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Predicting Shock Sensitivity of Energetic Compounds

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Shock sensitivity is one of the most important parameters for safe handling of pure and mixture of energetic materials. A simple correlation is introduced to determine large-scale gap thicknesses shock sensitivity of pure or mixed $C_aH_bN_cO_d$ explosives. This method does not require any experimental data. This procedure is based on initial density, calculated per cent void and a+b/2-d as well as the presence of C-N(NO_2)-C in the case of pure explosives. The predicted results using the method describing here has a root mean square (rms) deviation of 3.83 mm from 28 measured values (corresponding to 17 pure and mixed explosives).

Key Words: Sensitivity, Energetic compounds, Explosives.

INTRODUCTION

Elimination of any poor candidate due to sensitivity or performance problems through predictive capabilities at the early stages of development is highly desirable to scientists and explosive industries. Since synthesis, test and evaluation of a new energetic material is so costly in time and money, thus the methods for predicting the performance or sensitivity before synthesis or formulation would be needed. By achieving development capabilities for predicting various properties of a notional energetic material that are associated with the performance and sensitivity before expending resources in its synthesis, it is hoped the development procedure for energetic materials would be improved. Prediction tools help the chemists to develop systematic and scientific formulations of appropriate futuristic target molecules having important properties such as enhanced detonation performance and good sensitivity.

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Various empirical methods complemented the computer output can be used to determine detonation performance and structure-sensitivity relationships[1,2]. Some new empirical procedures have also been recently developed to predict detonation performance of ideal and non-ideal explosives[2] as well as impact sensitivity of different classes of pure energetic compounds[3-5]. Since the drop weight impact test is convenient and the most common method of assessing sensitivities, most of studies that have attempted to associate molecular properties with sensitivities rely on drop weight impact measurements[3]. Some simple relationships have been found that relate impact sensitivities with measured and predicted molecular properties such as the oxygen balance of the molecules[6,7], molecular electronegativities[8,9], elemental composition[3,4] and through artificial neural network[5].

Despite all of the uncertainty with experimental data of impact sensitivity, there exist numerous impact measurements for pure explosives[5]. Price[10] has studied a variety of factors important in shock wave sensitivity test. Storm and coworkers[11] have found that there is a linear correlation between the impact and shock sensitivity under specified conditions for five energetic compounds with closely related structure, *i.e.*, TNB, DIPM, TNA, DATB and TATB. Owen and coauthors[12] indicated that measured impact and shock sensitivities of seven polynitroaromatic molecule correlate with an approximation of the electronegativity potential at midpoint of the C-N bond for the longest C-NO_2 bond in each molecule. However, it is important to establish a correlation between molecular properties of explosives and shock sensitivity. The purpose of this work is to present a generalized new simple reliable method for both pure and mixed explosives which is still needed to explosive users in industry. Development a simple correlation for large-scale gap thicknesses shock sensitivity is of significant importance because safe handling of novel pure and mixed energetic molecules is one of the most important issues to explosive industries. This research reveals a new simple correlation for predicting large-scale gap thicknesses shock sensitivity of well-known pure and mixed explosives.

Large-scale gap thicknesses shock sensitivity

The gap test data can be used to indicate the shock sensitivity of an explosive. The gap test method is widely used to determine the shock sensitivity of explosive. A shock pressure of uniform magnitude is produced by a detonating charge of high explosive which is transmitted to the test explosive through an attenuating inert barrier or gap. The thickness of the barrier between the donor and test (acceptor) explosives can be varied. The values are reported as one can determine the barrier thickness required to inhibit detonation in the test explosive half the time (G_{50}). Different gap tests have been used to qualitatively measure the shock wave

amplitude required to initiate detonation in explosive. Los Alamos National Laboratory (LANL) has used two test configurations so that the diameter of the cylinder acceptor charge in the small-scale test is 12.7 mm and in the large-scale is 41.3 mm[13]. The large-scale has an advantage over the small-scale because the large-scale can be used in somewhere an explosive whose detonation failure diameter is near to or greater than the diameter of the acceptor charge. The small-scale can not be tested in this situation. The test method in large-scale is to fire a few preliminary shots to determine the spacer thickness that allows detonation in the test explosive. The spacer thickness, that allows 50 % probability detonation in the acceptor explosive, is determined when shots are fired with the spacer thickness alternately increased and decreased. Detonation of the acceptor charge is ascertained by the dent produced in a witness plate. However, a deep defined dent in the steel witness indicates the test explosive detonated.

