



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

SAFETY AND SENSITIVITY OF NITROGLYCERINE (NG) MIXTURES

P. C. Hsu, G. Hust, R. Schmidt

November 2, 2012

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Safety and Sensitivity of Nitroglycerine (NG) Mixtures

P. C. Hsu, G. Hust, and Robert Schmidt
Energetic Materials Center
Lawrence Livermore National Laboratory, Livermore, CA USA

October 24, 2012

ABSTRACT

Small scale (SSST) safety tests were conducted to determine impact sensitivity, friction sensitivity and spark sensitivity of nitroglycerine (NG) and its mixtures. The tests were done for the following formulations (totally 9): NG (1% stabilizer), NG with diluents (acetone and triacetin), and mixture of NG and nitrocellulose (NC). Aging study was also performed on NG/NC mixture to determine the effect of aging on sensitivity. The test results are summarized in this report.

Keywords: Explosives, impact sensitivity, drop hammer, friction sensitivity, spark sensitivity, nitroglycerine, and nitrocellulose.

1. INTRODUCTION

Nitroglycerin (NG) is fairly sensitive to impact and it often is diluted with solvents to reduce its sensitivity for handling safety. Mixtures of NG and NC are popular for specific applications. This report presents the test results of NG and NG-NC mixtures with standard techniques used at LLNL and other laboratories (LANL, SNL, IH and Tyndall) in which explosives are studied.

2. METHOD

Small-scale sensitivity testing was done to determine material response to various stimuli including impact, friction, and static spark. These tests, briefly described below, provide parameters for safety in handling.

2.1 Drop Hammer (*impact sensitivity*)

ERL Type 12 drop hammer equipment at LLNL, shown in Figure 1, was used to determine the impact sensitivity. [1] The equipment includes a 2.5-kg drop weight, a striker (upper anvil, 2.5 kg for solid samples and 1.0 kg for liquid samples), a bottom anvil, a microphone sensor, and a peakmeter. For each drop, sample (35 mg for solids or 35 microliter for liquids) is placed on the bottom anvil surface and impacted by the drop weight from different heights. Signs of reactions upon impact are observed and recorded. These signs include noises, flashes or sparks, smoke, pressure, gas emissions, temperature rise due to exothermic reaction, color change of the sample, and changes to the anvil surface (noted by inspection). For solid samples, a “GO” was defined as a microphone sensor (for noise detection) response of ≥ 1.3 V as measured by a peakmeter. The higher the DH_{50} values, the lower the impact sensitivity. The method used to calculate DH_{50} values is the “up and down” or Bruceton method [2,3]. PETN and RDX have impact sensitivities of 15 and 35 cm, respectively. TATB has impact sensitivity more than 177 cm. For liquid samples, a “GO” was determined by the noise levels as measured by the peakmeter, appearance of flashes, temperature rise of the anvil, and visual inspection of the anvil surface. Two liquid samples TMETN and FEFO have impact sensitivities of 14 and 32 cm, respectively.

2.2 Frictional Sensitivity

A BAM friction sensitivity test machine, as shown in Figure 2, was used to determine the frictional sensitivity.[4] The system uses a fixed porcelain pin and a movable porcelain plate that executes a reciprocating motion. Weight affixed to a torsion arm allows for a variation in applied force between 0.5 kg to 36.0 kg. The relative measure of the frictional sensitivity of a material is based upon the smallest load (kg) at which reaction occurs for a 1-in-10 series of attempts. The lower the load values, the higher the frictional sensitivity. PETN has a frictional sensitivity of 6.4 kg.

2.3 Spark Sensitivity

The static spark machine at LLNL is used to evaluate the electrostatic discharge hazards (human ESD) associated with the handling of explosives.[5] The machine was custom-built almost 30 years ago and consists of a capacitor bank (up to 20,000 pF), a voltage meter, and a discharge circuit, as shown in Figure 3. An adjustable resistor up to 510 ohms (chosen to simulate human body) is wired to the discharge circuit. A 5-mg sample is placed in a Teflon washer sealed to a steel disc and covered with a Mylar tape. High static voltage (up to 10 kv) is applied and discharged to the sample. Evidence of reaction is judged from the condition of Mylar tape, smokes, and color change of the sample. Voltage, capacitance, and resistance can be adjusted to achieve the desired static energy. The results obtained are expressed as a zero in 10 or one-in-ten at a specific voltage and joules. One reaction in ten trials at ≤ 0.25 joules is considered spark-sensitive. Primary explosives show reaction at 0.1 joule.



