

Primary explosives: Electrostatic discharge initiation, additive effect and its relation to thermal and explosive characteristics

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Abstract

All explosives, under all conditions must be considered vulnerable to generation, accumulation and discharge of static charge. The low energy static hazards of the order as low as 2–3 mJ need to be guarded against in case of highly sensitive compounds namely primary explosives. The hazard is normally associated with manufacturing and filling operations due to discharge of static charge accumulated on a person supplying energy up to 20 mJ. To reduce the risk associated with static initiation hazard in the processing and handling of the explosives, the electrostatic sensitivity tests can provide an important input regarding electrostatic hazards. This paper presents electrostatic sensitivity data in terms of zero ignition probability data (E_{SE0}) of some of the initiatory explosives such as nickel/cobalt hydrazinium nitrate, silver azide, lead azide and mercury salt of 5-nitro tetrazole. Similar data has also been presented for samples coated with polyvinyl pyrrolidone to study its effect on electrostatic sensitivity. The electrostatic spark sensitivity of some conventional and novel made to explain the increased spark sensitivity behavior on the basis of the possible primary explosives has been studied. The electrostatic spark sensitivity of primary explosives decreased in the order of $AgN_3 > NHN > PbN_6 > MNT > CoHN > BNCP$. A possible correlation of spark energy with approximation and assumption has been drawn with thermal, detonation and mechanical properties. The polyvinyl pyrrolidone coated samples followed the same order but interestingly with increased spark sensitivity. An attempt has been reasoning of dielectric nature of the materials or exothermic effects of decomposition products of PVP. The present work also reports the electrostatic spark sensitivity of cap compositions.

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1. Introduction

The hazards related to explosives due to static charge/electricity have been studied since long. All explosives are high nonconductors and electrostatic potentials are developed upon these explosives. This can readily produce spark discharge between them and earthed articles. If such spark discharge takes place in the vicinity of explosive materials, even low energy spark of the order of 2–3 mJ is enough to initiate the primary explosives, which may lead to detonation causing damage to surroundings. The static discharge hazard is normally associated with manufacturing and filling operations accumulated on a person supplying energy up to 20 mJ. In estimating such types of electrostatic hazards associated with explosives, the informa-

tion of minimum spark energy required for initiating the primary explosives is most essential. Recent papers [1–6] published in the field of electrostatic initiation of sensitive energetic materials, bring out that spark sensitivity depends not only on the chemical entity of the material given granulometry and grain shape, mechanical properties, temperature and moisture content but also on the configuration of electrodes and structure of circuit [7]. There is no standard apparatus available for estimating the deflagration energy levels of such explosives. Therefore, it has not yet been possible to devise an international standards test specifying these hazards. There are several methods used in USA organizations [8]. RARDE in UK [9], Mizushima [10] and Kuroda and Nagaiishi [11] have been reported. Dahn et al. [8] showed that electrostatic discharge sensitivity obtained for energetic materials is dependant on the combination of electrodes configuration and circuit structures of the test devise. Thus, the methodology of the test is a key factor as widely varying minimum initiation energy values for the same explosive may be

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obtained with different apparatus. It is also possible that the ranking of the sensitivities of explosives may vary with same apparatus when the parameters or rate of energy delivery is changed. Thus, the data presented by several workers may be at variance owing to these factors and consequently, it is not responsible to compare the sensitivities determined by different apparatus.

This paper presents electrostatic sensitivity data in terms of zero ignition probability data (E_{SEO}) of some initiatory explosives prepared under the set conditions. It is well known that polyvinyl pyrrolidone (PVP) is being used in several applications including as a coating agent [12]. Thus, similar data have also been presented for explosive samples coated with PVP to study its effects on electrostatic sensitivity using an electrostatic discharge apparatus set-up developed within the laboratory for such purpose. Therefore this paper describes the experimental set up and deflagration energy levels obtained for various primary explosives.

2. Experimental

2.1. Materials and methods

The raw materials used in the present investigation for the preparation of various primary explosives were obtained from trade (AR grade) and were used as such without further purification. The primary explosives such as lead azide (LA), silver azide (SA), mercury salt of 5-nitro tetrazole (MNT), bis-5-nitrotetrazolato tetra amino cobalt(III) perchlorate (BNCP), nickel hydrazinium nitrate (NHN) and cobalt hydrazinium nitrate (CoHN) have been synthesized on laboratory scale under strict controlled conditions.

