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SENSITIVITY TESTS ON LEADED GLOVE MATERIAL

EMRTC Report FR-95-15

Final Test Report submitted to:

Los Alamos National Laboratory
Business Operations Division
P.O. Box 1663, MS P274
Los Alamos, NM 87545

by

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Energetic Materials Research and Testing Center
New Mexico Tech
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SENSITIVITY TESTS ON LEADED GLOVE MATERIAL

1.0 SUMMARY

A series of small-scale safety and characterization tests was performed on material made by exposing leaded dry box gloves to nitric acid. This type of glove, used in handling radioactive materials, was made up of a central layer of a lead oxide (Pb_3O_4)/Neoprene mixture sandwiched between either Neoprene or Neoprene/Hypalon. In this study, the nitration products exhibited thermal and impact sensitivity which could lead to ignition or explosion. Water was used to separate the nitrated glove material into several fractions. Only the insoluble fraction (other than unreacted Neoprene/Hypalon) exhibited significant sensitivity to impact. Both the separated and mixed materials were thermally unstable. If heated to about 80°C, a kilogram quantity of the nitrated glove material would be expected to begin to self-heat and ignition would be expected. Whether this material might react violently is not known. Quantities larger than a kilogram would begin to self-heat at even lower temperatures.

The drop weight impact sensitivity of one sample was measured to be greater than for the explosive TNT. The electrostatic spark discharge sensitivity of the nitration products was measured to be less than for typical secondary explosives. No sensitivity to friction was measured. These results indicate that the nitrated gloves can probably be handled without extreme risk of ignition if handled carefully.

Washing the nitrated glove materials with room temperature water and separating the aqueous and residual solid phases was found to desensitize the materials, even when the solution was evaporated to dryness. This indicates that water could be used as a solvent to render the stored reactive glove materials less sensitive.

2.0 INTRODUCTION

A collection of waste drums is currently stored at the Rocky Flats Laboratory in Colorado. These drums contain contaminated leaded gloves which were used in dry box processing of radioactive materials. The gloves were fabricated with a central layer of a lead oxide (Pb_3O_4)/Neoprene mixture between either Neoprene or Neoprene/Hypalon. In their use at Rocky Flats, these gloves were exposed to nitric acid in both liquid and vapor form.

Previous work^{1,2} has shown that it is possible to form a sensitive, reactive material when the leaded glove material is exposed to nitric acid. Long and Smith¹ concluded: (a) that the material was comprised of nitrated carboxylic acids and lead nitrate; (b) the material was explosive when dry and had an initiation temperature of less than 70°C; and (c) that hot water could reduce the reactivity of the material. Johnson and Lindsay² also characterized the reactive material and found that it decomposed violently at 260°C.

The drums which contain the leaded gloves may also contain a potentially explosive gaseous atmosphere and a sensitive, flammable solid residue. Therefore, additional characterization of the sensitivity of the glove materials was performed.

3.0 TEST PROCEDURES

3.1 Impact Sensitivity

An ERL type 12 drop weight impact machine of 345 cm maximum height was used to test the impact sensitivity of the material. A series of 35 mg samples underwent testing in which each sample was placed on a piece of 180A grade garnet sandpaper. A sound-pressure level meter was used in conjunction with a peak-holding digital volt-meter to measure the difference between an ignition and no reaction. All the results in this work were obtained using a 2.5 kg drop weight. The data were analyzed using the Bruceton formula to give the drop height for 50 percent probability of ignition.

3.2 ESD Sensitivity

Electrostatic discharge (ESD) sensitivity of the material was measured using a capacitor discharge, travelling needle apparatus, following, generally, the procedure in MIL-STD-1751(USAF), Aug 1982. Each test sample was contained in a holder comprised of a size #10 screw and flat nylon washer with 0.48 cm id, a disc of 0.013 cm thick stainless steel disc held in place on the bottom by an annulus of double-sided tape, and covered on top by a disc of 0.005-cm thick Mylar tape (Scotch Magic tape). In this type of test, a nickel-coated brass needle connected to a selected capacitor (initially 0.1 μ F) and charged to a measured high voltage (2-8 kV), moves down rapidly, punctures the Mylar tape, and discharges a spark through the finely divided explosive sample. A clean puncture in the tape indicates no reaction. Torn Mylar tape is judged a positive ignition. The total energy reported is calculated according to the formula $E = 0.5 C V^2$, where E is the stored energy in Joules, C is the capacitance value in farads, and V is the voltage. An up-down method is used to determine the energy for a 50 percent probability of ignition.

