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Effects of Temperature and Aging on Emulsified Liquid Oxidizing Solutions Containing More Than 70 Percent Ammonium Nitrate Solutions with More Than 0.4 Percent Combustible Substances

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The shock and thermal sensitivity of three different emulsified liquid oxidizing solutions was examined using tests selected from the United Nations "Manual of Tests and Criteria." The solutions are used as raw materials in the manufacture of explosive blasting agents and were tested in the "as received" condition at ambient and elevated temperatures (150°F); tests were also conducted on samples aged for 30 and 60 days. None of the samples exhibited any marked sensitivity to explosive shock. However, there was some indication of thermal sensitivity in heavily confined samples exposed to the action of 20 and 10 g black powder igniters. None of the samples exhibited any significant increase in sensitivity when tested at elevated temperatures or after aging. Plans are being made to test additional samples.

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INTRODUCTION

This is an interim report on Agreement Number DTRS-56-97-0035 between the Research and Special Programs Administration of the U.S. Department of Transportation and the Pittsburgh Research Laboratory of NIOSH, the National Institute for Occupational Safety and Health. The agreement, titled "Effects of Temperature and Aging on Emulsified Liquid Oxidizing Solutions Containing More Than 70 Percent Ammonium Nitrate Solutions with More Than 0.4 Percent Combustible Substances," comprised two tasks:

1) Survey North American explosives manufacturers currently transporting emulsified liquid oxidizing solutions in bulk under a DOT exemption and summarize nominal weight percent ranges of ammonium nitrate and combustible substance and water typically shipped and the maximum elevated temperatures during transport.

2) Select and sample from 3 to 5 typical compositions from different manufacturers. Perform UN Series 1 and 2 testing on freshly prepared samples, both at ambient and maximum elevated temperatures; an added task called for tests on aged samples.

This report addresses these two tasks and contains test results on typical compositions from three different manufacturers.

SURVEY

Due to proprietary restrictions, the only records available to us for this survey were from the Bureau of Mines file of test reports on oxidizer solutions submitted for classification. Fifteen reports covering products from 8 different manufacturers were examined. The exact chemical compositions cannot be discussed in this report because of their proprietary nature. However, a generic composition consisting of 70 to 80 percent ammonium nitrate, 16 to 21 percent water, 5 to 7 percent fuel or mineral oil, and 1 to 2 percent emulsifier would cover most of the materials submitted for classification. Oxidizers other than ammonium nitrate are sometimes used and the exact nature of the oils and emulsifiers varied with the manufacturer.

These oxidizers are manufactured at elevated temperature and shipped, usually in bulk, at temperatures well above ambient. A telephone survey of several manufacturers indicated that the normal shipping temperature at the point of origin was 150°F or less. There is no arrangement for temperature control during shipment. Upon receipt at the shooting site, the oxidizer-emulsions are mixed in varying proportions with "dry" ammonium nitrate-fuel oil blasting agent; typical mixtures contain 60% ANFO with 40% emulsion. The emulsion serves to increase energy density and provide water resistance over that of ANFO used alone.

MATERIALS TESTED

Test samples were obtained from three different manufacturers. They were all emulsified mixtures of ammonium nitrate, water, oil, and emulsifier classified and shipped as Oxidizing Liquid, N.O.S., UN No. 3139, Class 5.1. For proprietary reasons, the suppliers of the three test samples will not be identified and the samples will be designated simply as samples A, B, and C.

The authors would like to express their appreciation for the cooperation of the three manufacturers in supplying the materials used in this project.

TESTS PERFORMED

The tests were selected from Test Series 1 and 2 of the UN test manual (1). They included the UN Gap test (Test 1(a) and 2(a); the Koenen test (Test 1(b) and 2(b); and the Time/pressure test (Test 1(c)(i) and 2(c)(i)). These three test types comprise recommended tests for test series 1 and 2. (see section 1.6 and table 1.2 of reference 1) Tests were also conducted with the Internal ignition test (Test 1(c)(ii) and 2(c)(ii)) which is an alternative to the Time/pressure test. This test, compared to the Time/pressure test, uses a larger sample and igniter and heavier confinement and was anticipated to be more severe than the Time/pressure test.

The gap and internal ignition tests were performed on the as received material and on the as received material heated to 150°F; the gap and internal ignition tests were also performed on (in most cases) the three materials aged for 30 and 60 days. The Koenen and time/pressure tests were performed on materials that were available after the gap and internal ignition tests were finished; in effect, on materials that had been stored for about 60 days.

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[1]United Nations Manual of Tests and Criteria, Second revised edition, United Nations, New York and Geneva, 1995.