Sensitivity of pure or mixed explosives is a complex matter and its understanding is large part of a chemical problem. Reliable shock sensitivity tests exist, but the results of impact sensitivity are often not reproducible because factors in the impact experiment that might affect the formation and growth of hot spots could strongly affect the measurements. However, reported data of impact sensitivities are extremely sensitive to the conditions under which the tests are performed. It should be mentioned that all of impact sensitivity correlations can be applied only for pure energetic compounds. Since large-scale shock sensitivities of various explosives depends on physical and chemical structural parameters, the main object of this work was to find a good correlation that can be applied for both pure and composite explosives.

It is found that large-scale shock sensitivities of various explosives depends on four main essential parameters which include initial density, per cent void, distribution of oxygen between carbon and hydrogen as well as structural parameter C-N(NO_2)-C for pure explosives. However, pure explosives containing C-N(NO_2)-C linkage are more sensitive than the other pure explosives containing only C-NO_2 linkage. The results indicated that the following general equation is suitable for various types of $C_aH_bN_cO_d$ pure and mixed explosives:

$$G_{50} = x_1 + x_2\rho_0 + x_3(a + b/2 - d) + x_4 Void_{theo} + x_5(C - N(NO_2) - C)_{pure} \quad (1)$$

where x_1, x_2, x_3, x_4 and x_5 are adjustable parameters which can be obtained by the best fit to experimental large-scale shock sensitivities data for different pure and composite $C_aH_bN_cO_d$ explosives, ρ_0 is initial density of explosive, a+b/2-d is a parameter that shows distribution of oxygen between carbon and hydrogen to form carbon monoxide and water, $Void_{theo}$ is theoretical calculated per cent void which can be obtained from

$\frac{(1/\rho_0 - 1/\rho_{TM})}{1/\rho_0} \times 100$ where ρ_{TM} is theoretical maximum density. As seen, this correlation has structural term C-N(NO_2)-C which can be considered only for pure explosives such as RDX. To obtain adjustable parameters, we have used a database given by Dobratz and Crawford[13], where the experimental values of large-scale gap thicknesses shock sensitivity for various pure and mixed well-known explosives have been collected.

TABLE-1
COMPARISON OF LARGE-SCALE GAP THICKNESSES SHOCK SENSITIVITY (G_{50}) OF THE NEW CORRELATION, EQN. 2, WITH MEASURED DATA[13]

Name[a]	ρ_0 (g/cc)	ρ_{TM} (g/cc)	$G_{50,exp}$	$G_{50,cal}$	Dev
COMP A-3	1.638	1.672	54.51	52.99	1.52
COMP B, Grade A	1.712	1.742	44.58	49.74	-5.16
COMP B-3	1.727	1.750	50.34	49.21	1.13
CYCLOTOL -75/25	1.757	1.770	43.15	48.37	-5.22
	1.734		45.74	48.71	-2.97
DATB	1.786	1.837	41.68	38.86	2.82
	1.705		45.36	40.22	5.14
EXP D	1.668	1.717	42.42	48.25	-5.83
	1.604		42.98	49.09	-6.11
HMX	1.070	1.905	70.70	67.74	2.96
NQ	1.609	1.775	50.00	48.69	1.31
OCTOL -75/25	1.822	1.843	49.45	43.48	5.97
	1.815		47.32	43.60	3.72
	1.795		43.56	43.94	-0.38
PBX-9007	1.646	1.697	52.91	51.87	1.04
PBX-9011	1.761	1.795	51.97	46.11	5.86
PBX-9205	1.682	1.720	50.83	50.80	0.03
PETN	0.810	1.780	69.40	70.96	-1.56
RDX	1.750	1.806	61.82	59.90	1.92
	1.090		70.20	70.38	-0.18
TATB	1.870	1.938	21.92	31.05	-9.13
TETRYL	1.690	1.730	59.82	60.89	-1.07
	1.666		60.60	61.21	-0.61
	0.850		69.20	72.27	-3.07
TNT	1.626	1.654	49.38	48.35	1.03
	1.631		46.43	48.29	-1.86
	1.505		54.92	49.68	5.24
	1.220		56.26	52.81	3.45
rms deviation					3.83

[a]See Appendix A for glossary of compound names.