3.3 Friction Sensitivity

An Allegheny Ballistics Lab type, sliding plate friction sensitivity apparatus was used to test the material following the procedure detailed in the United Nations *Recommendations on the Transport of Dangerous Goods*³. Each sample was placed on a heavy steel plate that slides upon impact by a pendulum-type hammer. Both the steel plate and the sample slide under a stationary friction disc at a force determined by a hydraulic cylinder and pressure gauge. The results for applied hydraulic pressure are given in psig. The pressure cylinder diameter was 2.54 cm, allowing a conversion to total applied load. The go/no-go judgment in the friction test is made by observing a flash of light or any other sign of reaction during the event. When no reaction is observed, the applied pressure is increased to the point where the sliding travel becomes less than 2.5 cm.

3.4 Henkin-McGill Thermal Runaway Tests

The critical temperature, T_c (i.e., the lowest temperature at which an explosive sample exhibits thermal runaway), and the time-to-explosion at various temperatures were determined using an apparatus similar to those described by Rogers.⁴ Samples were sealed inside aluminum blasting-cap shells using a hand-operated, hydraulic press and specially made hollow aluminum plugs. The nominal 40 mg samples had a geometry of a thin disc with average dimensions of 0.65 cm diameter with 0.05 cm thickness.

The temperature of a Wood's metal bath was controlled by an Omega Engineering, Inc. Model 920 proportional controller. The actual bath temperature was measured immediately prior to each test using a K-type stainless steel sheathed thermocouple and a Fluke model 52 digital thermometer readout. The sample was held in a heavy lid and lowered into the hot bath in a remote operation using an air-driven piston/cylinder. The time-to-explosion was measured using a digital stopwatch from the initial time when the sample was immersed in the molten metal bath to

the time, if any, at which the sample holder ruptured. The timing uncertainty was estimated to be about one second. To find the critical temperature, the time-to-explosion tests were repeated at various bath temperatures until the minimum temperature was found at which thermal runaway and shell rupture occurred.

4.0 RESULTS

4.1 Preparation of Test Material

New, uncontaminated lead-lined dry box gloves were received and cut into pieces for preparation of test samples. Small, approximately cm square samples of the glove material were treated with 70 percent nitric acid as well as with more dilute solutions (down to 35 percent HNO_3). The resulting material was then isolated and characterized. The only effect noted of varying the concentration of the nitric acid was on the material's rate of nitration; product sensitivities were unaffected.

Several methods were employed to isolate the nitrated material. Initially, the unreacted Hypalon was removed and the remaining material was air-dried and tested for sensitivity. This test material, denoted material #1, was inhomogeneous, inconsistent, and it separated during handling into two distinct layers in the sample bottle. The upper yellow-brown layer was drop-hammer sensitive (ca. 57 cm drop height) and was believed to be the nitrated Neoprene. The lower white layer was unreactive and consisted primarily of lead nitrate.

A second batch of glove material was nitrated. During the course of nitration it was observed that, after the Hypalon was removed, the remaining reacted material could be separated into three distinct phases.

- A white crystalline precipitate was recovered from the bottom of the reaction beaker. It consisted of lead nitrate with a small amount of nitrated Neoprene and was essentially unreactive.
- The material which was soluble in nitric acid was isolated and tested. It was found to be unreactive, and therefore was not further characterized.
- The yellow-brown material that floated on the surface of the nitric acid was skimmed off, collected in a Petri dish, and air-dried. This material, denoted material #2, was found to be drop-hammer sensitive, fairly homogenous, and it behaved in a much more consistent manner than the material that was not isolated in this manner. Because of its consistency and the fact that it was the most sensitive fraction identified, this material was used to characterize the maximum hazard potential associated with the nitrated glove waste.

