

## Electrostatic Discharge and Energetic Materials

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### Abstract

In this short review, excerpts from the literature on electrostatic discharge which includes physics of electric spark, charging of organic molecules, sensitivity measurements, some theory and predictions, and electrostatic discharge values of some group of explosives, including nitro compounds, nitramines, composites thermites, etc., have been presented.

**Keywords:** Electrostatic Discharge; Spark; Explosives; Sensitivity; Predictions.

### 1. Introduction

The decomposition reaction of energetic materials can be triggered by various external stimuli, such as impact, friction, heat, static compression, and electric spark. Electrostatic spark is a common ignition stimulus for both condensed and gaseous flammable substances [1,2]. Electrostatic discharge ignition of flammable gases was studied in great detail. Electric spark sensitivity is an important characteristic of explosives too, especially primers and propellants. However, this initiation of explosives has not attracted much attention in the past as it needs to have.

### 2. Physics of electric spark

Static electricity is a ubiquitous part of everyday life. It is one of the oldest scientific phenomena that people observed and described. Greek philosopher Thales of Miletus made the first account; in his sixth century B.C. writings. It took almost 2,000 more years to pass before the English word "electricity" was first coined, which had based on the Latin "electricus," meaning "like amber". Benjamin Franklin and Mikhail Vasilievich Lomonosow are to be remembered who made a great contribution to understanding of the underlying mechanism of electricity [3]. Although, tiny amount of charge in static electricity is rather innocent. Nevertheless, these little sparks can be fatal sometimes to sensitive electronics, such as the hardware components of a computer. A more serious threat is an electric discharge in the vicinity of flammable gases or explosive materials of conventional sense. It has been becoming increasingly important to understand the electro static discharge sensitivity of energetic materials. Probably the most common form of electrostatic discharge (ESD) is the spark, which occurs when the static electric field strength exceeds approximately 4-30 kV/cm (i.e., the dielectric field strength of air [1]). Invisible forms of ESD can also deliver sufficient energy to ignite an energetic material. Some electronic devices can be damaged by invisible ESD threshold energies as small as 0.082 nJ [4]. In fact, ESD is a main cause of ignition of powders such as dust [5], food [6], and textiles [7], as well as explosives [8-11].

Note that electrical resistivity of a material shares an inverse relation with its conductivity. These properties define how well a given material will dissipate charge. The electrical conductivity of mixtures may be altered by introducing additives or impurities. For example, aluminum (Al) is added as a metallic filler to increase electrical conductivity in epoxy coatings [12]; whereas, silica fume (fine grain SiO<sub>2</sub> particles) is added to cement paste to decrease its electrical conductivity which results in more corrosion resistance [13]. Similarly, additives affect the ESD sensitivity of energetic materials.

Electrons are retained in the atomic structure by the electrical attraction of the positive charge of the nucleus. In general, the outermost electrons are held less firmly in the atom structure than the inner electrons. The

outer electrons of atoms of metallic elements in particular are loosely held and are easily affected by outside forces. It is apparent that the external forces involved in generating electrification cannot influence the protons which are securely bound within the nucleus. When two appropriate materials are brought into close contact, some of the loosely held electrons may be transferred from one material to the other. In the case of molecules in the bulk, inter and/or intramolecular interactions influence the molecular orbital energies as compared to the free molecule in vacuum. All these interactions, affect the resistivity, dielectric constant, polarizability etc., thus the ESD character of the material changes (see the paragraphs below).

Although an electronic charge is easily transferred in a conductor material, insulators are such poor conductors that for the practical purposes they are considered to be nonconductors. Liquid solutions and confined gases conduct electricity in a different way than solids. Even though, the outermost electrons are rather firmly held within the atomic structure, an isolator still may have few free electrons. Nevertheless, the motion of free electrons is highly hampered by the strong nuclear charges. If an excess of electrons is transferred to one particular region of such an isolator material, the extra electrons remain in that region (local charges, bound charges) with little dispersion, in contrast to free electrons of a conductor which surge in the direction to reduce the intensity of the charge [14, 15].

Every object has an inherent electric field as a result of the electrons in the material. This includes conductive as well as nonconductive materials. The electric field around isolated objects are different than the electric field around two objects that are physically connected or in contact. When two connected objects are suddenly separated, the original initial electric field changes and the electrons must be redistributing themselves to form a new electric field. If both objects are conductive, the electrons are able to move rapidly/freely through and between the objects as they are being separated. The net result after separation is two objects at identical voltages. However, if one or more of the objects is nonconductive (insulators), the electrons are unable to move rapidly as the objects are being separated. Then, the final result after separation is two objects with opposite but equal charges. Separation is one mechanism for development of static charge generation [16].

In their natural state, gases do not conduct electricity and therefore are isolators. Thus, it is clear that a gas can be made conductive if free carriers of charge (charged particles) are introduced or created in it somehow. This can be done either by producing these charged particles by the action of an external factor or introducing them from outside (extrinsic conductivity) or by creating them in the gas by the electric field existing between the electrodes (intrinsic conductivity) [3].

### *2.1. Kinds of spark (electrostatic discharge process)*

Spark discharges may occur between conductors possessing different electrical potentials. A spark is a discrete discharge that leaks through a gap between two conductors in the form of an ionization path in which the stored energy is transferred swiftly (sometimes with sound and/or light but sometimes silent discharge occurs). The spark is triggered when the breakthrough field strength is reached at a certain point in the gap. Also, a sufficiently high field strength is required in the whole space between the electrodes so that the discharge can travel through that space. Thus, a homogeneous electrical field between the electrodes is an important requirement.

In contrast to spark discharges, corona discharges are typical one-electrode discharges which occur in an inhomogeneous electrical field at conductive and earthed sharp end points [16].

A material (generally solid) in an electric field acts as a dielectric material and when the field strength is sufficient, spark generation and the breakdown of the material occurs. The physical pattern of the breakdown of dielectrics may broadly vary in different cases. There are two main kinds of breakdown that is the electric and electro thermal breakdown (operative in ESD sensitivity tests).

## 2.2. Electric breakdown

It is simply nothing but the destruction of a dielectric by the forces of an electric field. The secondary processes (heating, chemical reaction, etc.) never take place with a purely electric breakdown [16].

An electric breakdown develops as a result of interaction of free charged particles (electron, ions, etc.) accelerated by an electric field with the particles of a dielectric or as a result of inelastic displacement of bound charges in a dielectric under the action of an electrical field.

The electric breakdown is characterized with small dependence of  $E_{BR}$  (electrical breakdown potential) or the frequency of the applied voltage, short time of development, small dependence of electric strength on temperature and low dependence of electric strength on the dimensions of the dielectric and the electrodes [16].

## 2.3. Electro thermal breakdown

At a given electric field intensity, dielectric losses increase with an increase in the conductivity ( $\gamma$ ). If alternating voltage is employed, the specific dielectric losses are higher, higher the frequency of the voltage.

An electro thermal breakdown develops when a voltage is applied to a dielectric which consequently liberates heat, thus the temperature of the dielectric rises and energy losses are therefore increase more, so that the process is intensified until the damage occurs. It is enough to heat some one spot of a dielectric. However, if the dielectric loss factor and the conductivity are small and the rate of them increase with increasing temperature is insignificant while the coefficient of thermal breakdown of the dielectric is high, then the thermal breakdown develops with difficulty [16].

Commonly a given dielectric material cannot be described by a definite mechanism of breakdown. Note that formation of spark should be a competitive process between the breakdown potential of air and the dielectric (such as an energetic material). Which one occurs first depends on the nature of the dielectric, temperature, humidity, pressure, etc.

In the case of spark discharge (intrinsic conductivity) when the potential between the electrodes increases and the intensity of field reaches to about 30000V/cm, an electric spark appears between the electrodes in the form of a bright tortuous channel connecting the two electrodes. The gas nearby the spark is heated to a high temperature and suddenly expands, producing sound waves perceived as a crackle [3]. Note that the appearance of an ionic avalanche not always lead to the formation of a spark, but may result in a different type of discharged called "corona discharge" [3].

A spark is well defined and has a sharp, needle like appearance. The charge exists and enters both conductors from a single point. Energy levels for spark can be as high as 1000 mJ, which is more than enough to ignite both combustible dusts and vapors. A brush discharge occurs between a conductor and a nonconductor. In this case the discharge exists from the conductor at a fixed point and has a fuzzy appearance towards the nonconductor as the charge is absorbed across a part of its surface [16] which is the case for most of the organic molecules.

A corona discharge is a special case of a brush discharge occurring between a charged nonconductor and a conductor having a small radius of curvature. These discharges have certain limited energy and capable of igniting the most sensitive gases (e.g., Hydrogen). A propagating brush discharge can occur between a grounded conductor and a charged insulator which is backed by a conductor. These discharges are very impressive and may ignite flammable vapors and dust [16,17].

### 3. Charging of organic molecules

Organic and inorganic molecules constitute the dielectric materials. Energetic materials, either primary or secondary type fall into one of these groups of molecules which have varying dielectric constants although conventionally they are not considered as dielectric materials. In general, dielectric or insulating materials are defined as the materials in which electrostatic fields can persist for a long time [18]. These materials offer a very high resistance to the flow of electric current under the action of the applied direct current voltage. Therefore, they sharply differ in their basic electrical properties from the conductive materials. However, it is to be noted that dielectric break down occurs if the applied potential is increased up to a certain voltage characteristic of the material.

The outer (valence) electrons of an atom at the levels of a filled (valence) band of a dielectric are not free. Therefore, they cannot participate in the transfer of the charge and the formation of electric current in mater. However, they can be free after passing through the forbidden band and reach the vacant band if they receive considerable amount of energy from outside. Because of this reason the conductance of dielectrics under ordinary conditions is negligibly small. Note that the forbidden band mentioned above is small for semiconductors and nil for metallic conductors.

The magnitude of resistivity of each dielectric material (as well as its other electrical parameters) is not strictly definite and invariable but depends on a number of factors such as the presence of impurities, humidity, temperature, applied voltage, time period of holding under voltage etc. [18]. When a moistened material is heated, the value of resistivity ( $\rho$ ) first increases (effect of drying predominates over the effect of increase in temperature) and begins to decrease only after a considerable portion of moisture is removed. On the other hand, the insulation resistance does not remain invariable when the applied voltage changes. Approximately, the conductivity ( $\gamma$ ) follows the Frenkel's equation.

$$\gamma = \gamma_0 \exp(\beta\sqrt{E}) \quad (1)$$

where  $\gamma_0$  is the conductivity of the material in a very weak field,  $E$  is the applied field strength and  $\beta$  is the parameter of the material [18].

When a direct current voltage is applied to a dielectric material, in most of the cases gradual drop occurs in the current in the course of time. Namely, the conductivity decreases and resistivity increases. The change in the conductivity in time is attributed to the effect of formation of space charges, electrolytic processes in a dielectric and some other causes.

The most important property of dielectrics is their ability to be polarized under the action of an external electric field. The state of a dielectric placed in an external electric field can be described by two vector quantities, namely intensity of an electric field  $\mathbf{E}$  and polarization  $\mathbf{P}$  which are interrelated as.

$$\mathbf{P} = k_e \epsilon_0 \mathbf{E} \quad (2)$$

Where the product  $k_e \epsilon_0$  is known as the absolute dielectric susceptibility [18]. The intensity of an electric field characterizes the force of this field exerted on electrically charged bodies or particles. Polarization is also defined as the surface density of a bound charges in a dielectric.

If the molecule is initially nonpolar, the polarization leads to the formation of an electric dipole moment. If it is already polar one then it leads to an additional component of the dipole [19]. Note that energetic materials due to the presence of explosophoric groups (e.g.,  $\text{NO}_2$ ) in their structures are generally highly polar molecules and characterized with quite high dipole moments as long as the geometrical factors allow.

For isotropic dielectrics, vectors  $\mathbf{P}$  and  $\mathbf{E}$  coincide at each other and the factor of proportionality between them is a scalar quantity. Whereas for anisotropic dielectrics the relation between them is tensorial ) [18].