2.2. Preparation of primary explosives

2.2.1. Lead azide (LA) [13]

Lead azide was prepared by adding a mixed solution of sodium azide and sodium hydroxide to a well stirred solution of lead acetate in presence of sodium carboxymethyl cellulose (CMC) at room temperature. The product obtained was free flowing 95% lead azide having bulk density of 1.6 g/cm³.

2.2.2. Silver azide (SA) [14]

Silver azide was prepared by adding silver nitrate solution to a mixed solution of sodium azide and barium acetate in presence of a crystal habit modifier. The product obtained was having purity 99% and bulk density of 1.25 g/cm³.

2.2.3. Mercury salt of 5-nitro tertazole (MNT)

MNT [15] has been prepared by treating copper salt of ethylene diamine nitro tertazole with mercuric nitrate, starting from 5-aminotertazole and via copper salt of nitrotetrazole.

2.2.4. Nickel hydrazinium nitrate (NHN)

NHN was prepared by a method reported by Talawar et al. [16]. It involves treatment of nickel nitrate solution with hydrazine hydrate.

2.2.5. Cobalt hydrazinium nitrate (CoHN)

CoHN was prepared by a method similar to that for NHN; only cobalt nitrate is used in place of nickel nitrate.

2.2.6. Bis-5-nitrotetrazolato tetraamine cobalt perchlorate (BNCP)

BNCP was prepared [17] by treating 5-nitrotetrazole solution with carbonato tetraamine cobalt nitrate (CTCN) in presence of perchloric acid (6%) at 80 °C. The 5-nitrotetrazole has been prepared by a method reported [18], while CTCN has also been prepared by a reported method [19].

2.2.7. Cap composition – A for small arms ammunition (SAA)

The following ingredients physically were mixed:

- basic lead azide (BLA),
- barium nitrate,
- antimony sulphide,
- tetrazene.

2.2.8. Cap composition – B for small arms ammunition (SAA)

The following ingredients physically were mixed:

- lead styphnate,
- barium nitrate,
- antimony sulphide,
- tetrazene,
- glass powder.

The above ingredients were sieved through BSS No. 85 to avoid particle size effect on the spark sensitivity. Some of the above primary explosives (~0.5 g each) were coated with PVP of 2.5% dissolved in 5 cm³ of methanol and then drying the content by slow evaporation swirling occasionally.

2.3. Instrumental set up

An electrostatic spark discharge apparatus was designed and fabricated in the laboratory (Fig. 1). The basic and major components of the system are high voltage power supply (30 kV, 5 mA), condenser bank of high energy storage capacitors, high voltage vacuum relays, charging and discharging circuit. The values of the condensers in the condenser bank are 0.001 microfarad to 0.1 microfarad. The pointed electrodes are specially designed from copper rod of 10 mm diameter. The lower electrode is flat and Teflon ring is fixed over that to form a cavity. Thus small cavity is filled with the sample powder under investigation and the gap between the lower and top pointed electrode is adjusted to about 2 mm. The condenser in the condenser bank is charged to a high voltage and with the actuation of the vacuum relay. The stored energy in the condenser is discharged through a spark gap during time interval which is governed by the time constant of discharge circuit.

$$E = \frac{1}{2} CV^2$$

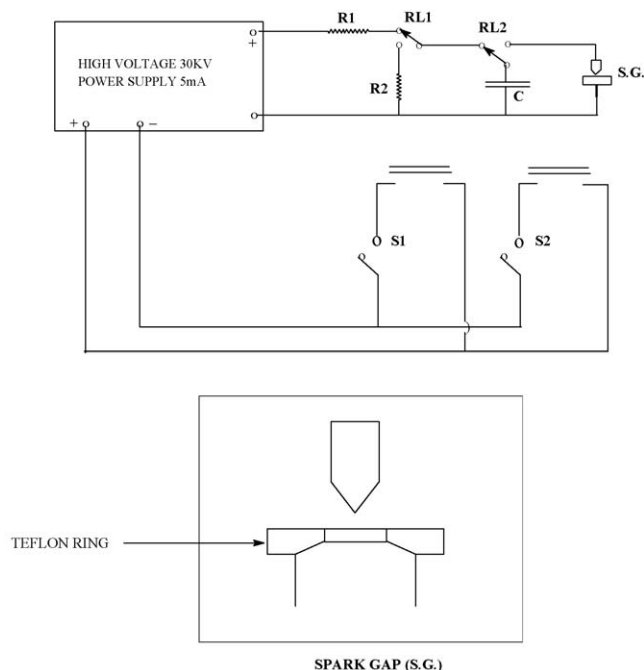


Fig. 1. Sparks sensitivity testing apparatus. R1: charging resistor – 10 M Ω ; R2: discharging resistor – 100 M Ω ; RL1: charging relay (high voltage vacuum); RL2: discharging relay (high voltage vacuum); SG: spark gap; C: high voltage energy storage capacitor; S1: switch for operating RL1; S2: switch for operating RL2.