4.2 Sensitivity of Leaded Glove Residue

The most reactive of the nitrated lead-glove residue, material #2, was heated in a spatula using an open flame. It immediately began a rapid combustion process that consumed the entire sample. The material appeared to be able to maintain combustion even in an inert atmosphere. Evolution of NO_2 was visually detected at temperatures as low as 70°C when unconfined samples were heated on a hot plate.

The most sensitive material was tentatively identified as having a drop-hammer sensitivity of 57 cm using a 2.5 kg weight, but there was not a clear transition between trials with reaction or no reaction. Even using the floated "Neoprene nitrate" layer, material #2, multiple tests from the same height ranged from 0 to 100 percent reaction, with most of the tests exhibiting some small patches of reaction on the order of 10 percent of the sample. This material did not appear to be at all sensitive to electrostatic discharge.

4.2.1 Drop Weight Impact Sensitivity

The impact sensitivity of two materials were measured: the crude mixed nitration product (material #1) and the low density material which floated on the nitric acid (material #2). Data results are given in Tables 1 and 2. Test conditions included using a 2.5 kg hammer, relative humidity of 57 percent, and temperature of 16°C. The drop heights for 50 percent probability of ignition were calculated for both materials using the Bruceton formula. The crude product had an impact sensitivity of 92 ± 26 cm compared to 75 ± 32 cm for the floated material. As discussed above, one sample of material #2 exhibited a preliminary impact sensitivity of about 57 cm, indicating that even when separated the material exhibits some variability. These impact sensitivities can be compared to other results from this apparatus:

Material	Impact Sensitivity (cm)
Ammonium Nitrate (AN)	200
Trinitrotoluene (TNT)	154
Ammonium Perchlorate (AP)	60
Trimethylene Trinitramine (RDX)	25

4.2.2 ESD Sensitivity

The electrostatic discharge sensitivity results for materials #1 and #2 are shown in Tables 3 and 4. Ambient conditions were relative humidity of 62 percent at 13°C. A Bruceton calculation was not done since many of the tests were performed at the maximum energy of 3.2 J. Four ignitions were obtained at 3.2 J, although thirteen no-go's were also obtained at this energy. Test material #1 was, in any case, very insensitive to ESD ignition.

The ESD sensitivity for 50 percent probability of ignition of material #2 was measured to be 2.0 ± 0.4 J, showing that it too was very insensitive to ESD ignition.

These results can be compared to other data from this apparatus:

Material	ESD Sensitivity (Joule)
Trimethylene Trinitramine (RDX)	0.14
Trinitrotoluene (TNT)	0.56

4.2.3 Friction Sensitivity

Ten samples each of materials #1 and #2 were tested for friction sensitivity. Up to the limit of the apparatus, no ignitions or any other signs of reaction were observed for either sample material.

4.2.4 Henkin Cook-off Tests

The experimental data for materials #1 and #2 are shown in Tables 5 and 6. The critical temperatures for these nominal 40 mg samples were almost identical—178 and 176°C for samples #1 (average sample thickness of 0.0506 cm) and #2 (average sample thickness of 0.0495 cm), respectively. These data show that neither material is very thermally stable and would likely generate decomposition heat and exhibit thermal runaway at relatively low temperatures for quantities of a kilogram or more. For example, if we assume a typical activation energy for the decomposition reaction of 1,600 kJ/mol, we can use the Frank-Kamenetskii⁵ formula, calibrated using the Henkin data, to predict minimum thermal runaway temperatures for various quantities of material #2. This exercise gave critical temperatures (i.e., temperatures above which the material would self-heat to ignition), of 83 and 61°C for a 1-kg sphere and a 55-gallon drum of material #2. However, it should be noted that these calculations are based on limited experimental data. Thermal tests on larger quantities of material would be needed to confirm this analysis.

However, the Henkin results definitely show that these materials are not stable when heated, even to relatively moderate temperatures for larger quantities. The least thermally stable secondary explosive tested in this laboratory is pentolite, which would have a critical temperature for similar 40 mg samples of about 188°C, showing that both leaded glove residue materials are less thermally stable than pentolite.