TEST RESULTS - UN GAP TEST

The results of the UN Gap test are presented in table 1. The UN Gap test involves confining the test sample in a steel tube (400 mm long, having a 4 mm wall thickness and a 48 mm outside diameter) and shocking it with a 160 g booster (RDX or Pentolite 50 mm diameter by 50 mm long) in direct contact with the material (UN Test 1(a)) or attenuated through a 50 mm long by 50 mm diameter plexiglass "gap" (UN Test 2(a)). A positive result is recorded if the tube is completely fragmented or if a hole is punched through a 3.2 mm thick steel witness plate placed over the downstream end of the tube.

Tests at elevated temperature were performed with the sample tube wrapped with a metallic resistive tape supplied with current from a variable alternating current power source. A single thermocouple on the axis of the sample tube midway along its length was used to monitor temperatures. Since heating time was relatively long (approximately 1 hour), the sample temperature was believed to be fairly uniform.

As shown in table 1, all three materials "as received" gave negative results in the gap test at "0 gap." Tube fragmentation lengths for sample A and sample C were approximately the same as observed with inert materials of equivalent density i.e. about 7 inches. Fragmentation lengths with sample B were somewhat larger indicating some reactivity. With the "as received" material at elevated temperature, the maximum tube fragmentation lengths for all three materials were larger than the corresponding lengths observed in the tests at ambient temperature. This may indicate some minor degree of sensitization associated with the increased temperature. Again, the trials with sample B resulted in the greatest tube fragmentation.

Due to an oversight, tests were not conducted on sample A aged for 30 days. Sample B aged for 30 days produced one positive result at "0 gap." Repeat trials with a two inch gap gave completely negative results with no damage to the confinement tube or witness plate. The tests with sample C aged for 30 days gave negative results with tube fragmentation lengths comparable (or even shorter) than those observed with the "as received" samples.

Results with the three materials aged for 60 days were all negative with sample B again producing the most tube damage.

Table 1. - SUMMARY OF UN GAP TESTS WITH EMULSIONS

Test Conditions	Gap Length	Substance/Results		
		Sample A	Sample B	Sample C
As received, ambient	0 in	N(7 ½); N(7 ¼); N(7)	N(11 ½); N(9); N(11 ½)	N(6 ¼); N(4 ¾); N(5)
As received, 150°F	0 in	N(12); N(6); N(6 ¼)	N(13); N(12 ¼); N(12 ½)	N(6 ¾); N(11); N(3 ¾)
Aged 30 days	0 in	NT	N(12 ½); N(15 ¼); P(18)	N(4 ½); N(4 ¼); N(3 ¾)
Aged 60 days	0 in	N(6); N(5 ½); N(6 ¾)	N(13 ¾); N(11 ¼); N(13)	N(3 ¾); N(9); N(5 ¼)

NOTES

1 - N = Negative (-); P = Positive (+); NT = Not tested.

2 - Numbers in parenthesis indicate pipe fragmentation length in inches.

3 - In view of the positive result with sample B aged 30 days, additional trials were made with a 2 in gap (UN Test 2(a)); the results were negative with no damage to the confinement tube or witness plate.

TEST RESULTS - INTERNAL IGNITION TESTS

The internal ignition tests in United Nations Test Series 1 and 2 (Tests 1(c)(ii) and 2(c)(ii)) involves ignition of the sample which is confined in a 45.7 cm long steel pipe having an inside diameter of 74 mm and a wall thickness of 7.6 mm capped at both ends with a forged steel pipe cap. For UN Test 1(c)(ii), an igniter consisting of 20 g of black powder contained in a cylindrical cellulose acetate container is used; for Test 2(c)(ii), the weight of black powder is reduced to 10 g. The igniter is positioned in the center of the sample tube and initiated with coil of resistance wire supplied with alternating current. A test result is considered positive (+) if either the pipe or at least one of the end caps is fragmented into at least two pieces.

The experimental results are presented in table 2. All three samples "as received" gave positive results with a 20 g igniter with sample B producing the most violent reaction. At elevated temperature, samples A and B produced positive results while three trials with sample C gave negative results. For samples aged 30 days, positive results were observed with sample B with a 20 g igniter while sample C produced negative results under the same experimental conditions. Similar results were obtained with samples B and C aged 60 days.

With a 10 g igniter, positive results were obtained with samples A and B in the "as received" condition while results with sample C were negative. With the 10 g igniter at elevated temperature, samples A and B produced positive results; sample C was not tested in view of the negative results with the 20 g igniter. Positive results were observed with sample B when aged for 30 and 60 days when tested against the 10 g igniter. Sample A aged for 60 days also produced a positive results with the 10 g igniter. Generally sample B appeared to be the most reactive in the internal ignition test with sample C the least reactive. The same ordering was observed in the gap tests.

From the data set in table 2, it is difficult to access the effect of elevated temperature and aging on the "sensitivity" of the three emulsions as reflected in the degree of damage observed under the different conditions. However, from the results with sample C which gave a weak positive result in the "as received" condition with a 20 g igniter and negative results in the trials at elevated temperature and with aged samples, the effect, if any, cannot be very significant.