where C is the capacitance in Farad, E the energy in Joules, and V is the charging voltage in volts.

After energy discharge, energy is gradually decreased either by charging the value of the capacitor or voltage or by combination of both as per requirement till no ignition/deflagration within the sample occurs.

3. Results and discussions

Using this system, a series of experiments have been systematically carried out for determination of spark sensitivity required for ignition/deflagration of prepared compounds as well as coated with PVP under controlled conditions of temperature and humidity. The results thus obtained are given in Table 1.

Table 1
Ignition energy values of explosive

Explosive	C (MF)	Voltage (kV)	Energy (J)	Temperature ($^{\circ}$ C)	RH (%)	Remarks
Lead styphnate	0.001	3.7	0.007	30	54	Ignited
Lead azide 1 (PVP coated)	0.001	10.0	0.050	26.3	53	Ignited
Lead azide 1 (PVP coated 97%)	0.01	6.8	0.231	26.1	57	Ignited
Lead azide 2 (uncoated)	0.001	11.0	0.0605	26.1	57	Ignited
Silver azide 1 (PVP coated)	0.003	5.0	0.0375	28.5	40	Ignited
Silver azide 2 (uncoated)	0.001	8.0	0.032	28.3	41	Ignited
Basic Lead azide	0.001	4.0	0.008	25	54	Ignited
MNT 1 (PVP coated)	0.003	8.6	0.111	26.7	49	Ignited
MNT 2 (uncoated)	0.01	8.4	0.353	26.6	51	Ignited
NHN	0.001	6.0	24.5	31.4	56	Ignited
BNCP	0.1	10	5.0	28.8	48	Not ignited
Cap comp. – A (for SAA)	0.03	4.0	0.240	32	55	Ignited
Cap comp. – B (for SAA)	0.001	10.0	0.050	30	50	Ignited

Table 2
Zero ignition probability data for primary explosive (PE)

Primary explosive	Zero ignition probability (mJ)	
	Uncoated PE	PVP coated PE
Silver azide	24	18
Lead azide	50	32
MNT	320	96
NHN	<5000	<1000
CoHN	<5000	<1000

The zero ignition data of each sample is obtained after establishing ten consecutive non-functioning of explosive sample. This indicated the insensitive limited character or zero ignition probability of the material. The ignition energy level for primary explosive like lead stephanie (LS), basic lead azide (BLA) and lead azide (LA) is less than 10 mJ, whereas NHN, BNCP and cap compositions based on BLA require ignition energy varies from 18 mJ to 5 J of BNCP. TNT and RDX require about 1.8 and 0.5 J energy for ignition/deflagration. The electrostatic spark sensitivity data obtained in the present study varies from the earlier reported data for the silver azide, lead azide and nickel hydrazinium hydrate. This is due to several factors including the type of instrument used for the study; particle size of the ingredients used, etc. The data obtained merits the in-depth studies on the electrostatic sensitivity of the materials/compositions used in the present study.

The electrostatic discharge ignition of explosives is considered to be dependant upon various physical characteristics of the energetic materials [20]. The ignition transient implies consumption of substantial amounts of available material. The energy delivered during the discharge lead to ignite the energetic materials depending on its levels and duration as well as the conditions related to confinement or pressure [21]. Therefore, it can be expected that the ignition energies may be responsible for setting the material to ignition depending on its deflagration/explosion or ignition temperature. Table 2 presents ignition energies along with the ignition/explosion temperatures, activation energy, velocity of detonation (VOD) and friction sensitivity for LA, SA, MNT, NHN and CoHN reported by various researchers [22–24]. The data indicates that it is not possible to