In general, when a molecule is placed in an electrical field, electron distribution and the molecular geometry are distorted [19-21]. The polarizability is a measure of the ease of this process. The atomic, electronic and the orientation polarizability are the contributors to the overall polarizability of a molecule in an electrical field [19]. When the molecules have a permanent dipole, the applied field orients these molecules and the entire sample acquires net polarization. Highly polarizable molecules respond strongly to the application of the field and they become highly polarized, thus the centroid of negative electronic charge is displaced [19,22]. At the molecular level, applied electric field,  $\mathbf{E}$ , interacts with the charge distribution of the system to produce a force ( $\mathbf{F}=\mathbf{q}\cdot\mathbf{E}$  where  $q$  is the charge) that causes displacement of the electron density away from the nuclear framework which consequently results in a separation of the positive and negative charge centers and consequently an induced dipole,  $\mu^{\text{ind}}$  arises [22]. Energy ( $\epsilon$ ) of polarizable molecule in a field  $\mathbf{E}$  is given by [19-22],

$$\epsilon(E) = \epsilon^0 - \mu^0 E - \frac{1}{2} \alpha E^2 - \frac{1}{6} \beta E^3 + \dots \quad (3)$$

Where  $\mu^0$  is the permanent dipole moment,  $\alpha$  is the polarizability and  $\beta$  is the first hyperpolarizability. The dipole moment in a field  $E$  is [19],

$$\mu = \mu^0 + \alpha E - \frac{1}{2} \beta E^2 + \dots \quad (4)$$

If the electric field increases sufficiently, polarization results in ionization of the molecule as a limiting case. In the literature there exist various studies about the charged forms of energetic materials [23-28]. The effect of static electricity on explosive materials was discussed in various articles [29,30].

Usually, experimentally obtained results of the spark energy are hard to interpret in terms of structure-activity relationship concept because very many factors (electric and/or electro thermal spark formation, involvement of bound charges, etc.) are operative. Also, it is a matter of question what mechanism of explosion at those conditions occurs. Usually, no idea can be obtained whether cations or anions are involved in some stage of the spark induced explosion mechanism.

When a substance is placed in an electric field, it might be polarized and then ionized before undergoing any possible decomposition to occur under the applied conditions. However, at the beginning logically it might be assumed that when sparking occurs over an organic molecule, the structure gains or loses electron(s) prior to disintegration of the molecule into fragments. In other words, decomposition of the molecule in an electric field should generally occur via its anionic or cationic form(s). So, the simplified possibilities for the fates of structures (initially neutral but in the electric field polarized and charged) could be some electron transfer (single or multiple) processes involving the HOMO or LUMO levels [23-30].

#### 4. Spark sensitivity measurements

In the case of energetic materials, the situation in electrostatic spark sensitivity (electric spark discharge, ESD) measurements are more complicated than most of the other sensitivity measurements. The problem lies in the fact that there are variety of testing instruments and modes of discharge units. Some of them are oscillating, some damped etc., [9,31,]. These ample cases make the comparison of the various relevant data present in the literature practically impossible [32].

There are several different approaches and types of apparatus reported in the literature for measuring electric spark sensitivity ( $E_{ES}$ ) [11, 33-37]. The  $E_{ES}$  values corresponding to these various options are to be found in the literature [31, 9, 36-39] (in decreasing order of magnitude [38, 39]). There are mainly two types of test apparatus/method commonly used to measure the ease of ignition of initiator materials by electric sparks. The first type, called fixed-gap method, in which a voltage is applied across two electrodes (one of which is

covered by the material steel) and the voltage is sufficient to break down the gap and causes a spark to pass. The second type, an approaching-electrode method, in which the gap is initially too idle for a discharge to take place with the voltage applied, but a spark is produced by moving one of the electrodes towards the other. The energy dissipated, in the discharge varied by changing the applied voltage or the capacity of the condenser used for the electrical energy.

Typically, a spark is generated by a high-voltage capacitor discharging over a gap between a sharpened electrode and a powder bed. The sharpened electrode can approach the surface or be fixed at a certain distance from it. The minimum capacitor energy at which the powder ignites is specified as the minimum ignition energy (MIE), which is a parameter defining the sensitivity of a powder to ESD ignition stimulation [1].

It has been suggested by Skinner that the spark represents primarily a thermal source capable of raising the temperature of a flammable powder above the point at which thermal runaway occurs [8]. However, it remains unclear how the spark heats the particles of the powder, what proportion of the spark energy is being transferred to the powder particles and by which mechanism [40]. Also, it remains unclear whether the polarity of the spark discharge is a factor affecting the ignition energy [40]. The thermal and electrical conductivities of powders are initially governed by the respective contact resistance between the particles. Then spark itself should behave as an unsteady heat source and the expected energy distribution should change as a function of time and location [40].

Presently, in literature, the current protocols used for ESD ignition sensitivity [39] testing mostly are not based on the understanding of the ESD ignition mechanism. Therefore, the reported results are often inconsistent between different testers and inconclusive in nature [40].

In short basically there are two types of instruments in ESD operation and there is a difference between their measurements. If there exists an air gap between the electrode(s) and the specimen being tested, the break down potentials of air and the sample (dielectric) have to be considered whether the electrostatic explosion is due to local heat induced by the spark [9,42] or electrostatically induced (via polarization followed by ionization of the sample molecules) decomposition. In the direct contact of electrodes with the sample mainly polarization followed by ionization process should be effective.

One of the instruments used for testing of electrostatic discharge behavior of powders is a model 931b Firing test system (FTS) by Electro-Tech Systems Inc., described in the literature [41]. FTS includes a capacitor bank with capacitance variable in the range of 100-10000 pF. The capacitors can be discharged through the spark gap directly or through an additional resistor varied from 500 to 5000 Ohm. The capacitors can be charged to a voltage varied from 100 V to 26 kV. Also, the polarity of the electric output can be changed so that the high-voltage electrode can be either positive or negative. For a typical test, the material is placed into a grounded stainless-steel cup, then the high voltage pin-electrode (stainless steel) is placed 0.2 mm above the surface of the specimen. Providing sufficient energy, ignition takes place.

In quite recent years, Zeman and coworkers [36,38,39,42,44] have described details of measurements with two instruments marked as RDAD and ESZ KTTV. For the RDAD instrument, they reported the electric spark sensitivity of 15 polynitro compounds and compared their results with some of the literature data [36]. They found a linear relationship between their own experimental data ( $E_z$ ) with some other authors ( $E_{pub}$ ) [36].

$$E_z = AE_{pub} + B \quad (5)$$

Where A:3.821, B:3.015 and R: 0.8925.  $E_{pub}$  data belong to Larson et al., [11]. Another relationship they found makes use of the data of Amari et al., [43] having A: 0.128, B: 1.885 and R: 0.8368 [36]. Zeman et al., additionally reported electric spark sensitivity of a large set of polynitro compounds of secondary explosive type [39,42,44-49]. Since the outputs from the RDAD instrument satisfactorily correlated with those obtained by other methods of determination of the electric spark sensitivity in some recognized laboratories [49], in recent years different predictive models have been developed for nitramines [50-52]. Zeman and coworkers

tried to establish a correlation between electric spark sensitivity of 32 polynitroarenes and their detonation velocities [48]. A similar research was reported for 12 nitramines [49]. Moreover, the reported electric spark sensitivities for nitramines have also been correlated with detonation performance [53], impact sensitivity [54], thermal stability [55], and shock sensitivity [56]. All of these studies were used as the outputs of the RDAD instrument. Since the RDAD instrument is not suitable for determination of the sensitivity of primers and pyrotechnics, Zeman et al. [36, 39] have developed the ESZ KTTV for measurements of energetic materials within the whole scope of technically attractive sensitivities. They compared differences between outputs of both instruments from the point of view not only numerical values but also molecular structure [36,39].

An ESZ KTTV instrument is a new, relatively simple construction and has been applied to determination of electric spark sensitivity ( $E_{ES}$ ) of 34 polynitro arenes and their derivatives. The results obtained by Zeman and coworkers were compared with those from measurements made by means of older RDAD instrument. The analysis of relationship between the  $E_{ES}$  values obtained by measurements on these two instruments have revealed that the relationship is not unequivocal. The results made Zeman and coworkers come to the conclusion that the mechanisms of spark energy transfer into the reaction centre of molecule should be different in measurement on the two alternative instruments. Measurement by means of the ESZ KTTV system is more sensitive to molecular structure of the studied polynitro compounds [45].

The RDAD and the ESZ KTTV instrument differed mainly in the construction of their spark gaps because the discharge in the spark gap for the RDAD has gone through an air gap whereas the electrode of the ESZ KTTV [36, 39] (e.g. in ESD 2008A [57]) has a direct contact with the sample. Since considerable electrical energy losses in the air gap between the upper electrode and the sample surface occurs in the case of the RDAD, a large part of the discharge energy should have been converted into the expressive thermal component.

As for the details of RDAD instrument; its wiring and its spark gap are presented in the related papers [58,59]. The bottom electrode is a steel base which has an attached screw as a leak electrode in the centre. To this screw a plastic cylinder is attached with a cut for fastening a piece of flexible tubing of 5 mm height and 5 mm diameter serving as a container of the sample tested. The top electrode is a steel cylinder having a conical shape with attached resistance wire protected by a plastic distance stop, which presses an Umafol lid to the flexible tubing. The capacity of the capacitors was chosen so as to allow measurements in the voltage range of 8 to 14 kV. If the initiation was successful, the next measurement was made with a voltage lowered by 0.2 kV; if it was unsuccessful, the voltage was increased by the same value. The authors considered an initiation as successful if the sample disappeared or the flexible tubing was torn. Altogether 25 measurements were made with each substance and the results were treated in the sense of eq.6 by means of the "up and down method".

$$E_{ES} = 0.5 \cdot C \cdot U^2 \quad (6)$$

The energy of electric spark,  $E_{ES}$ , required for 50% initiation probability was calculated (up and down method) from the know capacity  $C$  (in F) of the circuit and voltage  $U$  (in V) at the condenser [45].

The instrument named ESZ KTTV is designed for a small-scale sensitivity testing of energetic materials [60-62]. Basically, a high voltage power supply (variable operating voltage of 4-10 kV) and a set of capacitors of overall variable capacity in the range from 100 pF to 350 nF produce an electrostatic discharge having total energy from 10 mJ to 16 J. In the experiment, a sample of 1 mm height is fitted into an isolation tube which is mounted on the lower cylindrical metal electrode. The upper electrode is equipped with manually adjustable vertical positioner. The micro container itself is placed in a separate test box having ventilation. The time behavior of the voltage and current at the spark gap was registered with a scope and then the data were evaluated using a microcomputer to yield the effective energy transmitted to the sample.

On the other hand, standardization of electrostatic test methods attracted attention as well. In the article of Smallwood, these efforts are summarized [63]. Progress in world standards developed by the International Electro technical Commission (IEC) Technical Committee 101 (Electrostatics) has so far been mainly driven by

the needs of the electronics industry, but has also laid down basic materials test methods, test methods for specific applications, and requirements for protection of electronic devices from electrostatic damage [63].

## 5. Theoretical methods and calculations

Often electrostatic discharge ignition of explosives, pyrotechnics, or propellants is considered to be mainly dependent upon various physical characteristics of those energetic material. The work by Skinner and coworker, shows that ESD ignition of secondary explosives tested in powdered form is primarily dependent upon the chemical characteristics of the energetic material (i.e., the decomposition rate kinetics of the materials) [8]. It was proposed that ignition occurs when a spark raises the temperature of the explosive particles to the point where thermal runaway occurs. The ESD sensitivities of explosives falling in to diverse series of samples were measured using a traveling needle test apparatus with the powders slightly confined by Mylar tape to prevent formation and ignition of a dust cloud.

Using global thermal decomposition rate coefficient expressions, two parameters were calculated for each explosive. These are the critical temperatures according to the Frank-Kamenetskii formula for 20  $\mu\text{m}$  particles of each explosive and the temperatures at which the rate coefficient equaled to  $10^3 \text{ s}^{-1}$ . These two sets of collected data were correlated with the observed ESD sensitivities for 50 percent probability of ignition,  $E_{50}$ . Some excellent correlations have been obtained for ESD ignition under these conditions, that the spark discharge is primarily a thermal source [8].

