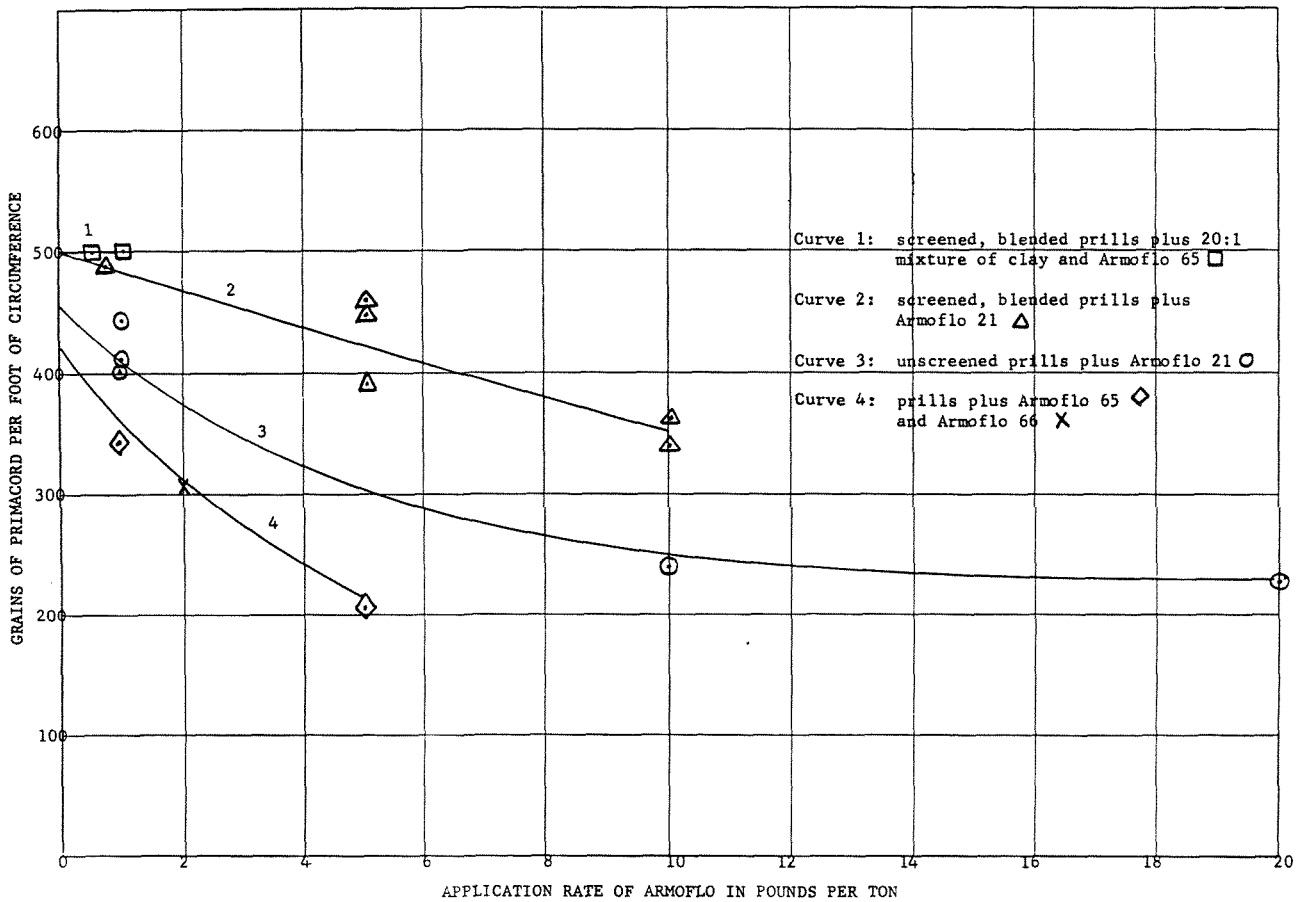

Figure 2. Explosive sensitivity of Armoflo coated AN prills.

With this test we were unable to detect any difference in behavior between these samples during heating. In no case was there indication of gas evolution or temperature differential prior to sustained decomposition beginning at 180°C. Rapid decomposition or "fume-off" raised the sample temperature to the self-limiting temperature of 290°C in each case without flame in the decomposition products.

We made a comparison between uncoated prills and prills coated with 5 and 10 pounds per ton of Armoflo 21 when heated in a beaker on a hot plate. The only observable difference noted was the presence in the coated sample of small black specks on the surface of the prills after melting, also a fatty odor at 130 C during heating. Samples tested in this way did not develop flames during fume-off.