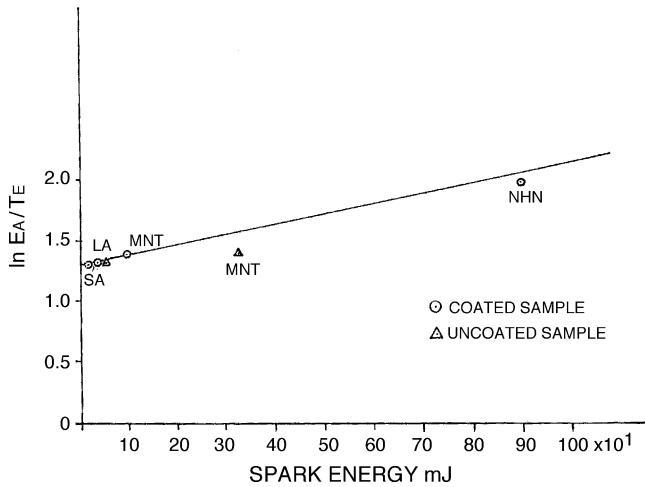


Fig. 2. Relation between spark sensitivity and activation energy.

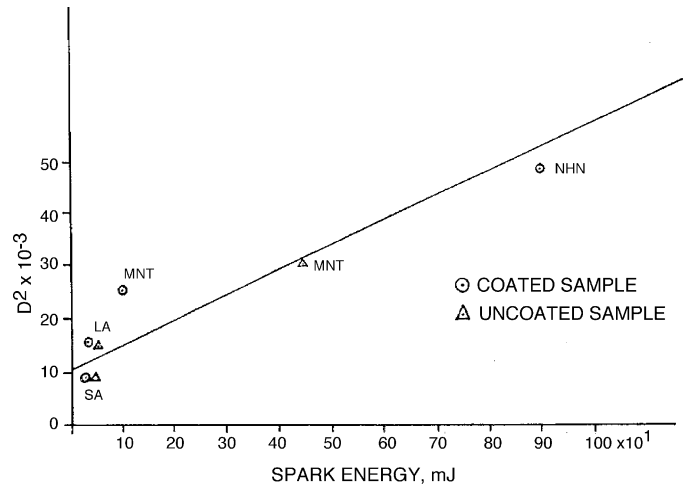


Fig. 3. Relation between spark sensitivity and velocity of detonation.

correlate ignition energies with explosion temperature or activation energies as Skinner et al. [20] also made similar observation. Present study brings out that the ignition spark energies for silver azide and lead azide is lower whereas respective explosion temperatures are higher than those of MNT, NHN and CoHN. The ignition spark energy and respective explosion temperature for energetic materials do not appear to have direct relationship. However, in spark initiation process [25] it appears that when explosive is heated to a critical temperature (thermal explosion temperature) and then subsequently the heated material self ignites, self ignition characteristics of the compound distinguishes the energetic material with respect to spark sensitivity characteristic [24].

The existence of general formula given below represents a motivating fact for evaluation of mutual relationship between the electrostatic spark sensitivity and detonation characteristics

$$\ln(E_p T_D^{-1}) = aX + b \quad (1)$$

where T_D is the temperature of the onset of their thermal decomposition and X is the spark energy for 50% probability of initiation. Assuming the E_{SEO} close to initiating spark energy and taking ignition/explosion temperatures as T_D , Fig. 2 indicates that in spite of the approximation and assumption there appears to exist reasonably close relationship between spark energy and the expression $E_a T_D^{-1}$, where E_a is activation energy. This is in agreement with a successful correlation made between the observed ESD sensitivity critical temperature for thermal run away and thermal decomposition rate coefficient of explosives.

The expression $E_p T_D^{-1}$ and $E_a T_D^{-1}$ correlates well by means of the general form of Eq. (1) with detonation characteristics where E_a is the activation energy of decomposition. In this case X is the square of detonation velocity D^2 or the heat of explosion Q or the ratio of detonation pressure P and density ρ of the compound ($P\rho^{-1}$)

$$D^2 = AE_{ES} + B \quad (2)$$

Thus, it is very interesting to note that ignition energies (ESE) varies with velocity of detonation (Fig. 3) which depends