Wang and coworkers employed the DFT method (B3LYP/6-31G(d)) to optimize molecular geometries and electronic structures of thirty-nine nitro arenes [64]. The averaged molar volume ( $V$ ) and theoretical density ( $\rho$ ) were estimated using the Monte-Carlo method, based on 0.001 electrons/bohr<sup>3</sup> density space. The detonation velocity ( $D$ ) and pressure ( $P$ ) of the explosives were estimated by using the Kamlet–Jacobos equations on the basis of the theoretical density and heat of formation ( $\Delta_f H$ ), which was calculated by using the PM3 method. The reliability of this theoretical method and results were tested by comparing the theoretical values of  $\rho$  and  $D$  with the experimental or referenced values. Then the theoretical values of  $D$  and  $P$  were correlated with the experimental values of electric sensitivity ( $E_{ES}$ ). Table 1 displays the electric sensitivities of various nitroarenes.

No	Name	Code	$E_{ES}$ (J)
1	1,3-Dinitrobenzene	1,3-DNB	3.15
2	1,4-Dinitrobenzene	1,4-DNB	18.38
3	1,3,5-Trinitrobenzene	TNB	6.31
4	1-Methyl-2,4,6-trinitrobenzene	TNT	6.85
5	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	11.1
6	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	8.98
7	1-Hydroxy-2,4,6-trinitrobenzene	PA	8.98
8	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	12.3
9	1-Methoxy-2,4,6-trinitrobenzene	TNA	28.59
10	1-Methyl-3-Hydroxy-2,4,6-trinitrobenzene	TNCr	5.21
11	1-Amino-2,4,6-trinitrobenzene	PAM	6.85
12	1,3-Diamino-2,4,6-trinitrobenzene	DATB	10.97

13	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB	17.75
14	2,6-Diamino-3,5-dinitropyridine	DADNPY	12.4
15	2,6-Dimethoxy-3,5-dinitropyridine	DMDNPY	20.57
16	2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitropyridine	PYX	8.9
17	1-Chloro-2,4,6-trinitrobenzene	CTB	6.71
18	1,3-Dichloro-2,4,6-trinitrobenzene	DCTB	2.55
19	1,8-Dinitronaphthalene	1,8-DNN	13.9
20	1,5-Dinitronaphthalene	1,5-DNN	11.2
21	1,4,5-Trinitronaphthalene	TNN	10.97
22	1,4,5,8-Tetranitronaphthalene	TENN	8.26
23	2,2',4,4',6,6'-Hexannitrobiphenyl	HNB	5.03
24	3,3'-Dimethyl-2,2',4,4',6,6'-Hexannitrobiphenyl	BiTNT	4.28
25	2,2',2'',4,4',4'',6,6',6''-Nonanitro-m-terphenyl	NONA	16.44
26	2,2',4,4',6,6'-Hexanitrodiphenylmethane	DPM	4.1
27	2,2',4,4',6,6'-Hexanitrodiphenylethane	DPE	3.89
28	2,2',4,4',6,6'-Hexanitrostilbene	HNS	5.32
29	2,2',4,4',6,6'-Hexannitroazobenzene	HNAB	8.2
30	3,3'-Dimethyl-2,2',4,4',6,6'-hexannitroazobenzene	DiMeHNAB	13.37
31	2,2',4,4',6,6'-Hexanitrodiphenylamine	DPA	5.02
32	2,2',4,4',6,6'-Hexanitrooxanilide	HNO	14.58
33	2,2',4,4',6,6'-Hexanitrodiphenylsulfide	DIPS	2.56
34	3-Methyl-2,2',4,4',6,6'-hexanitrodiphenylsulfide	MeDIPS	5.71
35	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrodiphenylsulfide	DiMeDIPS	8.57
36	2,2',4,4',6,6'-Hexanitrodiphenylsulfone	DIPSO	10.54
37	1,3,7,9-Tetranitrophenothiazine-5,5-dioxide	TNPID	5.78
38	1,3,7,9-Tetranitrophenoxazine	TENPO	5.12
39	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	6.5
E <sub>ES</sub> is determined by the electrostatic discharge energy required for 50% initiation probability [65] and the values are excerpted from Ref. [46].			

It was found that, for the nitro arenes considered, there was a linear relationship between the square of detonation velocity ( $D^2$ ) or detonation pressure ( $P$ ) and electric sensitivity ( $E_{ES}$ ). The result suggests that the theoretical approach can be used to predict or judge the magnitude of  $E_{ES}$ , which is difficult to measure in the molecular design of energetic materials. They also have discussed the influence of the substituted groups and the parameters of the electronic structure on density, detonation velocity, pressure, and electric sensitivity. The result has shown which of the substituted groups have exhibited the effect of activity or insensitivity, and also the influence of  $Q_{-NO_2}$  and  $E_{LUMO}$ .

Wang and coworker published a similar work this time for nitramines [53]. To optimize molecular geometries and electronic structures of eighteen nitramines, the DFT-B3LYP method, with basis set 6-31G(d) was employed. The averaged molar volume ( $V$ ) and theoretical density ( $\rho$ ) were estimated by means of the Monte-Carlo method based on 0.001 electrons/bohr<sup>3</sup> density space. Then, the detonation velocity ( $D$ ) and pressure ( $P$ ) of the explosives were estimated by using the Kamlet-Jacobs equation on the basis of the theoretical density and heat of formation ( $\Delta_f H$ ), which had been calculated using the PM3 method. By comparing the theoretical values of  $\rho$  and  $D$  with the experimental or referenced values, the reliability of this theoretical method and results were tested. The theoretical values of  $D$  and  $P$  were compared with the experimental values of electric spark sensitivity ( $E_{ES}$ ). It has been found that for the compounds with methylenenitramine units ( $\text{CH}_2\text{N}(\text{NO}_2)$ ) in their molecules (such as ORDX, AcAn and HMX) or with the better symmetrical cyclic nitramines but excluding methylenenitramine units (such as DNDC and TNAD), there exists an excellent linear relationship between the square of detonation velocity ( $D^2$ ) or the logarithm of detonation pressure ( $\log P$ ) and electric spark sensitivity ( $E_{ES}$ ). Thus, in a molecular design of energetic materials, such a theoretical approach can enable one to predict their  $E_{ES}$  values prior to synthesis and testing.

Politzer and coworkers examined computationally the effects of external electric fields upon their "trigger linkage" bonds, the breaking of which is believed to play a key role in detonation initiation [66]. For that purpose, five prototypical energetic molecules (nitrobenzene, methyl azide, methyl nitrate, nitromethane, and dimethylnitramine) were considered. The level of calculations was at the B3PW91/6-31G (d, p). They have found that electric fields along reactive bonds that reinforce the molecules' intrinsic polarities also lower their energies and increase the stretching vibration frequencies of the bonds. This suggests a strengthening of the bonds whereas fields in the opposite direction do the reverse.

### 5.1. Predictions and correlations

Energetic compounds are substances containing metastable molecules capable of undergoing very rapid and highly exothermic reactions. So, it is important in energetic materials technology to be able to predict sensitivity of new energetic materials before their synthesis or to have some preliminary information before any measurement. The classification of sensitivity is based on the nature of stimuli such as electric spark, impact, and shock. Some research has been made significantly in order to find the relationship between molecular structure of energetic materials and their sensitivities to specific stimuli.

#### 5.1.1. Nitroaromatics

Keshavarz and Pouretedal in their paper introduced a new simple method to predict the electrostatic sensitivity of nitroaromatic compounds [67]. This technique makes use of the calculated detonation velocity at the maximum nominal density and the contribution of some structural parameters. A training set was used to optimize the new correlation. The predicted results for 17 explosives were also compared with the quantum mechanical computations. The root means square deviations (rms) between the experiment and the introduced model and the complicated quantum mechanical computation were the same, i.e. 2.0 J [67].

Another new simple correlation was introduced by Keshavarz for predicting electric spark sensitivity of nitroaromatic compounds [68]. This approach is based on the number of carbons and hydrogens as well as the ratio of hydrogens to oxygens and the presence of certain groups, i.e. alkyl or alkoxy groups, attached to an aromatic ring. The model was optimized using a set of 17 polynitroaromatic explosives as the training set and then it was applied to 14 explosives having a variety of chemical families as test set in order to assess the predictive capability of the new method. The results have indicated that the following general equation (eq.7) with four variables is suitable for various types of nitroaromatic compounds:

$$E_{ES} = z_1 + z_2 n_C + z_3 n_O + z_4 R_{nH/nO} + z_5 C_{R,OR} \quad (7)$$

where  $z_1$ ,  $z_2$ ,  $z_3$ ,  $z_4$  and  $z_5$  are adjustable parameters which can be obtained by the best fit to experimental electric spark sensitivities data and  $n_C$ ,  $n_O$ ,  $R_{nH/nO}$ , are the number of the respective atoms and their ratio

( $R_{nH/nO}$ ), respectively.  $C_R$ ,  $O_R$  are certain parameters, respectively. The equation (eq.7) with numerical values of the parameters is

$$E_{ES} (J) = 4.60 - 0.733n_C + 0.724n_O + 9.16R_{nH/nO} - 5.14C_{R,OR} \quad (8)$$

The predicted results were found to be reasonably close to the measured values for both training and test sets [68].

Also, a new model has been constructed to predict the electric spark sensitivity of nitramines [52]. Genetic algorithm was employed for selection of the optimal subset of descriptors which possess significant contribution to the electric spark sensitivity from various calculated molecular structure descriptors. The novel modeling method was then applied in order to model the best possible quantitative relationship between some selected descriptors and electric spark sensitivity. Five most relevant molecular descriptors (selected by genetic algorithm) are;

- 1) Broto-Moreau autocorrelation of a topological structure - lag 1/weighted by atomic Polarizabilities ( $X_1$ ).
- 2) Moran autocorrelation - lag 8/weighted by atomic polarizabilities ( $X_2$ ).
- 3) Geary autocorrelation - lag 6/weighted by atomic van der Waals volumes ( $X_3$ ).
- 4) Number of double bonds ( $X_4$ ).
- 5) Mean absolute charge (charge polarization) ( $X_5$ ).

The regression equation (eq.9) has the form of;

$$E_{ES} = 16.477 + 48.392 X_1 - 1.414 X_2 - 2.854 X_3 + 1.472 X_4 - 72.448 X_5 \quad (9)$$

having the following regression characteristics.

$$n = 18; R^2 = 0.912; SD = 1.707; F = 24.824; p < 0.001$$

The equation indicates that the electric spark sensitivity is mainly dictated by molecular connectivity and charge distribution. The results indicate satisfactory prediction capability, robustness, and generalization. The new model has also been compared with the previous ones. Comparison of the results indicate the superiority of the present model over the others and reveals that it can be effectively used to predict the electric spark sensitivity of nitramines from their molecular structures alone [52].

A study by Zohari and coworkers presents a novel relationship between electric spark sensitivity of various nitroaromatic energetic compounds and their activation energies of thermal decomposition [69]. The new correlation can give some insight to elucidate the mechanism of initiation of energetic materials by electric spark. It can be used to predict the magnitude of electric spark sensitivity of new nitroaromatics, which is difficult to measure. The methodology originates from the assumption that electric spark sensitivity of a nitroaromatic energetic compound with general formula consisting of CHNO can be expressed as a function of its activation energy of thermal decomposition, the optimized elemental composition and the contribution of certain specific structural parameters.

The study has shown that it is possible to relate these parameters if a suitable combination of the number of carbons, oxygen, and nitrogen atoms as well as non-additive correcting functions are considered. Thus, using multiple linear regression method the following equation (eq.10) has been obtained as a suitable correlation.

$$E_{ES} = -9.72 + 0.034E_a + 7.41W + 3.49E_{ES}^+ - 2.50E_{ES}^- \quad (10)$$

where

$$W = (N_N + N_O) / N_C$$

$E_{ES}^+$  and  $E_{ES}^-$  are some parameters (see below).