Figure 1. Drop hammer system at LLNL

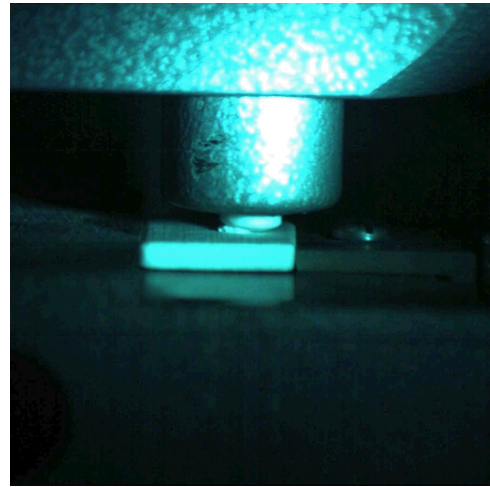
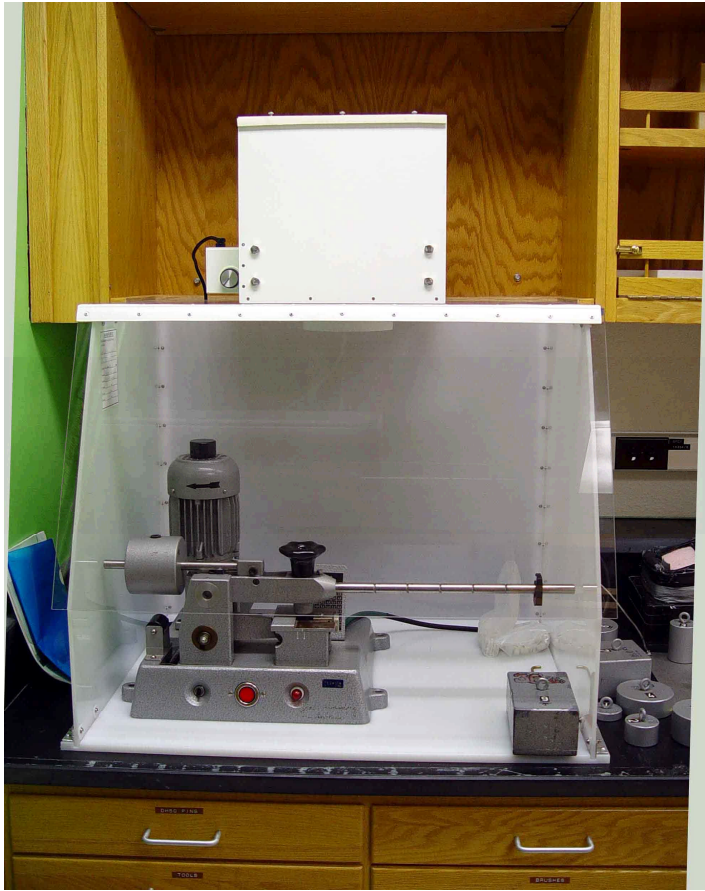


Figure 2. Friction sensitivity test machine; (a) front view, left; (b) pin and plate with sample in between in a close-up view, right.



Figure 3. Spark test system

2.4 Sample compositions

All 9 mixtures were prepared and tested for their sensitivities. Table 1 lists compositions of the mixtures. Mixture 9 was chosen for aging study.

Table 1. Composition* of Mixtures 1 to 9

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8	Mix 9**
Surface for impact testing	Bare anvil	Bare anvil	Bare anvil	Bare anvil	Bare anvil	Bare anvil	Bare anvil	Bare anvil	120 grit sand paper
NG	99%	88%	80%	71%	88%	79%	71%	59%	80%
NC	1%								20%
Stabilizer (NDPA)									
Acetone		12%	20%	29%		21%			
Triacetin					12%		29%	41%	

*All percentages are by weight. ** selected for aging study

3. RESULTS

3.1 Sensitivities of mixtures

The 9 mixtures were freshly prepared (mixing) immediately before performing the sensitivity testing except for the aging study. Sample size of 35 microliters (liquids) or 35 mg (gel) was precisely measured and placed on the bottom anvil surface (bare anvil for mixtures 1 to 8, 120 grit sand paper for mixture 9) for impact sensitivity testing. The drop weight was set at different heights for impacting the samples. Signs of reaction for determining ‘GO’ or ‘NO-GO’ were noise levels recorded by the peakmeter, flashes, temperature measurement with an IR probe, and changes noted through visual inspection of anvil surface. The tests were performed at ambient condition (72°F, 20% R.H.) by the same technician. Figure 4 shows a ‘GO’ event with an appearance of flashes as the drop weight impacted the sample. The impact sensitivity test results are listed in Table 2. Impact sensitivities for some commonly used explosives are also listed in the table for comparison. Table 2 shows that neat NG without dilution is impact-sensitive. But after diluted with acetone or triacetin, the impact sensitivities (mix 2 to 8) were similar to those of secondary explosives, values ranging from 15 cm to more than 177 cm.