Multiple linear regression method[14] was used to find adjustable parameters. The left-division method for solving linear equations uses the least squares method because the equation set is overdetermined[14]. The optimized correlation for predicting large-scale gap thicknesses shock sensitivity can be given as follows:

$$G_{50}(/\,mm) = 171.47 - 69.10\rho_0 - 2.61(a + b/2 - d) - 0.961 Void_{theo} + 12.32(C - N(NO_2) - C)_{pure} \quad (2)$$

As indicated, eqn. 2 requires no prior knowledge of any measured physical, chemical or thermochemical properties of explosive. Calculated large-scale gap thicknesses shock sensitivity is presented in Table-1 and compared with corresponding measured values[13]. The new correlation, which is based on some physical and structural parameters, shows good agreement with experimental values. Due to large uncertainty in experimental data, R-squared value or the coefficient of determination of this correlation is 0.87[14]. This equation provides new and simple empirical available procedure for estimation of large-scale gap thicknesses shock sensitivity of pure and composite explosives.

Difference of predictions from experiments, *e.g.,* Dev = measured-predicted, as well as root mean square (rms) of deviations for new method are also given in Table-1, which can be defined as follows:

$$\text{rms deviation} = \sqrt{\frac{1}{N}\sum_{i=1}^{N} Dev_i^2} \quad (3)$$

where N represents the number of large-scale gap thicknesses shock sensitivity measurements. As shown in Table-1, the rms deviation of the new correlation is 3.83 mm which shows relatively good predictions.

Limitations of new correlation: The new correlation can be applied for pure and composite mixtures that are prepared under vacuum cast, cast, hot-pressed and pressed conditions. Deviations may be large for creamed, granular and flake situations.

Conclusions

This work introduces novel approach for prediction shock sensitivity of pure and mixed explosives based on Los Alamos National Laboratory large scale gap tests. The new correlation has several major advantages: (i) Since high percentage errors generally attributed to reported experimental measurements from different sources for impact sensitivities, there is large uncertainty in different methods of impact sensitivity predictions as compared to new correlation for large-scale gap thickness shock sensitivity (ii) Different correlations of impact sensitivity can be applied only for pure explosives but eqn. 2 can be used for both pure and mixed explosives.

However, the results indicated that the accuracy of prediction is not necessarily enhanced by greater complexity.

Appendix A: Glossary of compound names

1. COMP A-3: 91/9 RDX/wax ($C_{1.87}H_{3.74}N_{2.46}O_{2.46}$)
2. COMP B: 63/36/1 RDX/TNT/wax ($C_{2.03}H_{2.64}N_{2.18}O_{2.67}$)
3. COMP B-3: 60/40 RDX/TNT ($C_{2.04}H_{2.50}N_{2.15}O_{2.68}$)
4. CYCLOTOL -75/25: 75/25 RDX/TNT ($C_{1.78}H_{2.58}N_{2.36}O_{2.69}$)
5. DATB: 1,3-Diamino-2,4,6-trinitrobenzene ($C_6H_5N_5O_6$)
6. DIPM: Dipiramide ($C_{12}H_6N_8O_{12}$)
7. EXP D: Ammonium picrate ($C_6H_6N_4O_7$)
8. HMX: Cyclotetramethylenetetranitramine ($C_4H_8N_8O_8$)
9. TNA: Trinitroaniline ($C_6H_4N_4O_6$)
10. NQ: Nitroguanidine ($CH_4N_4O_2$)
11. OCTOL-75/25: 75/25 HMX/TNT ($C_{1.78}H_{2.58}N_{2.36}O_{2.69}$)
12. PBX-9007: 90/9.1/0.5/0.4 RDX/Polystyrene/DOP/Rosin ($C_{1.97}H_{3.22}N_{2.43}O_{2.44}$)
13. PBX-9011: 90/10 HMX/Estane ($C_{1.73}H_{3.18}N_{2.45}O_{2.61}$)
14. PBX-9205: 92/6/2 RDX/Polystyrene/DOP ($C_{1.83}H_{3.14}N_{2.49}O_{2.51}$)
15. PETN: Pentaerythritol tetranitrate ($C_5H_8N_4O_{12}$)
16. RDX: Cyclomethylene trinitramine ($C_3H_6N_6O_6$)
17. TATB: 1,3,5-Triamino-2,4,6-trinitrobenzene ($C_6H_6N_6O_6$)
18. TETRYL: N-Methyl-N-nitro-2,4,6-trinitroaniline ($C_7H_5N_5O_8$)
19. TNB: Trinitrobenzene ($C_6H_3N_3O_6$)
20. TNT: 2,4,6-Trinitrotoluene ($C_7H_5N_3O_6$)

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