The new correlation, having a pool of 22 nitroaromatic energetic compounds with different molecular structures, has the root mean square and the average deviations of 1.43 and 1.17 J, respectively. The proposed new method has also been tested for eight nitroaromatic energetic compounds, which possess complex molecular structures, e.g., 1,3,7,9-tetranitrophenoxazine, 2,4,6-tris(2,4,6-trinitrophenyl)-1,3,5-triazine, and 1-(2,4,6-trinitrophenyl)-5,7-dinitrobenzotriazole [69].

Definition of  $E_{ES}^+$  and  $E_{ES}^-$ .

Two different situations can be considered for prediction of  $E_{ES}^+$  and  $E_{ES}^-$  which depend on the attachment of some increasing and decreasing electrostatic sensitivity groups to 2,4,6-trinitrophenyl (TNP). The following intricate rules are given.

- I. The existence of one TNP. For the compounds with general structure TNP(X)<sub>2</sub> or TNP(X)<sub>3</sub>, where X is –CH<sub>3</sub>, –NH<sub>2</sub>, or –OH, the values of  $E_{ES}^+$  equal 1.75, 0.75 and 1.25, respectively. For the presence of –Cl, the value of  $E_{ES}^-$  is 2.0.
- II. The presence of two TNP. For energetic compounds with general formula TNP-Y-TNP, where Y is –SO<sub>2</sub><sup>-</sup>, –HN-COCO-NH or TNP, the value of  $E_{ES}^+$  equals 1.40. For the existence of –NH–, –S–, or the attachment of two TNP groups directly together, the value of  $E_{ES}^+$  equals 1.25.

The authors have also noted that measuring of activation energy of thermal decomposition of energetic materials is easier and safer than measurements of their electrostatic sensitivity values.

A study by Zohari, et al., presented a linear relationship between the impact sensitivity of nitroaromatic energetic compounds and their electric spark sensitivity (measured using an RDAD instrument) [70]. It was assuming that the impact sensitivity of a nitroaromatic energetic compound with the general formula C<sub>a</sub>H<sub>b</sub>N<sub>c</sub>O<sub>d</sub> could be expressed as a function of the electrostatic sensitivity, the number of NH<sub>2</sub> groups present in the 2,4,6-trinitrophenyl ring and certain non-additive structural parameters [70].

The root mean square and absolute standard deviation of a newly introduced correlation were found to be 2.4 and 2.0, respectively for 27 nitroaromatic energetic compounds. They tested the proposed correlation also for 7 additional nitroaromatic energetic compounds, which have complex molecular structures such as 1-(2,4,6-trinitrophenyl)-5,7-dinitrobenzotriazole and 1,3,7,9-tetranitrophenoxazine [70].

They showed that it is possible to correlate the impact sensitivity data of nitro aromatic compounds with their electric spark sensitivity. Analysis of the relationship between impact sensitivity and electrostatic sensitivity results in a linear equation (Equation 11). In the equation, the impact sensitivity ( $E_{IS}$ ) is only a linear function of the electrostatic sensitivity ( $E_{ES}$ ), the number of NH<sub>2</sub> groups, and certain non-additive structural parameters.

$$E_{IS} = 2.572 + 0.942E_{ES} + 34.175F_{n-NH_2} + 17.105F_{IS^+} - 8.272F_{IS^-} \quad (11)$$

where  $E_{IS}$  is the impact sensitivity in J,  $F_{n-NH_2}$  is the number of NH<sub>2</sub> group substituted into the 2,4,6-trinitrophenyl (TNP) ring,  $E_{ES}$  is the electrostatic sensitivity in J, and  $F_{IS^+}$  and  $F_{IS^-}$  are the increasing and decreasing contribution of non-additive structural parameters, respectively. A value of 0.99 was obtained for the coefficient of determination,  $R^2$ , for Equation 11. They gave some rules to define  $F_{IS^+}$  and  $F_{IS^-}$  for nitro aromatic compounds [70].

Definition of  $F_{IS}^+$  and  $F_{IS}^-$ 

For nitro aromatic compounds  $F_{IS}^+$  and  $F_{IS}^-$  can be determined according to the following conditions:

- I. For the nitro aromatic energetic compounds with general formula TNP-(NH<sub>2</sub>)<sub>n</sub>, the  $F_{n-NH_2}$  is 0.75, 2 or 3 for  $nNH_2 = 1, 2$  or 3 positions in the molecule, respectively.
- II. For molecules which have 2,4,6-trinitrophenyl (TNP) in the form TNP-X, the value of  $F_{IS}^+$  is 1.0 for X = -R or -OR.
- III. If the nitro aromatic molecule has the general formula TNP-X-TNP, the value of  $F_{IS}^-$  is 1.0 for X = SO<sub>2</sub>, TNP. If X is CH=CH or two TNP attached directly together, the value of  $F_{IS}^-$  is 0.5.

The present method can be helpful to elucidate the mechanism of initiation of energetic materials by impact and electric spark sensitivity. Moreover, this new relationship can be employed to design novel ideal energetic materials.

Impact and electric spark sensitivities of energetic compounds are two important parameters, which are closely related to many accidents. Impact sensitivity can be easily measured in contrast to electric spark sensitivity. In the article of Keshavarz and Keshavarz, a new simple method has been introduced which correlates electric spark and impact sensitivities of nitroaromatic compounds [71]. For reliable prediction of electric spark sensitivity through the measured / estimated impact sensitivity of nitroaromatics, two correcting functions were proposed to consider several molecular moieties. The model was optimized using a set of 28 polynitroaromatic explosives composed of CHNO and then tested for some nitroaromatics containing the other atoms such as sulfur.

The following general equation (eq.12), which was obtained by the best fit to experimental electric spark and impact sensitivities data through multiple linear regression method [18] can correlate two types of sensitivities ( $E_{ES}$  and  $E_I$ ) as:

$$E_{ES} = 6.17 + 0.0797E_I + 10.1E_{cor}^+ - 3.21E_{cor}^- \quad (12)$$

where  $E_{ES}$  is electric spark sensitivity (J),  $E_{cor}^+$  and  $E_{cor}^-$  are two correcting functions that were used to adjust large deviation of  $E_{ES}$  and  $E_I$ . The values of  $E_{cor}^+$  and  $E_{cor}^-$  can be determined as follows:

- (i) Prediction of  $E_{cor}^+$ : the values of  $E_{cor}^+$  equal to 1.8, 0.5, and 0.9 for the presence of -OR, two -OH, and/or the attachment of more than one nitroaromatic ring to the other nitroaromatic ring.
- (ii) Prediction of  $E_{cor}^-$ : The value of  $E_{cor}^-$  equals 1.0 for the attachment of only one CH<sub>x</sub>- or Ar- to aromatic ring in the case of CHNO nitroaromatic compounds. The parameters  $E_{cor}^+$  and  $E_{cor}^-$  are equal to zero if above conditions are not satisfied.

In the article the predicted electric sensitivities of the new method were also compared with the reported results of a new quantum mechanical approach. For 22 CHNO nitroaromatics considered, quantum mechanical calculations were within  $\pm 3.0$  J of 18 measured values and more than  $\pm 3.0$  J for remaining 4 experimental data. Meanwhile, the predicted results of the method were less than  $\pm 3.0$  J for 28 CHNO nitroaromatics. The root-mean-square (rms) deviations of the new model and quantum mechanical results were calculated to be 1.55 and 2.51 J, respectively [71]. The method can be exploited for reliable estimation of electric spark sensitivity of new nitroaromatic explosives, for which no measured or predicted impact sensitivity data exist.

### 5.1.2. Nitramines

Keshavarz and coworkers introduced, a general correlation for nitramines to predict the electric spark sensitivity through detonation pressure [72]. The new method uses maximum obtainable detonation pressure as a fundamental relation and it can be corrected for some nitramines having some specific molecular structure. In the approach, there is no need to use crystal density and heat of formation of nitramine explosives in order to predict the detonation pressure and electric spark sensitivity. The predicted electric spark sensitivities for some nitramines were compared with the results of the calculated ones, on the basis of some quantum mechanical computations. The root mean square (rms) deviations from the experiment for new method and the predicted results of the complicated quantum mechanical method are 1.18 and 3.49 J, respectively [72].

Another structure-property relationship has been published by Keshavarz and coworkers [73]. In this paper, a new approach was introduced to predict the electrostatic sensitivity of nitramines based on their molecular structures. The essentials for the correlation to predict the electrostatic sensitivity of nitramines are the ratio of carbon to oxygen and the existence of two specific structural parameters. The results were also compared with quantum mechanical computations so that the new method gives better predictions with respect to the measured data. Electrostatic sensitivities calculated by the new method for two new nitramines CL-20 [2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane] and TNAZ [1,3,3-trinitroazetidine] were also found to be close to the experimental values.

The study published by Keshavarz and coworkers presents a new simple correlation between electric spark sensitivity of certain nitramines and their activation energies of thermolysis, which are important for safety measures in industrial processes [[55]. It enables one to predict the magnitude of electric spark sensitivity of new nitramines, which is generally difficult to measure. The methodology is based on the assumption that electric spark sensitivity of a nitramine possessing a general formula of  $C_aH_bN_cO_d$  can be expressed as a function of its activation energy of thermal decomposition as well as optimized elemental composition and the contribution of specific molecular structural parameters.

Note that there is no unique idea of initiation mechanism of energetic materials by electrostatic spark sensitivity because the initiation can be considered as a multidisciplinary problem. The study of various nitramines by Keshavarz and coworkers has shown that mechanism of the spark energy transfer can be related to their activation energy of thermal decomposition as given by eq.13.

$$E_{ES}(J) = 9.826 - 0.047 E_a + 7.432 n_C/n_O + 7.680 E_{ES}^+ \quad (13)$$

where  $E_{ES}$  is electrostatic sensitivity;  $E_a$  is activation energy in kJ/mol;  $n_C$  and  $n_O$  are the number of carbon and oxygen atoms, respectively whereas  $E_{ES}^+$  is an increasing electric spark sensitivity factor. As indicated in the equation (eq.13), the ratio of  $n_C/n_O$  and  $E_{ES}^+$  are two effective parameters (have high coefficients) to correlate  $E_{ES}$  with reported values of  $E_a$  of nitramines.

The root means square and the average deviations for the new correlation are 1.37 and 1.09 J, respectively, for 21 nitramines belonging to different molecular structures. The proposed new method has been also tested for 16 nitramines for which there is no experimental data of electrostatic sensitivity for them [[55].

The present method by Keshavarz and coworkers can help to elucidate the mechanism of initiation of energetic materials by electric spark because it confirms that the primary fragmentation reactions in the electric spark initiation can be supposed identical with the primary splitting processes of low temperature

thermolysis. Furthermore, this new relationship can be used to in order to design new cyclic or acyclic nitramines.

Electric spark and impact sensitivities of energetic compounds are two important sensitivity parameters, which are closely related to many accidents in working places. Impact sensitivity can be easily measured or predicted by various methods so can be for nitramines, in contrast to their electric spark sensitivity. Keshavarz et al., proposed a new approach to correlate electric spark and impact sensitivities of nitrammite type energetic compounds by the use of three structural parameters [54]. In the cited article, the predicted results of the novel model for 20 nitramines were compared with two of the best available models, which were based on complex quantum mechanical approach and the measured values of activation energies of thermolysis. The root-mean-square (rms) and maximum deviations of the new model are 1.06 and 2.41 J, respectively. The article also considered further 14 nitramines, for which the measured electric spark or impact sensitivities were not available. The estimated electric spark sensitivities by the new model were found to be close to those predicted based on experimental data of activation energies of thermolysis [54].