upon the physical properties of the energetic materials, density, thermal characteristics, etc. Similarly like detonation property, friction sensitivity also appears to vary with spark sensitivity in the high sensitive range (Fig. 4). The role of the mechanical properties [26] in facilitating ignition by maintaining surface hot spot pressure developed by the discharge and the products of the reaction appears to be an important phenomenon. The spark sensitivity data on coated and uncoated samples indicate that the PVP coated samples become more sensitive to electrostatic energy in comparison to uncoated samples. It reveals that the PVP coat surrounding the explosive crystals probably modifying the energy discharge through the spark. There is a possibility that PVP layer may act as a dielectric media which may be modifying the spark sensitivity. Similar phenomenon has been reported for epoxy coating on a steel, waxed paper and filter paper placed on a cathod [27]. This can also be supported by the fact that some pyrotechnic or propellant compositions have been found sensitive to spark with the energy level even below 10 mJ. Therefore, we can say it is probably dependant on the nature of coating material. This is further supported when we take an example of ammonium perchlorate (AP) and aluminum based composition

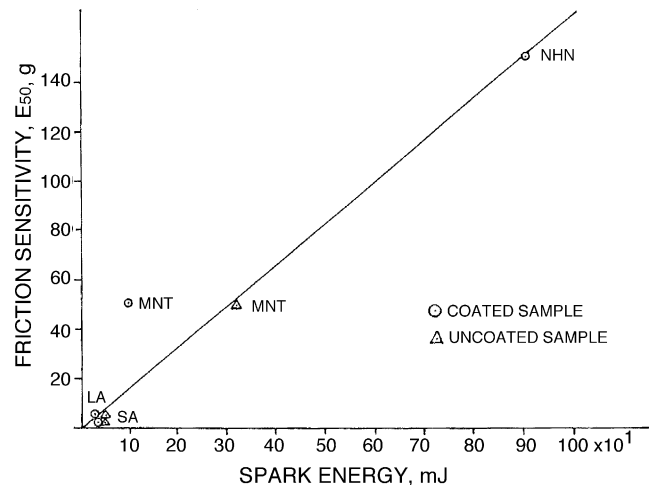


Fig. 4. Relation between spark sensitivity and friction sensitivity.

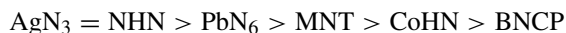
Table 3
Properties of primary explosives studied under present investigation

Primary explosive	E_{SEO} (mJ)	Deflagration temperature (K)	Friction sensitivity, E_{50} (g)	Activation energy (kcal/mol)	VOD (m/s)
Silver azide	18	548	5	165	3000
Lead azide	32	623	50	165	4500
MNT	320	503	500	113	5000
NHN	<1000	493	1000	75	7000
CoHN	18	463	6000	160	6500
BNCP	5000	535	1000	33	5700
Comp. A	150	620	10000	–	–
Comp. B	100	575	8000	–	–

where there is no initiation up to spark energy 541 mJ as against 37 mJ for similar formulation with binder (AP/Al/Binder) [20]. Therefore a polymerized material like PVP/epoxy resin markedly increase the spark sensitivity character. Similarly the author has tried probable correlation of spark energy with thermal, detonation and mechanical properties (Table 3).

4. Conclusion

The electrostatic spark, mechanical sensitivities, thermal and velocity of detonation (VOD) of some conventional and new developed energetic materials have been studied in detail. From the findings, a probable comparative nature of the primary compounds with respect to electrostatic spark sensitivity is in the decreasing order as follows:



A possible correlation of spark energy with approximation and assumption has been drawn with thermal, detonation and mechanical properties. The polyvinyl pyrrolidone coated samples followed the same order but interestingly with increased spark sensitivity. An attempt has been made to explain the increased spark sensitivity behavior on the basis of the possible reasoning of dielectric nature of the materials or exothermic effects of decomposition products of PVP.