Since neat NG with 1% stabilizer NDPA was not friction sensitive and not spark sensitive, no friction and spark tests were performed on diluted mixtures 2 to 8. Table 2 also lists results of frictional sensitivity tests and spark sensitivity tests. All mixtures tested showed no reaction to spark.

Table 2. Impact sensitivities, friction sensitivity, and spark sensitivity for the 9 mixtures

Mixtures and compositions	Impact sensitivity, DH_{50} , cm	Friction sensitivity	Spark sensitivity
Mix 1, NG 99%, 1% NDPA	9.1	1/10 @ 27 kg	0/10 @ 1.0 Joule
Mix 2, NG 88%, acetone 12%	15.6	NT*	NT
Mix 3, NG 80%, acetone 20%	48.1	NT	NT
Mix 4, NG 71%, acetone 29%	154.5	NT	NT
Mix 5, NG 88%, triacetin 12%	14.6	NT	NT
Mix 6, NG 79%, triacetin 21%	58.6	NT	NT
Mix 7, NG 71%, triacetin 29%	140.9	NT	NT
Mix 8, NG 59%, triacetin 41%	> 177	NT	NT
Mix 9, NG 80%, NC 20%	13.3	1/10 @ 9.6 kg	0/10 @ 1.0 Joule
PETN	15	1/10 @ 6.4 kg	0/10 @ 1.0 Joule
HMX	32	1/10 @ 11.6 kg	0/10 @ 1.0 Joule
RDX	35	1/10 @ 12.4 kg	0/10 @ 1.0 Joule
TATB	> 177	0/10 @ 36 kg	0/10 @ 1.0 Joule

* NT- not tested because diluted nitroglycerine was not expected to be friction and spark sensitive

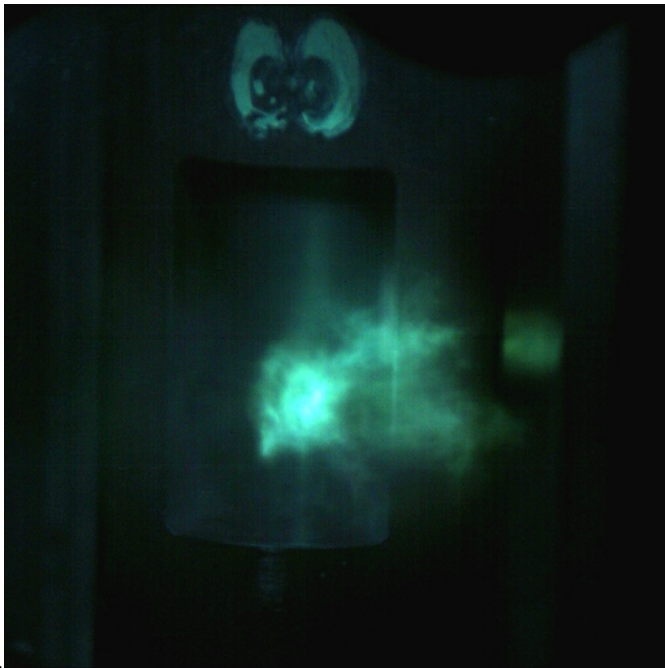


Figure 4. A “GO” event observed during the impact sensitivity test; flashes appeared as the drop weight impacted the sample.

3.2 Effect of material aging on impact sensitivity

After NC was added to NG, the mixture (mixture 9) jelled slowly and the viscosity and density changed. In an effort to understand the effect of aging on its handling safety, we conducted a series of impact testing on

aged samples with the results shown in Table 3. Table 3 shows the sample became very impact sensitive after it aged for a few hours (DH_{50} dropped to 7.3 cm in 4 hours). After 4 days, the impact sensitivity was 2.0 cm, very sensitive to handle. This was probably due to the formation of air bubbles (up to several hundred microns) as a result of nitrocellulose dissolution into nitroglycerin (see Figure 5), making the sample more porous and hence increased the impact sensitivity. No friction and spark testing was performed on the aged samples because no sufficient amount of aged samples were available at the time.