The thermal stability of a mixture of materials is typically dominated by the thermal stability of the least stable component. Thus a 90/10 mixture and a 10/90 mixture of a stable and an unstable material would be expected to show similar thermal stabilities. This is probably the situation for the two materials tested here. Material #1 probably contained some of the sensitive component that made material #2 more easily ignited.

4.3 Solubility of Leaded Glove Material

A portion of material #2 was placed in an Erlenmeyer flask with excess room temperature water, swirled briefly, and then poured into a Hirsch funnel and vacuum filtered. Both the filtrate and the liquor were evaporated to dryness and the samples tested. Neither the filtrate nor the evaporated aqueous phase (lead nitrate was the only material identified from the liquor) was drop hammer or ESD sensitive. These materials were recombined and intimately mixed using an agate mortar and pestle. This recombined material was tested and found to have a greatly reduced drop-hammer sensitivity; drop height on the order of 100 cm greater than was required to initiate a similar level of reaction as the unwashed material #2. The water-washed material burned only as long as the flame was in direct contact with it. When the individual water-washed components were remixed, the sample exhibited identical combustion characteristics identical to those of the unwashed material. The water-washed material did not react in Henkin tests, but the behavior of the remixed material appears very similar to the untreated substance.

Further evidence of a change in the character of the water-insoluble "Neoprene nitrate" due to washing was a difference in color. When first isolated, this layer was described as having a moderately dark, yellow-brown to tan hue, but after the brief water washing this changed to a light, pale yellow. It seems likely that a prolonged wash in hot water would result in a white material which would be even less reactive when remixed with the dried aqueous lead nitrate

extract. This result would indicate that another reaction was occurring during the aqueous neutralization process besides just the removal of lead nitrate. The aqueous phase was evaporated slowly, yielding large crystals of lead nitrate and an amorphous yellow substance that appeared to be a mixture of water-soluble organic compounds. None of these compounds was individually drop-hammer sensitive. The mixture of the unidentified aqueous-phase yellow substance and the lead nitrate was not drop-hammer or ESD sensitive, but it could be made to burn with difficulty.

The initial water- washing test of the nitrated leaded glove material was performed in such a manner that the time allotted for dissolution of material was small compared to the time required to agitate, filter, and wash the sample. This initial test indicated that water was effective enough at room temperature that reasonable care in processing the gloves (i.e. water wash and stir, then filter or decant), would result in an inert product. Repeating the test more rapidly and with less agitation also yielded effectively inert products, leading to the conclusion that high water temperature and long soak times are not required for effective desensitization of the material. It appears likely that simply filling the contaminated drums with warm water, allowing to soak, and then pouring or filtering off the liquid would result in two unreactive phases. Based on this premise, methods involving more mechanical agitation or the use of other solvents would not be needed.

No evidence of lead fulminate was detected in any of the samples generated in this work.

5.0 REFERENCES

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2. Johnson, T.C. and Lindsay, J.W., "Flammability of Leaded Dry-Box Gloves," Dow Chemical Co. report RFP-1354 (June 1969).
3. *Recommendations on the Transport of Dangerous Goods: Tests and Criteria*, (1990) Second Edition, United Nations.
4. Rogers, R.N., "Thermochemistry of Explosives," *Thermochimica Acta*, 11, 131 (1975).
5. Frank-Kamenetskii, D.A., *Diffusion and Heat Exchange in Chemical Kinetics*, Princeton University Press, 1955.

Table 1. Drop Hammer Data on Material #1

Trial No.	Height (cm)	Noise	Go/No-Go
1	95	1.04	go
2	90	0.90	go
3	85	0.94	go
4	80	0.70	no-go
5	85	0.87	no-go
6	90	0.84	no-go
7	95	0.81	no-go
8	100	0.81	no-go
9	105	0.93	go
10	100	1.05	go
11	95	0.95	go
12	90	0.64	no-go
13	95	0.57	no-go
14	100	0.89	no-go
15	105	0.97	go
16	100	0.92	go
17	95	0.81	no-go
18	100	1.05	go
19	95	0.90	go
20	90	0.88	go
21	85	0.84	go
22	80	0.91	go
23	75	1.00	go
24	70	0.74	no-go