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References

- [1] T.E. Larson, P. Dimas, C.E. Hannaford, Electrostatic sensitivity testing of explosives, at Los Alamos Inst. Phys. Conf. Ser. No. 118 Section 2 (Electrostatic 91) IOP Publishing Ltd., 1991, pp. 107–117.
- [2] M. Roux, M. Auzanneau, C. Brassy, Propell. Explos. Pyrotech. Part I 18 (1993) 317–324.
- [3] M. Auzanneau, M. Roux, Propell. Explos. Pyrotech. Part II 20 (1993) 99–101.
- [4] M. Roux, A. Trevino, M. Auzanneau, C. Brassy, 'Sensible des substances explosives' 16th Annual Conference ICT, Karlsruhe, 1985, pp. 3.1–3.15.
- [5] J.P. Chaumat, AUSSOIS (1996) 173–179.
- [6] T. Hasegawa, E. Kawashima, K. Satoh, T. Yoshida, "Correlation Between Screening Test Results of energetic materials", 22nd International Pyrotechnic Seminar, Fort Collins, Colorado, July 1996, pp. 195–207.
- [7] S. Amari, F. Hosoya, Y. Mizushima, T. Yoshida, "Electrostatic Spark Ignitability of energetic materials", 21st International Pyrotechnic Seminar, Moscow, September 1995, pp. 13–31.
- [8] C.J. Dahn, A. Kashani, M. Nguyen, "New Concepts in Studying Electrostatic Discharge Hazards of Propellants, Pyrotechnics and explosives" 17th International Pyrotechnic Seminar, Beijing, China, 28–31 October 1997, pp. 941–944.
- [9] RARDE, Sensitiveness Collaboration Committee Manual of Tests No. 6 Electrostatic Spark Test, March 1966.
- [10] Y. Mizushima, Electrostatic Spark Sensitivity of explosives, Kogyo Kayaku 39 (3) (1978) 129.
- [11] E. Kuroda, T. Nagaishi, "Ignition Mechanism of Pyrotechnic Materials by Electrostatic Discharge" 18th International Pyrotechnic Seminar Breckenridge, Colorado, USA, 13–17 July 1992, pp. 511–523.
- [12] H.W. Voigt Jr., Polyvinyl Pyrrolidone surface alteration of fine crystalline explosives for desired effects, Int. Symp. Povidone (1983) 456–470 (Eng).
- [13] L.M. Dennis, A.W. Browne, Inorg. Chem. 40 (1904) 68.
- [14] Costain, S. Thomas, U.S. 394,323,509 (1976).
- [15] W.H. Gilligan, M.J. Kamlet "Synthesis of Mercuric-5-Nitrotetrazole" US NTIS AD Report 1976. AD-A036086 15pp. (Eng) available NTIS, From Govt. Rep Annance Index (US) 1977, 77(10), 248. Chem. Abstr., 87 (1977) 154288.
- [16] J.S. Chhabra, M.B. Talawar, P.S. Makashir, S.N. Asthana, Haridwar Singh, J. Hazard. Mater. A 99 (2003) 225–239.
- [17] M.B. Talawar, A.P. Agrawal, S.N. Asthana, J. Hazard. Mater. 120 (1–3) (2005) 25–35.
- [18] Jenkins J.M. and white, J.R. (1970). ERDE-TN-21, Jenkins, J.M. and White, J.R. (1974) ERDE – TR – 172.
- [19] J. Fronabarger, A. Schuman, R.D. Chapman, W. Fleming, W.B. Samborn, T. Massis, "Chemistry and development of BNCP, a novel DDT Explosive", AIAA 95-2858, Presented at the 31st Joint propulsion conference and Exhibit, San Diego, CA, July 1995, pp. 10–12.
- [20] D. Skinner, D. Olson, A.B. Boltan, Propell. Explos. Pyrotech. 23 (1998) 24–42.
- [21] R. Roger, I. Jean, "The static Electricity Hazards: Methods of assessing Pyrotechnics Sensitivity and Approach for Hazard Reduction", 26th International Conference of ICT July 4–7, Karlsruhe, Federal Republic of Germany, 1995, pp. 38.1–38.10.
- [22] M.A. Schrader, M.W. Leeuw, A.C. Vander Steen, "The Thermal Step Test: A Key to High Temperature Behaviour of Explosives" 9th International Pyrotechnic Seminar, IIT Research Institute, Chicago, IL 60616, 1984, pp. 881–890.
- [23] J.S. Chhabra, M.B. Talawar, K.U.B. Rao, S.N. Asthana, Haridwar Singh, Mercuric-5-Nitrotetrazole: A Thermally Sensitive Promising Primary Explosives (unpublished work).
- [24] M. Auzanneau, M. Roux, Propell. Explos. Pyrotech. 20 (1995) 96–101.
- [25] S. Zeman, Thermochem. Acta 41 (1980) 199–212.
- [26] A.M. Mellor, P.J. Baker, J. Energetic Mater. 12 (1994) 1–62.
- [27] M.S. Kirshenbaum, "Functional Circuit Parameter Approach to the Electrostatic Sensitivity of Primary Explosives", International conference on "Research on Primary Explosives" Editors, ERDE, Waltham Abbey, England, 1975.