Literature cited

(1). Brinkley, Sykes, and Meyers, 5th Symposium on Mining Research, Bulletin of the University of Missouri School of Mines, Technical Series No. 98, 1960.
(2). Statistics Manual, Crow, Davis, and Maxfield, Dover Publications, 1960, page 93.
(3). Arthur D. Little, Inc., Report to Commandant, U.S. Coast Guard Hq., Contract No. Teg 38528 (CG20-003A), 1952.

Questions and answers

JOHN PARKS—Monsanto Chemical Co. Do you have data on the precision of the sensitivity levels and the significant differences between them?

SYKES—Table II (reproduced herewith) gives data obtained for various types of uncoated prills.

TABLE II

Uncoated A N

No.	Treatment	50% detonations	Standard Deviation	Number of Tests
1	As Received (1)	420	30	19
2	As Received (II)	450	50	75
3	Screened (+ 20 M)	400	30	24
4	Screened (- 20 M)	300	40	26
5	Hammermilled	350	20	10

The standard deviation of the "As Received" prills is highest, apparently due to the random distribution of fines. The hammermilled product is probably the most uniform and as a result shows the lowest standard deviation.

PARKS—Does this data indicate that there is a significant difference between the "As Received" AN and the hammermilled AN?

SYKES—Using the "t" test to test for difference, we first calculate entries No. 1 and No. 5 in Table II. We obtain an estimate for t of 6 to 7. This result indicates high confidence (>.999) that the two samples are different. As a further example, the value of "t" for the difference between entries No. 1 and No. 2 in the Table is about 2.5. Then the confidence level for significant difference between samples is 99 + % indicating that our test can detect different sensitivity levels due to fines in a sample of prills.

PARKS—Referring to your experiment for the determination of the thermal stability of ammonium nitrate, I think you will agree that the experiment described in my paper is not the same thing.

SYKES—I think that our thermal stability test is more severe than the conditions used for your calculations since we simulate an infinite mass by raising the outside temperature of our container slowly enough for the inside temperature to follow closely, while in your calculations the outside temperature is set at a fixed value.

PARKS—Referring to the slide accompanying my talk showing the temperature rise as a function of time in the center of a mass of ammonium nitrate, you suggest that the temperature rise would not continue to 800°C as shown on my curve.

SYKES—That is correct. Since you did not include the temperature-limiting process as such, the computer did not have enough information to calculate a temperature-time curve on the proper basis.

PARKS—In any event, under our conditions the time required to reach a temperature over 200°C would still be about 10 days.

SYKES—Yes.

PARKS—I would like to clear up a possibility of confusion that arose in my talk yesterday. The size of the critical masses that I computed for pure ammonium nitrate were supported by the values computed by Arthur D. Little, Inc., in the report to the U. S. Coast Guard and were on the order of 10^{15} tons when stored under warehouse or ship conditions at ambient temperature. In the experiment I proposed, on the other hand, I used rate values for a nitro-carbo-nitrate, an entirely different material from pure AN. I chose a nitro-carbo-nitrate to make the critical mass required as small as possible. We do find that the critical mass at 165°C is less than that of pure ammonium nitrate at the same temperature.

Q. In coating your prills with Armoflo 21 and kaolin clay, were the two materials mixed before application to the prills, or were all the materials mixed as a common stream?

SCOTT CHANDLER—Armour Chemical Co. The clay and Armoflo were mixed prior to the prill coating process.

Q. Have you noted any correlation between prill density and sensitivity?

SYKES—I would expect such an effect to exist, but we have not done any experimental work to explore it.

Q. Quoting from memory, I recall an article by Professor Melvin Cook that about 0.3% of Petroag applied to prills made them sensitive to a No. 8 cap. How would you relate this to your results?

SYKES—When talking about ammonium nitrate or nitro-carbo-nitrate the term "cap sensitivity" must be carefully defined. Under the right conditions even pure ammonium nitrate is cap sensitive. However, if you were to detonate a No. 8 cap in a bag of Petroag coated prills, or even prills and 6% fuel oil, nothing would happen. On the other hand, prills and 6% fuel oil blown into a 2 inch borehole under pressure are well known to be No. 8 cap sensitive. It is true that for any ammonium nitrate, pure or fueled, some material near a cap would decompose. The amount decomposed would depend on the physical state of the material and the amount of fuel present.

In a bag, unconfined, the amount that decomposed would be insufficient to initiate a detonation into the rest of the nitrate.