Electric spark sensitivity and shock sensitivity based small-scale gap test for nitrammite energetic compounds are two important sensitivity parameters, which are needed for assessment of their safety in working places. A novel method has been introduced for reliable prediction of electric spark or shock sensitivities of desired nitrammite type energetic compounds when reliable data for one of the sensitivities is available [56]. A novel correlation with a high value of correlation coefficient ( $R^2 = 0.998$ ) is derived between electric spark and shock sensitivities of 20 cyclic and acyclic nitramines (eq.14).

$$E_{ES} = 24.83 - 1.166(\text{Al Gap})_{90\%TMD} - 8.219CN(n_{CH_2} = n_{NNO_2}; 2 < n_{CH_2} < 5) \quad (14)$$

where  $(\text{Al Gap})_{90\%TMD}$  is the thickness of aluminum gap (shock-initiated aluminum gap critical thickness values based on the measured data of the improved small scale gap test set),  $E_{ES}$  and  $(\text{Al Gap})_{90\%TMD}$  are in J and mm, respectively;  $CN(n_{CH_2} = n_{NNO_2}; 2 < n_{CH_2} < 5)$  is a correcting function, where its value is equal to 1.0 for cyclic nitramines with equal number of  $CH_2$  ( $n_{CH_2}$ ) and  $NNO_2$  ( $n_{NNO_2}$ ) groups as well as  $2 < n_{CH_2} < 5$ .

For these nitramines, the predicted results of electric spark sensitivities of the novel model are compared with two of the best available models. The root-mean-square (rms) and maximum deviations of the new model are 0.20 and 0.51 J, respectively, which are much less than two comparative methods considered in the article. The reliability of the new method for prediction of electric spark sensitivity of further 14 nitramines was also compared with one of the best available methods, where the measured electric spark or shock sensitivities were not available in the literature. Thus, it is possible to have an accurate model for prediction of electric spark or shock sensitivity of a new nitramine without using complex calculations.

Spark sensitivity of explosives is obviously an important subject. To shed some light on the mechanism for the behavior of molecules in an electric field Türker [29] tried to obtain some correlations between the experimental spark sensitivity excerpted from the literature and certain molecular orbital characteristics of some nitramine type explosives calculated by the author. For that purpose, certain semi empirical and DFT calculations have been carried out (UB3LYP/6-31G (d, p)//UHF/PM3, UB3LYP/6-31G (d, p) or UB3LYP/6-31+G(d)) together with some statistical analysis. Investigations within the limitations of the level of calculations have revealed that the nitramine type compounds considered preferentially decompose via anionic states in an electric field. DFT calculations showed that TETROGEN decomposition in electric field also should occur by the cleavage of C-H bond in addition to N- $NO_2$  bond rapture.

### 5.1.3. Nitroaromatics and nitramines

For nitroaromatics and nitramines, Keshavarz, considered some recent developments in predicting impact, shock and electric spark sensitivity through different approaches [74]. Also, a novel simple correlation has been introduced to predict electric spark sensitivity of energetic compounds, which has some advantages with respect to the other available predictive methods. This approach has been based on only the molecular

structures of energetic compounds in which the ratios of the number of carbon and hydrogen to oxygen atoms as well as the existence of some specific functional groups or molecular fragments are important contributing factors. Comparison of the predicted electric spark sensitivity by new method gives good results with respect to available experimental data. Additionally, the results of this method were also compared with calculated results of the best available methods in date such as quantum mechanical computations. This method can be easily used for two important classes of energetic compounds including nitroaromatics and nitramines [74].

Ferdowsi et al., in their article considered two well-known stimuli for initiation of energetic compounds, namely electric spark and impact, which are closely related to many accidents in working places [75]. Obviously, it is valuable to correlate electric spark sensitivity and impact sensitivity of energetic compounds through their molecular structures. To correlate impact and electric spark sensitivities of energetic compounds, including nitroaromatics and nitramines, a general approach was introduced which was based on the usage of three structural functions. The predicted results of the novel model for 45 energetic compounds containing 31 nitroaromatics and 14 nitramines have been compared with two of the best available models, which are based on complex quantum mechanical approaches. The root-mean-square (RMS) and maximum deviations of the new model are 1.31 and 2.97 J, respectively, which are less than the total predictions by two quantum mechanical models. Additionally, 9 energetic compounds, having complex molecular structures, for which the calculated electric spark sensitivities by quantum mechanical approaches were not available, were considered. The estimated electric spark sensitivities by the new model were close to the experimental data, i.e. the RMS and maximum deviations were 1.12 and 1.58 J, respectively.

Before closing this section about the predictions, a final remark for correlative studies is necessary which originates from the difference between a regression and correlation. Although, both are some sort of mathematical equations and useful, it is questionable whether apparently independent variables of a correlation reflect the truth. In general, as the number of independent variables is increased, better and better fits of the regressed equation to experiment are obtained. To find out how realistic a regression is, at least a detailed statistical analysis of it (regression statistic) has to be done. Unfortunately, most of the regression work in the literature has lack of it.

## 6. Energetic materials and the spark sensitivity

### 6.1. Experimental ESD characteristics of some classes of energetic materials

It has long been known that most of explosives are non-conductors, easily accumulate charge when contacting with and separating from other materials, and are sensitive to electrostatic discharge. Thus, explosives can be ignited by electric sparks due to local charge accumulation. Compounds such as lead styphnate are particularly sensitive, and electric discharges, rarely visible to the naked eye, are capable of igniting them. However, ESD sensitivity measurements show scatter [76].

A review of the literature followed by some experimental determinations, showed that widely varying values of ignition energy could be obtained for the same substance by using different experimental test methods and conditions [76].

Various factors may have influence and change the behavior of the material, depending on the nature of the additive. Slight amounts of inert impurities having high melting temperatures and high hardnesses (glass, corundum, etc.) are known to increase the sensitivity of explosives to shock and friction; on the other hand, additives having a low melting temperature and high plasticity (wax, paraffin, etc.) reduce the sensitivity of the same explosives to the same factors [77]. One such effect is that of additives on the sensitivity of explosives ignited by an electric discharge.

The most probable mechanism for the ignition of secondary explosives by an electric discharge is the ignition of explosive particles as the result of the thermal effects of the discharge plasma [8]. Of course, in this case the

sensitizers would have to be substances which could ignite in the discharge channel, releasing a large amount of heat and increasing the burning temperature. The reaction of metallic additives in the shock wave from a discharge is less probable because of the lower temperature and the relative slowness of this mechanism in comparison with that based on the discharge plasma. Also, the additives must have a high electrical conductivity and a sufficiently small particle size (on the order of a few microns). These properties ensure that the discharge will flow through these particles and that there will be a rapid heating to the evaporation temperature of the particles. Such additives could be powdered (finely dispersed) metals, such as aluminum, magnesium, zirconium, titanium, etc. These metals are characterized by a high heat of combustion, a high combustion temperature and a high electrical conductivity.

Many researchers have studied electrostatic discharge sensitivities of high explosives using an apparatus that discharges a spark into a sample. Larson et al., [11] specifically looked at explosive grain sizes and their effect on ignition sensitivity. They have concluded that as the particle size decreases, the ESD sensitivity increases. Particles with greater surface area tend to be less sensitive but as the surface area to volume ratio increases, ESD sensitivity correspondingly increases. They have explained that the spark is forced to take a longer time, in more circular path through large grain size media, thus resulting in a lower energy density in the spark. Studies simulated the static electric energy output of the human body that can dissipate up to 8.33 mJ of energy [78]. Simpson and Foltz [10] tested high explosive powder samples ranging from 3 to 5 mg, and concluded that the samples' minimum ignition energy exceeded 1 J, (above the human body threshold) are to be classified as spark insensitive. Another study [8] revealed that RDX is the most ESD sensitive powder, igniting at 0.15 J and TATB is the least sensitive of the tested materials with ignition energy of 2.56 J. They link this behavior to the thermal properties of the material such as critical temperature for thermal runaway and temperature for thermal decomposition, but did not examine electrical properties [8].

Decades ago, an experimental study by Roux et al., showed that spark energy transfer mechanisms were different for the explosive alone (HMX) and for the explosive containing 1% of graphite [35]. Their study was completed by the literature data. The work indicated the need for parametric studies by systematically varying the electrodes gap, as well as the spark duration to determine the true minimum value of the ignition energy. Grain size and shape were found to be very important factors. The influence of the electrode shape was also discussed, as well as the environmental conditions. Moreover, for ionic solids or substances made of an electrically insulating matrix containing conductive inclusions, particular phenomena appeared when they were submitted to electric fields for a certain period of time [35].

In another publication, Roux and Auzanneau considered the energy transfer mechanism from the electric spark to the reactive solid sample in powder form [79]. Only a small portion of the solid was heated to the explosion critical temperature through a resistive heating by electric current. In fact, hot spots develop at the thinnest part of the solid, i.e., at intergrain contact points. They studied the evolution of thermal diffusivity and of sensitivity to electric spark as a function of powdered HMX granulometry. It allowed them to specify the respective importance of the grain size and shape in this evolution [79].

In one of the earliest works by Wang, experimental results of a systematic study on electric spark sensitivity of ignitable gases and explosive powders were reported by using a new type of sensitivity testing apparatus, which consisted of a test bomb, a dual switch spark circuit and a photoengraved electrode sheet [80]. The ranking of electric spark sensitivity of hydrogen (typical of ignitable gases) and lead styphnate (typical of explosive powders) had been obtained for the first time. Through some careful sensitivity comparison tests, a conclusion was drawn that hydrogen was more sensitive than lead styphnate. Additionally, in the work, the electric spark sensitivity of black powder was investigated in depth and the minimal value (26.4 mJ) of the minimum energy for 50% ignition was obtained. By systematic studies on the optimum ignition condition of hydrogen, lead styphnate and black powder, the minimal value of the ignition energy was found, existing regularly for different materials. On the other hand, in the study of determining the effects of humidity and ambient temperature on the ignition energy, a linear correlation was found [80].

In general, all explosives, under all conditions must be considered vulnerable to generation, accumulation and discharge of static electric 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/or filling operations due to discharge of static charge accumulated on a person supplying energy up to 20 mJ. Note that to reduce the risk associated with static initiation hazard in the processing and handling of the explosives, the electrostatic sensitivity tests are needed which can provide an important input regarding electrostatic hazards. Talawar et al., documented various electrostatic sensitivity data in terms of zero ignition probability data ( $E_{SE0}$ ) including some of the initiatory explosives such as nickel/cobalt hydrazinium nitrate, silver azide, lead azide and mercury salt of 5-nitro tetrazole [9]. Similar data also were presented for samples coated with polyvinyl pyrrolidone to study its effect on the electrostatic sensitivity. The electrostatic spark sensitivity of some conventional and novel made energetic materials (to explain the increased spark sensitivity behavior on the basis of possible primary explosives) was 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 some approximations and assumptions) with thermal, detonation and mechanical properties was drawn. The polyvinyl pyrrolidone coated samples followed the same order but interestingly with increased spark sensitivity. Also, an attempt was done for reasoning of dielectric nature of the materials or exothermic effects of decomposition products of PVP. The work also reports the electrostatic spark sensitivity of cap compositions [9].

In the work of Gerber et al., a series of experiments were performed to evaluate and document the effect of a TASER ("stun gun") on triacetone triperoxide (TATP), which is an easily manufactured explosive and used often in suicide bombing vests [81]. TATP samples were synthesized and subjected to several tests of their sensitivity. These samples were run through an electrostatic discharge test with a result of  $0.073 \pm 0.018$  J. In addition, TATP was shocked with a TASER in a variety of configurations. The TATP reacted in 17/17 tests when the TASER arced through the TATP and 0/4 times when the TATP was configured in such a way that the TATP was not subjected to the electrical arc. Based on the experimental data, it has been concluded that TATP will readily explode in a variety of configurations by a TASER or similar device. However, testing should be expanded, because as the data presented in the work are limited to a single formulation of TATP. Also, just one of a large array of TASER-like devices by a single manufacturer were tested. Other devices, scenarios and formulations of TATP and other likely threat materials should be assessed.