Table 2. - SUMMARY OF INTERNAL IGNITION TESTS WITH EMULSIONS

Test Conditions	Igniter Weight	Substance/Results		
		A	B	C
As received, ambient	20 grams	P(5); P(5)	P(11); P(8)	N(1); P(2)
	10 grams	N(1); N(1); P(7)	P(14)	N(1); N(1); N(1)
As received, 150°F	20 grams	P(20)	P(14)	N(1); N(1); N(1)
	10 grams	N(1); N(1); P(7)	P(13)	NT
Aged 30 days, ambient	20 grams	NT	P(11)	N(1); N(1); N(1)
	10 grams	NT	P(23)	NT
Aged 60 days, ambient	20 grams	NT	P(4)	N(1); N(1); N(1)
	10 grams	N(1); P(11); P(14)	P(2)	NT

NOTES 1 - N = Negative (-); P = Positive (+); NT = Not tested.
2 - Numbers in parenthesis indicate number of pipe fragments.

TEST RESULTS - KOENEN AND TIME/PRESSURE TESTS

Tests were also performed using the Koenen test and the Time/pressure test on samples that had been aged for 60 days.

The Koenen test (UN Test 1(b) and 2(b)) involves heating the substance in a metal cylinder closed with a disc having a small orifice. Heating is accomplished by a prescribed gas flame and the orifice size is varied until an "explosion" is observed as witnessed by container damage. The largest orifice diameter at which explosion occurs is the limiting diameter. If no "explosion" is obtained with a diameter of 1.0 mm, the limiting diameter is recorded as being less than 1.0 mm. A positive result (+) is recorded for Test 1(b) if the limiting diameter is 1.0 mm or more; for Test 2(b) a positive result is recorded if the limiting diameter is 2.0 mm or more.

The Time/pressure test (UN Test 1(c)(i) and 2(c)(i)) involves confinement of a small sample of the test substance (5 g) in a special container equipped with a pressure gage. The sample is exposed to the action of a special short duration igniter and the pressure pulse generated by the reacting substance is recorded. A result is considered positive (+) in Test 1(c)(i) if the minimum pressure reached is 2070 kPa (300 psi). In Test 2(c)(i) a positive result is recorded if the pressure rise time from 670 kPa to 2070 kPa is less than 30 ms. The result is negative (-) if the rise time exceeds 30 ms of if 2070 kPa is not reached.

The results of the Koenen and Time/pressure tests are presented in table 3. Positive results were observed with samples B and C in the Series 1 version of the Koenen test while the sample A results were negative. However, both B and C gave negative results in Test 2(b), i.e. the limiting diameter was less than 2.0 mm. All three samples passed the Time/pressure test producing peak pressure considerably below the 2070 kPa required for a positive result.

There was no obvious correlation between the Koenen and Time/pressure test results or between these results and the results of the gap or internal ignition tests.

Table 3. - RESULTS WITH THE KOENEN AND TIME/PRESSURE TESTS

Sample Designation	Koenen Test Limit dia (mm), remarks	Time/pressure Test Max pressure (kPa)	Rise time (ms)
A	< 1.0, mild jetting	551	250
B	< 1.5, mild jetting (1.0, "explosion")	420	280
C	<1.5, mild jetting (1.0, "explosion")	551	380

CONCLUSIONS

UN Test 1(a), the UN Gap test, yielded negative results with all three samples in the "as received" condition. Sample B was somewhat more reactive than samples A or C based on tube fragmentation length. Sample B also gave a weak positive result when tested after aging 30 days; repeat trials with UN Test 2(a), the UN Gap test with a 50 mm gap were negative. Aside from this one result, there did not appear to be any significant effect of aging or elevated temperature on shock sensitivity.

UN Test 1(b), the Koenen test, gave positive results with samples B and C and negative results with sample A. However, all three samples passed UN Test 2(b), the test series 2 version of the Koenen test.

UN Test 1(c)(i), the Time/pressure test, produced negative results with all three samples; the three samples also met the criteria for negative results in UN Test 2(c)(i).

UN Test 1(c)(ii), the Internal ignition test, which is an alternative to Test 1(c)(i), yielded positive results with all three samples. Two of the samples, A and B, also failed test 2(c)(ii). This indicates that the Internal ignition test is more stringent than the Time/pressure test (Test 1(c)(i) and 2(c)(i)). Disparities of this sort led to the selection of the "recommended tests" given in the UN test manual.

In conclusion, all three samples passed the recommended tests in UN Test Series 2, but two samples, A and B, failed the alternative test 2(c)(ii). Additional tests selected from the "assignment" side of the UN Classification Flow Chart would probably resolve this ambiguity.