Table 2. Drop Hammer Data on Material #2

Trial No.	Height (cm)	Noise	Go/No-Go
1	50	0.58	no-go
2	60	0.76	go
3	55	0.51	no-go
4	60	0.62	no-go
5	65	0.69	no-go
6	70	0.60	no-go
7	75	0.69	no-go
8	80	0.96	go
9	75	0.93	go
10	70	0.70	no-go
11	75	0.84	go
12	70	0.67	no-go
13	75	0.90	go
14	70	0.75	no-go
15	75	0.87	go
16	70	0.66	no-go
17	75	0.79	no-go
18	80	0.68	no-go
19	85	0.88	no-go
20	90	0.63	no-go
21	95	0.96	go
22	90	0.91	go

Table 3. ESD Sensitivity Data on Material #1

Trial No.	Energy (J)	Voltage	Go/No-Go
1	0.5	3162	no-go
2	0.8	4000	no-go
3	1.5	5477	no-go
4	2.0	6325	no-go
5	3.2	8000	no-go
6	3.2	8000	go
7	3.1	7874	no-go
8	3.2	8000	no-go
9	3.2	8000	no-go
10	3.2	8000	no-go
11	3.2	8000	go
12	3.1	7874	no-go
13	3.2	8000	go
14	3.1	7874	no-go
15	3.2	8000	no-go
16	3.2	8000	no-go
17	3.2	8000	no-go
18	3.2	8000	no-go
19	3.2	8000	go
20	3.1	7874	no-go
21	3.2	8000	no-go

Table 4. ESD Sensitivity Data on Material #2

Trial No.	Energy (J)	Voltage	Go/No-Go
1	3.2	8000	go
2	0.8	4000	no-go
3	1.5	5477	no-go
4	2.0	6325	go
5	1.9	6164	go
6	1.8	6000	no-go
7	1.9	6164	go
8	1.8	6000	no-go
9	1.9	6164	no-go
10	2.0	6325	no-go
11	2.1	6481	go
12	2.0	6325	go
13	1.9	6164	no-go
14	2.0	6325	no-go
15	2.1	6481	go
16	2.0	6325	no-go
17	2.1	6481	no-go
18	2.2	6633	go
19	2.1	6481	no-go
20	2.2	6633	no-go
21	2.3	6782	no-go
22	2.4	6928	go

Table 5. Henkin Data on Material #1

Trial No.	Thickness (mm)	Temp. (°C)	Weight (mg)	Time-to-Ignition (seconds)	Go/No-Go
1	0.536	250.8	40.1	0.5	go
2	0.443	238.5	40.3	0.5	go
3	0.496	226	40.7	0.5	go
4	0.450	212.8	40.6	0.76	go
5	0.499	195.8	40.6	1.03	go
6	0.439	183.5	40.3	5.45	go
7	0.530	175.5	40.7	1260	no-go
8	0.543	180.2	40.8	1.08	go
9	0.615	178	40.0	3.24	go
10	0.545	176.3	40.4	1060	no-go
11	0.558	177.8	40.8	1000	no-go
12	0.471	178.2	40.5	1020	no-go
13	0.454	180	40.9	5.3	go
14	0.504	179	39.9	1.65	go

Table 6. Henkin Data on Material #2

Trial No.	Thickness (mm)	Temp. (°C)	Weight (mg)	Time-to-Ignition (seconds)	Go/No-Go
1	0.464	179.6	40.2	11.1	go
2	0.529	175.5	40.0	1080	no-go
3	0.518	177.7	40.2	9.78	go
4	0.498	176.9	40.5	9.24	go
5	0.502	175.9	40.5	7.46	go
6	0.479	175	40.5	1000	no-go
7	0.444	176.5	40.7	1040	no-go
8	0.534	177.5	40.0	1020	no-go
9	0.514	179.5	40.3	980	no-go
10	0.468	180.9	40.5	5.52	go
11	0.458	179.7	39.9	1060	no-go
12	0.491	182.4	40.2	5.15	go
13	0.510	180.8	40.3	1100	go
14	0.516	183.5	40.0	3.44	go