One of the papers by Zeman provides an overview of the main developments over the past nine years in the study of the sensitivity of energetic materials (EM) to impact, shock, friction, electric spark, laser beams, and heat [44]. Attention is also paid to performance and to its calculation methods. Summaries are provided of the relationships between sensitivity and performance. On the basis of current knowledge existing, it is possible to state that a single universal relationship between molecular structure and initiation reactivity does not yet exist. However, it has been confirmed that increasing the explosive strength is usually accompanied by an increase in the sensitivity. In the case of nitramines, although this rule is totally valid for friction sensitivity, for impact sensitivity there are exceptions to the rule. It has to be noted that with certain explosives the relationship works in the opposite direction. With respect to the QSPR approach there might be some reasonably good predictions but it provides little insight into the physics and chemistry involved in the process of initiation.

### 6.1.2. Nitroaromatics

Usage of explosive materials for many purposes in aerospace applications requires investigation of ESD effects at those extreme conditions. Couple of decades ago Hosoya et al., studied thermally stable explosives (polynitroaromatic compounds) using an electric-spark generating device to determine their sensitivities for aerospace applications [82]. The explosives tested were DATB, TATB, HNS and ONT. In addition, TNT as a reference nitro compound was used. The ignition energy of HNS and ONT was found to be not depending on the initial temperature of the samples as much as does DATB. In electric-spark test, underwater small-scale

gap test and drop hammer test, HNS and ONT were found to be more sensitive than DATB and TATB and they also showed high adiabatic flame temperature.

Some empirical relationships were sought in the literature from time to time. One of the earliest efforts along this direction belonged to Zeman and coworkers [47]. In their work, the electric spark sensitivity of 32 polynitro arenes was determined as the spark energy,  $E_{ES}$ , required for 50 per cent initiation probability. A relationship between the  $E_{ES}$  values and the squares of detonation velocities of the polynitro arenes was established. The relationship obtained seems to be a certain form of Evans - Polanyi - Semenov equation. Therefore, it implies an identity (at least a high similarity) of chemical mechanisms of the primary fragmentation processes in the molecules of polynitro compounds during their detonation and in the initiation of their decomposition and/or explosive transformation by the stimulus of electric spark. However, the way of energy transfer from the spark to reaction centre of molecule of the said compounds was not explicitly clarified.

An ESZ KTTV instrument which was a new, relatively simple construction has been applied to the determination of electric spark sensitivity ( $E_{ES}$ ) of 31 polynitro arenes and their derivatives by Zeman et al., [83]. The results obtained have been compared with the theoretical DFT Mullikan net charges of nitro groups,  $Q_{NO_2}$  (B3LYP/6-31G (d, p) level). Nitro groups are considered as the primarily reacting moieties in the initiation by spark. Based on the analysis of the results obtained, it has been observed that intermolecular interaction plays a considerable role in this initiation. However, generally accepted presumption, that most positive  $Q_{NO_2}$  value represents a sensitivity of the given molecule, is not valid without some reserve within the limitations of the theory. If the polynitro aromatic molecule contains several potential reaction centers, the proper initiation might then be realized selectively (depending on the kind of initiation impulse).

A similar study on various polynitroaromatic compounds has been performed by Zhi et al., [84]. After the detailed investigation on the molecular structural and electronic parameters for many polynitroaromatic explosives for a relationship between electric spark sensitivity and molecular electronic properties, they found that there is a quantitative relationship between the electric spark sensitivity and the lowest unoccupied molecular orbital (LUMO) energy and the Mulliken charges of the nitro group, and the number of the aromatic rings as well as certain substituted groups attached to the aromatic ring. Electric spark sensitivities calculated by such a correlation were found to be reasonably close to the experimental data for both 17 polynitroaromatic explosives as training set and 11 polynitroaromatic explosives as test set. The optimized eq. is,

$$E_{ES}(J) = (-1)^{n_1} 10.16 Q_{nitro} - 1.05 n_1 n_2 E_{LUMO} - 0.20 \quad (15)$$

where  $n_1$  is the number of aromatic rings, and  $n_2$  is the number of substituted groups attached to the aromatic ring, such as alkyl (-R) or amino (-NH<sub>2</sub>) groups. Note that the substituted groups mentioned here do not include the nitro group. In eq.15,  $Q_{nitro}$  (in e) is the minimum Mulliken charges of the nitro group, and  $E_{LUMO}$  (in eV) is the lowest unoccupied molecular orbital energy.  $Q_{nitro}$  is calculated according to eq.16.

$$Q_{nitro} = Q_N + Q_{O1} + Q_{O2} \quad (16)$$

On the whole, the electric spark sensitivity augments with the increase of  $Q_{nitro}$ , while it decreases with the increase of  $E_{LUMO}$ .

Quantitative structure-property relationships are quite often sought by various researches in order to predict certain property by using the others (descriptors). A quantitative structure-property relationship (QSPR) model was proposed for predicting electric spark sensitivity of 39 nitro arenes [85]. The genetic function approximation (GFA) was employed for selection of the descriptors that have significant contribution to electric spark sensitivity from various descriptors. A fitting relationship was obtained between the eight selected descriptors and electric spark sensitivity. The correlation coefficients ( $R^2$ ) together with correlation coefficient of the leave-one-out cross validation (Q2CV) of the model are 0.924 and 0.873, respectively. Thus,

the model is highly significant statistically. Moreover, the robustness as well as the internal prediction capability of which is satisfactory. Thus, the results have indicated that the predicted electric spark sensitivity values are in good agreement with the experimental values [85].

In some cases, ESD value(s) is/are reported for individual explosives of course without any correlative effort by the investigators. For example, in one of the articles by Klapötke synthesis 2,6-Bis(picrylamino)pyridine (1; pre-PYX) and 2,6-bis(picrylamino)-3,5-dinitropyridine (2; PYX) were reported using an improved literature method. Compounds 1 and 2 of the articles were reinvestigated in detail and the X-ray structures are given [86]. Various reactions of 2 with different bases were reported. The sensitivities towards impact, friction, and electrostatic discharge (1.00 J) were also determined.

### 6.1.3. Nitramines

Some time ago, Zeman and coworkers employed an ESZ KTTV instrument (at that time a new, relatively simple construction) for determination of electric spark sensitivity ( $E_{ES}$ ) of 16 nitramines [38]. Results obtained are compared with those from measurements by means of an older instrument (RDAD). They focused their attention both on the relationships between the  $E_{ES}$  values from both instruments and the theoretical (B3LYP/6-311+G(d,p)) N-NO<sub>2</sub> bond dissociation energies, B3LYP/6-31G(d,p) Mulliken net charges of the nitro group, heats of fusion and <sup>15</sup>N NMR chemical shifts of the nitrogen atoms of the most reactive nitro groups, respectively. Although, large differences existed between the results of both instruments, the  $E_{ES}$  values from both of the instruments correlated with certain characteristics of molecular structure, that primarily leaving group in a nitramine molecule was the nitro group. It has been found that these relationships for ESZ KTTV results are strongly affected by molecular structural factors. It was also found that the dislocations in the crystals should have some relation to electric spark sensitivity. They arrived at the conclusion that the mechanisms of spark energy transfer into the reaction centre of a molecule should be different while measuring on the two alternative instruments (RDAD and ESZ KTTV). The thermal component of discharge in the RDAD instrument may be one of the reasons for this difference. This assumption has also been supported by the differences (in an order of magnitude) between the  $E_{ES}$  values obtained from the individual instruments. Further, the considerable electric energy losses should exist in the space between the upper electrode and the sample surface in the RDAD system measurements which contribute to the difference mentioned above (most likely a large part of discharge is enacted in the air) [38].

Klapötke et al., have synthesized the highly energetic 1,5-di(nitration) tetrazole and its salts [87]. The neutral compound was found to be very sensitive and representing one of the most powerful non-nuclear explosives to date. Selected nitrogen-rich and metal salts were prepared. It has been noticed that the potassium salt can be used as a sensitizer in place of tetracene. The obtained compounds have been characterized by using various techniques. Calculated energetic performances using the EXPLO5 code based, on the calculated (CBS-4M) heats of formation and X-ray densities support the high energetic performances of the 1,5-dinitraminotetrazolates as energetic materials. In the article, the sensitivities towards impact, friction, and electrostatic discharge were also explored [87].

Li et al., tested the responses of high-density HMX-based and PETN-based explosives to electrostatic discharge by using a JGY-50 electrostatic spark tester [88]. Two discharge modes, including penetrating discharge and surface discharge were employed to simulate the different ESD scenarios. The results have showed that the materials possess response of high-density explosives included heat and shock effects. The heat effect of PETN-based explosive and the shock effect of HMX-based explosive appear to dominate under ESD conditions. No detonation was probably observed because there was less accessible surface area and low permeability of high-density solid explosive, thus allowing little convective burning, and the energy of ESD could not be coupled effectively to high-density solid explosives.

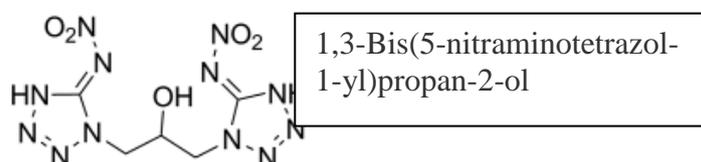
The electrostatic hazards of nitramine explosives (RDX, HMX) were reported in the paper by Peng et al., [51]. The electrostatic resistivities of different particle-size RDX and HMX were tested by a device designed and

manufactured according to the standard ISO/IEC 80079-20-2:2016. They used an ESD sensitivity test device designed according to US military standard MIL-STD-1751A. This work shows that the resistivities of uncompacted RDX and HMX increase as the particle size decreases. Charging characteristics of the test experiments were also carried out using a so-called "sieve method". By employing this method, the influence of aperture size on charge accumulation of RDX was studied. The characteristics of electrostatic accumulation of different particle-size RDX and HMX sieved with 50 mesh standard sieve were compared. The results showed that the charge accumulation (in absolute value) increases as the mesh number increases (i.e. the aperture size decreases). It also increases as the particle size is decreased, indicating that Nano-sized RDX and Nano-sized HMX have tendency to accumulate static electricity more easily as compared to the conventional micron-sized ones. Additionally, the electrostatic discharge sensitivity of Nano-sized RDX and Nano-sized HMX was investigated. In the experiments, the 50% ignition probabilities of RDX and HMX, having different particle sizes, were tested by 25-time tests in which the discharge voltage of the capacitor was varied in each case. The results indicated that Nano-sized nitramine explosives had a higher ESD sensitivity than micron-sized ones [51].

The article by Fischer et al., describes the synthesis of 1,1'-Dinitramino-5,5'-bitetrazole and 1,1'-dinitramino-5,5'-azobitetrazole for the first time [89]. The neutral compounds have been found extremely sensitive and powerful explosives. Also, some selected nitrogen-rich salts were prepared in order to adjust sensitivity and performance values. The compounds were characterized by IR and Raman spectroscopy, multinuclear NMR spectroscopy, low-temperature X-ray diffraction, elemental analysis, and DTA/DSC. The sensitivities toward impact, friction, and electrostatic discharge were also explored. Most of the compounds exhibited ESD sensitivities (0.03-0.1 J) which are in the range of primary explosives and therefore should only be handled with great care.

Melt-cast explosives are extensively used in mortars, grenades and artillery shells and also in civil applications. The melt-cast technology nowadays is based on 2,4,6-trinitrotoluene (TNT), 2,4-dinitroanisole (DNAN) and 1,3,3-trinitroazetidine (TNAZ). Numerous efforts are ongoing to replace TNT as the melt-cast matrix in explosive charges because of its low performance and security issues [90]. In this study by Klapötke et al., the syntheses and full structural as well as spectroscopic characterizations of 2-nitrazapropyl substituted polynitroazoles have been presented as potential melt-cast explosives. The method of derivatization of the heterocyclic N-H function by introducing a further energetic group improved the stability and also the energetic properties of the products. All the compounds were characterized in terms of their sensitivities towards impact, friction and electrostatic discharge, and their thermal stabilities. The ESD values for 12 compounds have been reported which range between 0.1-0.6 J. The highest value belongs to 1-(5-amino-3-nitro-1,2,4-triazol-1-yl)-2-nitrazapropane. Note that the corresponding value for TNT is 0.7 J.