Table 3. Effect of aging on sensitivities of NG/NC mixture (80%/20%)

Aging time	Impact sensitivity, DH_{50} , cm	Friction sensitivity	Spark sensitivity
1 hour	13.3	1/10 @ 9.6 kg	0/10 @ 1.0 Joule
3 hours	11.1	NT	NT
4 hours	7.3	NT	NT
23 hours	4.6	NT	NT
4 days	2.0	NT	NT

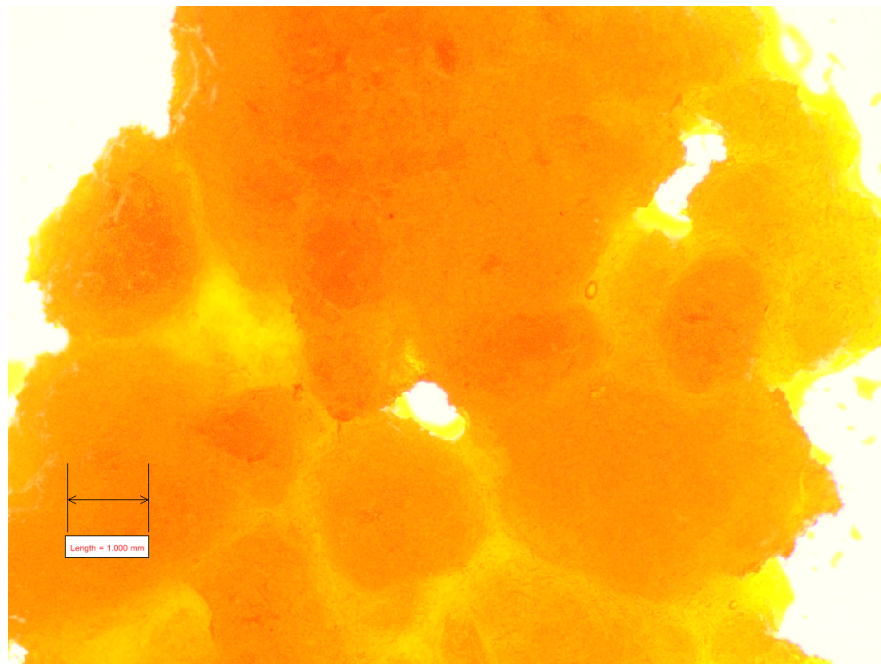


Figure 5a. NG/NC mixture after one hour of preparation; DH_{50} was 13.3 cm.

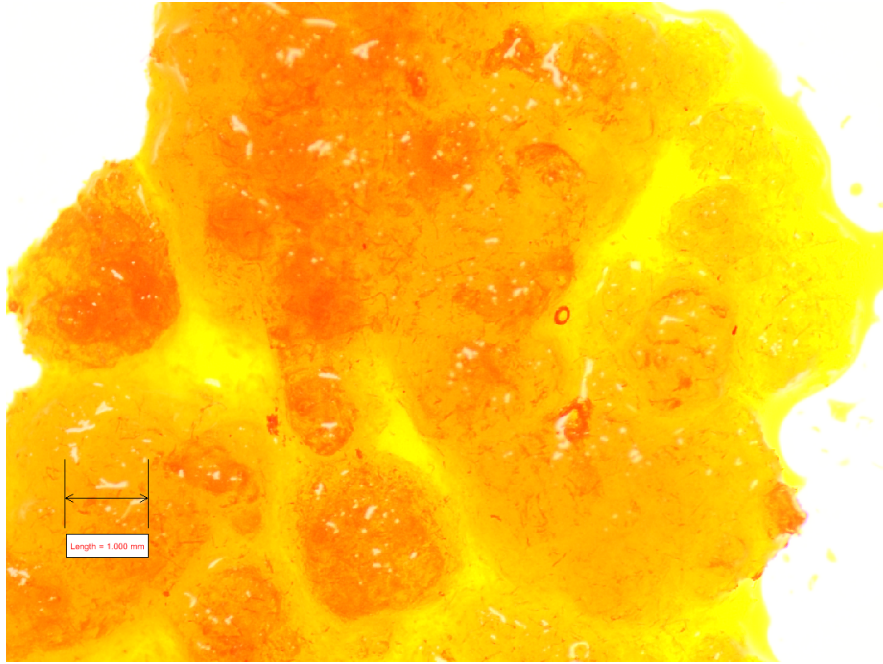


Figure 5b. NG/NC mixture after aging for 23 hours, many air bubbles formed; DH_{50} was 4.6 cm.