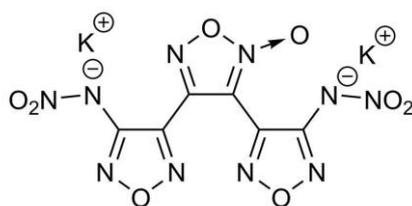
Another nitramine, 1,3-Bis(5-nitraminotetrazol-1-yl) propan-2-ol, was prepared by Klapötke et al., starting with 5-aminotetrazole and 1,3-dichloroisopropanol under basic conditions [91].



1,3-bis(5-aminotetrazol-1-yl) propan-2-ol was obtained and nitrated afterwards with 100 % nitric acid. Then, the hydrolysis of the nitrate ester was studied. Metal and nitrogen-rich salts of the neutral compound 1,3-Bis(5-nitraminotetrazol-1-yl)propan-2-ol were prepared and analyzed. Various alkali and earth alkali salts were also synthesized and the sensitivities toward impact, friction and electrostatic discharge were determined as well. The electrostatic discharge values were found to be greater than 1.5 J (OZM ESD tester). Additionally, the performance values of the compounds were calculated using the EXPLO5 program. A detailed comparison of the different salts is also enclosed.

Potassium salt of 1,1'-dinitramino-5,5'-bitetrazolate is one of the most promising recently synthesized primary explosives which has been currently under investigation for different applications [92]. This interest is simply because of its high initiation power and the exclusion of heavy metals. To close the gap, the research group synthesized the remaining alkali metal salts (such as the lithium, sodium, rubidium and cesium salts) [92]. In addition, the highly explosive silver salt as well as several other transition metal amine complexes with nickel, copper and zinc were prepared. The sensitivities toward impact, friction, heat and electrostatic discharge as well as their behavior on laser irradiation of the transition metal complexes were explored [92].

Gospodinov et al., synthesized the following furoxan starting from 3,4-bis(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-furoxan (BAFF) and nitrating it in 100 % HNO<sub>3</sub> at -10 °C. Then, it was reacted with KOH to produce the corresponding energetic dipotassium salt of 3,4-bis(4-nitramino-1,2,5-oxadiazol-3-yl)-1,2,5-furoxan (K<sub>2</sub>BNAFF) whose structure of is shown below [93].



The neutral nitramino-furoxan compound (H<sub>2</sub>BNAFF) is unstable at room temperature. Several nitrogen-rich salts (e.g. ammonium, guanidinium, aminoguanidinium, hydrazinium and hydroxylammonium) were prepared from K<sub>2</sub>BNAFF and characterized. In addition, the sensitivities of all the above mentioned BNAFF salts toward friction, impact and electrostatic discharge were determined. The electrostatic discharge values of all the compounds considered rang in between 0.19J -1 J (OZM research). Note that the value for RDX is 0.2 J.

#### 6.1.4. Composites

Lu et al., searched the electrostatic charge accumulation caused from RDX explosive and RDX/Al composite explosive friction with a one-meter long flume [94]. The results show that RDX gains electrons while sliding on flume, and the electrostatic charge accumulation (which is from -3.0 μC·kg<sup>-1</sup> to -5.0 μC·kg<sup>-1</sup>) has a linear relationship with the mass of RDX. In the experimentation, the characteristic of static electricity and electrostatic accumulation changed after the addition of aluminum powder. The maximum electrostatic accumulation of RDX/Al is 1.19 μC·kg<sup>-1</sup> while that of RDX is -4.89 μC·kg<sup>-1</sup>. Whereas, the electrostatic charge accumulation varies from 0.35-0.50 μC·kg<sup>-1</sup> to 0.70-1.20 μC·kg<sup>-1</sup> as the proportion of Al powder increases from 20% to 30%. The electrostatic charge accumulation of RDX/Al composite explosive increases from 0.50 μC·kg<sup>-1</sup> to 1.20-1.50 μC·kg<sup>-1</sup> after addition of 3%-8% organic solvents, such as ethyl acetate or petroleum ether.

The paper by Thiruvengadathan et al., gives details of the synthesis and combustion characteristics of silicon-based nanoenergetic formulations [95]. Silicon nanostructured powder (with a wide variety of morphologies such as nanoparticles, nanotubes and nanowires,) were produced by direct current plasma arc discharge route. Then, these nanostructures were passivated with oxygen and hydrogen post-synthesis. Their structural, morphological, and vibrational properties were investigated using various techniques. The silicon nanostructured powder (fuel) was mixed with varying amounts of sodium perchlorate (NaClO<sub>4</sub>) nanoparticles (oxidizer) to form nanoenergetic mixtures. The NaClO<sub>4</sub> nanoparticles with a size distribution, ranging between 5–40 nm were prepared by using a suitable surfactant in a mixed solvent system. The observed correlation between some basic material properties and the measured combustion characteristics is presented. It has been observed that these silicon-based nanoenergetic formulations exhibit reduced sensitivity to electrostatic discharge [95].

In the experiments, the ESD sensitivity measurements were performed with a test system fabricated by Electro-Tech Systems (ETS) Inc (Model: 931). The instrument includes a capacitor bank (300–20,000 pF), which can be charged to a voltage ranging between 100 V to 26 kV. The nanoenergetic powder (typically 2–4 mg) was placed in a stainless steel sample holder. The high-voltage pin electrode (a stainless steel needle) was placed 1 mm above the surface of the sample powder prior to subjecting the powder to 24 consecutive discharge cycles at a known energy level (typically beginning with the lowest energy). If no ignition occurred, the voltage and/or capacitance were increased, and the same sample was again subjected to 24 consecutive discharges at a slightly higher energy level until the ignition occurred. It was observed that the ESD energy of CuO/Al and Bi<sub>2</sub>O<sub>3</sub>/Al for passing the ESD test (meaning fail to ignite upon charging at high voltage) is less than 100 mJ. On the other hand, the nanoenergetic formulations comprising of nanosilicon and NaClO<sub>4</sub> as ingredients passed ESD tests with at least 16 mJ. Thus, relatively reduced sensitivity of these silicon-based nanoenergetic formulations (in comparison to CuO/Al, Fe<sub>2</sub>O<sub>3</sub>/Al MoO<sub>3</sub>/Al, and WO<sub>3</sub>/Al nanothermite formulations) occurred.

Very often unintentional ignition of composite energetic materials (CEM) occurs when

static electricity is discharged onto the CEM. A recent report has showed that for micron sized particle of CEM formulations, only aluminum (Al) combined with copper oxide (CuO) was electrostatic discharge ignition sensitive, whereas commonly used Al combined with molybdenum trioxide (MoO<sub>3</sub>) seemed not ESD ignition sensitive [96]. However, in practice frequent unintentional ESD ignition events occur with Nano Al/MoO<sub>3</sub>. A study by Weir et al., examines the role of size of Al particles on ESD ignition sensitivity and measures electrical conductance for each CEM [96].

A CEM containing Al, (characterized with varying average particle diameter) as the fuel and MoO<sub>3</sub> were examined. The MoO<sub>3</sub> content was maintained constant in all the mixtures so that the electrical conductivity and ignition energy became more strongly as a function of the fuel particle diameter. Each mixture was combined to a stoichiometric equivalence ratio. Electric energy was delivered and discharged into a 10 mg powder sample through a capacitor. In the experiment, the sample was placed directly under the capacitor and energy stored in the capacitor was discharged on to the sample. Each powder was tested at 10,000 V (i.e., corresponding to 100 mJ). If ignition occurred, the powder was tested at a lower voltage until minimum ignition energy was observed.

Results have showed that as Al particle size is reduced, electrical conductance increases dramatically as does ESD ignition sensitivity. Overall, electrical conductance has been shown to increase linearly with increasing ratio of aluminum surface area to its volume. The alumina passivation shell surrounding Al core particles plays a significant role in enhancing ignition sensitivity.

The response of composite energetic material to electrical stimuli was investigated and a correlation between electrical conductivity and ignition sensitivity was examined by Weir et al., [97]. In the work, the composites used consisted of micrometer sized aluminum particles combined with another metal, metal oxide, or fluoropolymer.

The approach used for energetic material ESD ignition testing was based on a human body model (HBM) [98]. The HBM uses a capacitor that is charged to a certain voltage, and discharges the stored electrical energy through a resistive network into the material being tested.

Of the nine tested mixtures, aluminum (Al) with copper oxide (CuO) was the only mixture susceptible to ignition by electrostatic discharge. Under the loose powder conditions of these experiments, the minimum ignition energy (MIE) for Al–CuO composite was 25 mJ and exhibited an electrical conductivity, two orders of magnitude higher than the next composite. A mixture having combined properties of electrical conductivity greater than 0.45 n's/m and also high capacity for thermal energy storage, conducts electrical energy accumulating joule heating to trigger an ESD ignition. It is interesting to note that three orders of magnitude greater energy level are required to produce the MIE using a hot wire than ESD. This may be because of the ESD stimulus is more locally concentrated [98].

This study has revealed a similar trend in MIE for ignition triggered by a discharged spark compared with a thermal hot wire source [98]. Overall, ESD ignition requires significantly less energy than thermal ignition but, electrostatic discharge creates more power than the hot wire, such that only 27% of the power generated from the electrostatic stimuli may produce joule heating and ignite the mixture.

Composite propellants based on the solid nitrate ester, 2,3-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate (SMX), were theoretically and experimentally examined by Reese et al., and compared with the formulations based on ammonium perchlorate (AP) [99]. In the experiment, the ignition sensitivity value was obtained to be 172 mJ (neat SMX) and >250 mJ (SMX-HTPB-Al), respectively and compared with those of the AP-based formulations. However, the SMX-based formulation could be detonated using a high explosive donor charge in contact with the propellant. Hence, with good performance and high density, SMX-based composite propellants may offer a promising candidate for perchlorate-free alternative to the existing AP-based formulations.

Energetic films may be affected by electrostatic discharge. In the work of Plummer et al., nanoporous silicon (pSi) films on a silicon wafer were loaded with perfluoropolyether (PFPE) and sodium perchlorate oxidizing agents [100]. Sensitiveness to impact, friction and electrostatic discharge of the resulting energetic thin films was investigated. The ESD sensitiveness was measured on a custom-built high-voltage discharge instrument with pre-determined spark energy levels of 0.045, 0.45 and 4.5 J. It was observed that nanoporous silicon loaded with perchlorate was sensitive at the lowest limit of detection for the available equipment (<45 mJ ESD spark energy). On the other hand, when loaded with perfluoropolyether, the material was moderately sensitive to ESD (between 45 and 100 mJ). During the sensitiveness testing, pSi loaded with either perchlorate or PFPE displayed behavior similar to other primary explosive materials [100].

Zirconium metal powder has been of interest as an energetic material because of its high density and good combustion performance, which affords an opportunity for usage of zirconium powders as fuel in solid propellants [101]. Unfortunately, the application of zirconium powders is limited due to its high electrostatic discharge sensitivity which makes the zirconium powders more pyrophoric and less amenable to functionalization. To improve the security, glycidyl azide polymer (GAP) (a kind of energetic binder as coating material) was selected in the work, and coated on the surface of zirconium powder directly to obtain Or/GAP composite particles possessing reduced electrostatic discharge sensitivity. The measured results have showed that 50% firing energy ( $E_{50}$ ) of Or/GAP is increased from 5.13 mJ to 24.91 mJ, meanwhile reserving the good combustion performance and high density of Zr powder. This work provides a kind of technology support for its application in high density propellant [101].