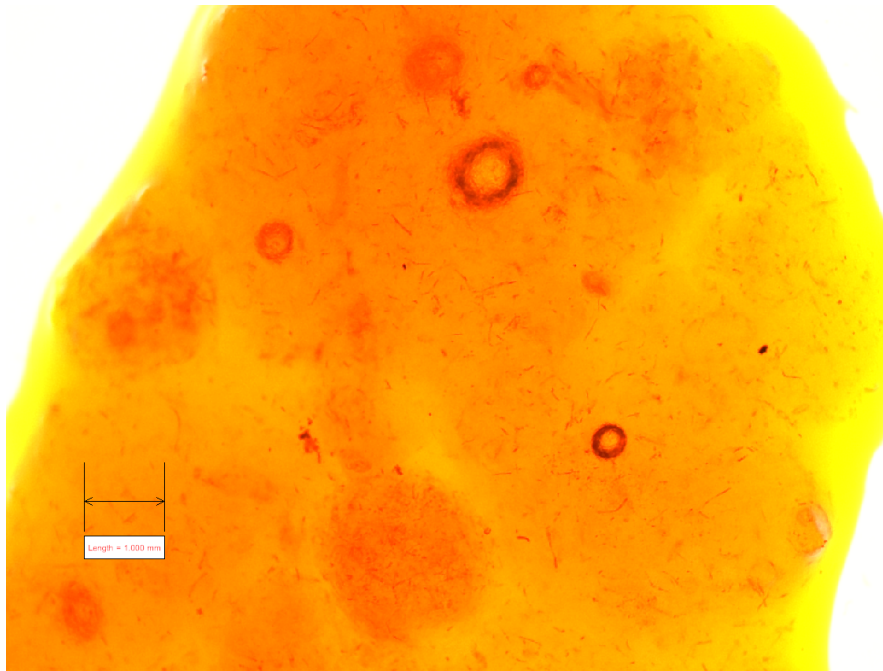


Figure 5c. NG/NC mixture after aging for 4 days, larger air bubbles were visible; DH_{50} was 2.0 cm.

4. CONCLUSIONS

8 NG/diluents mixtures and 1 NG/NC mixture were formulated and sent for evaluation for their sensitivities to various stimuli with LLNL's drop hammer (drop weight) system, friction test machine, and the spark test machine. These tests were performed on the samples immediately after formulation, thus eliminating the variable of side reactions. Neat nitroglycerine with 1% stabilizer NDPA was impact sensitive. After dilution, test results showed that DH_{50} values for the NG/diluent mixtures were between 15 cm and greater than 177 cm, behaved like secondary explosives. All mixtures tested showed no reaction to spark testing. Gelled NG/NC mixture (80%/20%) was somewhat impact sensitive when tested right after formulation but not sensitive to friction and spark. Impact sensitivity of gelled NG/NC increased greatly after a few hours of aging. In 4 days, the impact sensitivity of the sample was only 2 cm. it must be handled very carefully. More experiments are recommended to determine the effect of aging on friction sensitivity and spark sensitivity of gelled NG/NC samples.

NOMENCLATURE

BAM	<i>Bundesanstalt für Materialprüfungen</i>
DH	drop hammer values
HMX	Cyclotetramethylenetetra-nitramine
NC	Nitrocellulose
NG	Nitroglycerine
PETN	Pentaerythritol tetranitrate
pF	pico-Faraday
RDX	Cyclotrimethylenetrinitramine
TATB	1,3,5-triamino-2,4,6-trinitrobenzene

REFERENCES

1. Simpson, L. R. and Foltz, M.F., "LLNL Small-Scale Drop-Hammer Impact Sensitivity Test," UCRL-ID-119665, 1995.
2. Dixon, W.J. and Massey, F.J., "Introduction to Statistical Analysis, 2nd ed., McGraw-Hill, New York, pp 318-327, 1957.
3. Dixon, W.J., "The Up and Down Method for Small Samples," J. Am. Statistical Assoc., 60, pp 967-978, 1965.
4. Simpson, L.R. and Foltz, M.F., "LLNL Small-Scale Friction Sensitivity (BAM) Test," UCRL-ID-124563, 1996.
5. Simpson, L.R. and Foltz, M.F., "LLNL Small-Scale Static Spark Machine: Static Spark Sensitivity Test," UCRL-ID-135525, 1999.