Highly energetic novel coordination polymers (ECPs), based on the graphene oxide (GO)-copper(II) complex, have been synthesized by Cohen et al., by using 5,5'-azo-1,2,3,4-tetrazole (TEZ) and 4,4'-azo-1,2,4-triazole (ATRZ), as linking ligands between GO-Cu layers [102]. The molecular structures, detonation performances and sensitivity of these ECPs were determined. They observed that these energetic nanomaterials are insensitive and highly thermostable, because GO sheets have high heat and impact dissipation capacity. Particularly, the GO-TEZ-Cu(II) ECP exhibits low sensitivity to impact as well as to electrostatic discharge ( $I_m = 21$  J; ESD of 1995 mJ). It has a comparable detonation performance to RDX. Also, their novel GO/Cu(II)/ATRZ hybrid, ECP GO-Cu(II)-ATRZ ECP, has high density ( $2.85 \text{ g}\cdot\text{cm}^{-3}$ ), remarkably high thermostability ( $T_p = 456$  °C), and low sensitivity ( $I_m > 98$  J; ESD of 1000 mJ).

The ESD sensitivity values, for materials explored in this study were found to have a range. The most insensitive material was found to be GO/Cu(II)/ATRZ hybrid ECP, which is even less sensitive than TATB. The ESD results measured for their ECPs were found to be higher than 205 mJ, showing insensitivity to electrical discharge. It is due to electron conductivity of GO sheets, where the GO-Cu(II)-TEZ ECP achieved a very impressive 1995 mJ value.

Due to its good combustion performance, and high density, zirconium metal prepared as powder is of interest as an energetic material as fuel in solid propellants. Unfortunately, the current zirconium powders have some

limited applications due to its high electrostatic discharge sensitivity. Thus, it makes the zirconium powders more pyrophoric and less amenable to functionalization. Glycidyl azide polymer (GAP) is a kind of energetic binder as coating material. It was selected by Jiang et al., to improve the security, and coated on the surface of zirconium powder directly to obtain Zr/GAP composite particles possessing highly reduced electrostatic discharge sensitivity [101]. The measured results indicated that 50% firing energy (E50) of Zr/GAP was increased from 5.13 mJ to 24.91 mJ, meanwhile the good combustion performance and high density of Zr powder were also reserved.

The electric spark induced ignition mechanism for explosives studied by Lyu et al., [103]. In the study, the ignition of powdery and bulky TATB by electrostatic discharge was investigated. Up to 200 kV ultra-high voltage ESD was applied to powdery and bulky explosives of two TATB-based polymer-bonded explosives (named PBX-1 and PBX-2).

The results revealed that powdery and bulky explosives have extremely different spark sensitivities for the same formulation. The 50% ignition voltages of powdery PBX-1 and PBX-2 were 10.8 kV and 8.5 kV, respectively, while the values for the bulky samples (tablets) were not less than 200 kV. Note that both heat and the electric field can be transmitted into the powdery samples, on the other hand only the electric field can be transmitted into the bulk samples. Also note that the electric field should have a smaller contribution while the heat has a larger contribution to the ignition during an ESD, namely, the thermal effect plays a main role in the ignition process. Their experimental results are reported as in good agreement with recent results calculated by density functional theory.

Poper et al., showed that small concentrations of carbon nanotubes (CNT) added to the highly reactive mixture of aluminum and copper oxide (Al+CuO) significantly reduces ESD ignition sensitivity [104 (See safety section below!).

#### 6.1.5. *Thermite*s

It had been previously postulated that the ESD ignition threshold could be affected by altering a material in three ways either increasing the conductivity of the sample, having the energy from the discharge absorbed by an endothermic reaction or increasing the electrical resistance of the material. Foley et al., briefly gave the description of an apparatus suitable for testing the electrostatic discharge ignition threshold for sensitive materials [105]. This apparatus was used by the authors to demonstrate how fluorocarbons could alter the propensity of a nanothermite to ignite. In addition to these findings, the effect of the fluorocarbon on the pressure output of the material is reported.

In the article of Shaw et al., nanocomposite, 8Al MoO<sub>3</sub>, thermite particles were prepared by using arrested reactive milling and ignited performing two experimental techniques [106]. In the spark ignition, a monolayer of powder was placed on a conductive substrate and heated in air by a pulsed electrostatic discharge. Whereas, in shock ignition, an individual particle was targeted by a miniature, laser-driven flyer plate which was accelerated to a speed in the range of 0.5-2 km s<sup>-1</sup>. In both of the experiments, time-dependent optical emission produced by the ignited material was monitored and recorded. The heating rates achieved in the above mentioned experiments were on the order of 10<sup>9</sup>–10<sup>11</sup> K s<sup>-1</sup>. These ignition methods result in a very fast combustion with characteristic burn times reduced by 1-3 orders of magnitude compared to the burn times measured previously for the same material ignited in the CO<sub>2</sub> laser beam, where it was heated at a much lower rate of about 10<sup>6</sup>–10<sup>7</sup> K s<sup>-1</sup>. The ignition delays observed in both shock and spark ignition experiments have been found to be close to each other and vary in the range of 120-200 ns. The times of characteristic rapid increase in the optical emission of the ignited particles were also found to be close to each other for the two experiments. However, these times were somewhat shorter (less than one μs) for the spark ignition tests compared to few μs observed for the shock initiated particles. In the article, preliminary ideas enabling one to interpret the present results were discussed. The work establishes an approach for systematic studies of high rate ignition and respective combustion of nanocomposite reactive materials.

In the research by Abraham et al., four bimetal Al–Ni nano-powders having compositions varied from 5 to 45 at % of nickel were synthesized by explosion of electrically heated twisted pure Al and Ni wires in argon atmosphere [107]. The nano-powders were characterized using various techniques. The materials were ignited using an electrically heated filament (which was coated with powder) and electrostatic discharge. The results were compared with those of the pure nano-aluminum powder (n-Al) prepared using the same wire explosion technique. The nano-powders with high nickel concentrations contain fully reacted intermetallic phases, which are difficult to oxidize making them unattractive for energetic formulations. Nano-powders with lower nickel concentrations do not contain significant amounts of the intermetallic phases. No intermetallics were detected in the powder with 5 % at Ni, which oxidized qualitatively similar to n-Al.

The experiments for ignition of nano-powders, Al95–Ni05 and n-Al by electro-static discharge were performed in air using a 2000 pF capacitor allowed to characterize the minimum ignition threshold for both of the nano-powders. It was observed that at voltages below 4 kV, some of the Al95–Ni05 powder remained in the sample holder after the spark discharge. However, all n-Al was always ejected. The recorded emission pulse structure typically includes a relatively weak prompt ignition event, with characteristic times of about 2–4 ms, and a stronger delayed ignition, occurring typically after 10 ms. The prompt ignition is not discernable for all recorded traces. Its timing is comparable to that observed in experiments with individual aluminum nanoparticles [108,109]. Thus, the initial weak maximum in the emission signal probably represents particles which are directly ignited by ESD. The stronger, delayed maximum occurring at 15–60 ms may be associated with ignition of an aerosolized powder cloud. It was stronger for n-Al at lower ESD voltages, because the larger amount of powder was ejected from the sample holder. However, in contrast, the maximum emission intensity at ESD voltages greater than 5 kV, was consistently stronger for Al95–Ni05 composite.

The overall mass gain during oxidation for the bimetal powder was nearly identical to that of n-Al, which suggests the same heat release anticipated from their combustion. Oxidation kinetics assessed for this material accounting directly for the measured particle size distribution was compared to that of n-Al. In the experiment the observed bimetal powder oxidized slower than n-Al, indicating its greater stability during the handling and storage. The bimetal powder was less sensitive to ESD-ignition than n-Al was, but generated a stronger emission signal when ignited. Therefore, the bimetal powder with 5 at % Ni is an attractive replacement of n-Al for advanced energetics with lower ESD sensitivity, better stability, and improved combustion performance.

The sensitivity of nanothermites to electrostatic discharge has been noted by many authors. In the work of Kelly et al., various nanothermites have been prepared using aluminum fuels with oxide (O-Al), palmitic acid (L-Al) and Viton (V-Al) passivation and CuO, Fe<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> oxidants (as well as binary oxidant mixtures) [110]. The fuel- and oxidant based ESD sensitivity trends of were obtained, with binary oxidants affording some intermediate sensitivities. In the majority of cases, with the exception of high proportions of MoO<sub>3</sub> oxidant, the nanothermites containing V- Al fuel were found to be the least sensitive to ESD at > 0.156 J.

Resistivity measurements have been made for the fuels and oxidants which follow

the trends V-Al > O-Al ≈ L-Al and MoO<sub>3</sub> > Fe<sub>2</sub>O<sub>3</sub> > CuO. It was observed that V-Al resistivity of ca.1011 Ω·cm exceeds that of the oxidants studied.

#### 6.1.6. Miscellaneous

Most primary explosives are non-conductors, have tendency to accumulate charge easily when contacting with and separating from other materials. They are sensitive to electrostatic discharge. In order to reduce the risk of accidents caused by ESD initiation of primary explosives, obviously some studies on their electrostatic hazards are necessary. In the work by Li et al., comprehensive experimental results of electrostatic discharge sensitivity and chargeability of tris(carbohydrazide)zinc perchlorate (ZnCP) under different conditions have been presented [111]. The influences of the testing conditions, of devices, ambient

temperature, particle size and relative humidity on the electrostatic discharge sensitivity and chargeability have been investigated in detail, and some quantitative regression equations obtained.

It has been observed that the  $E_{50}$  decreases with decreasing electrode gap, and a linear relationship exists which can be described by the following equation, where "gap" is the magnitude of the electrode gap, in millimeters.

$$E_{50} = 0.0956 + 0.9516 \text{ gap} \quad (17)$$

ZnCP can be ignited by an electronegative discharge with an  $E_{50}$  of 0.25 J ( $C = 0.22 \mu\text{F}$ ,  $R = 100 \text{ k}\Omega$ ,  $V_{50} = -1.5 \text{ kV}$ ,  $R$  is an additional resistance in the discharge circuit). However, when using an electropositive discharge, ZnCP cannot be ignited by 62.5 J ( $C = 0.22 \mu\text{F}$ ,  $R = 100 \text{ k}\Omega$ ,  $V = 25 \text{ kV}$ ). This may be attributed to the high density of electrons around the needle electrode causing ZnCP to decompose quickly when ignited by an electronegative discharge.

The relation between the  $E_{50}$  of ZnCP and the capacitance can be regressed to yield eq.18.

$$E_{50} = 1.5130 - 12.2697 C + 27.7419 C^2 \quad (18)$$

The relation between the  $E_{50}$  of ZnCP and its particle size can be described by:

$$E_{50} = 0.2692 + 5.6683 \times 10^{-5} \exp(d/28.1188) \quad (19)$$

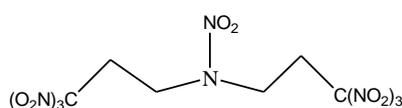
The linear equations for the dependence of the  $E_{50}$  of ZnCP on temperature ( $T/^{\circ}\text{C}$ ) and relative humidity ( $H/\%$ ) can be described by:

$$E_{50} = 0.4052 - 0.0049 T \quad (20)$$

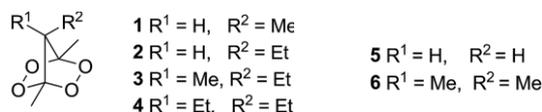
$$E_{50} = -0.0744 + 0.0063 H \quad (21)$$

respectively.

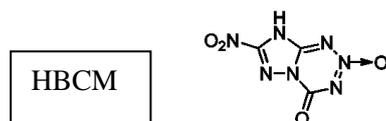
The authors of a quite recent article, considered the chemistry of energetic materials containing 3,3,3-trinitropropyl group which has been less investigated regarding its chemical and energetic properties [112]. Note that 2,2,2-trinitroethyl group is well-established in the chemistry of energetic materials. Thus, investigations on the syntheses of several compounds containing the 3,3,3-trinitropropyl group were performed and their properties compared with the 2,2,2-trinitroethyl group. All the materials were thoroughly characterized, including single-crystal X-ray diffraction studies. The thermal stabilities were examined and the sensitivities towards impact, friction, and electrostatic discharge were tested using a drop hammer, a friction tester, and an electrical discharge device, respectively. The best compound, with excellent detonation parameters, is the nitramine whose structure is depicted below, which has a very high detonation velocity ( $9119 \text{ ms}^{-1}$ ) and a strong detonation pressure. The both values significantly exceed those of TNT, RDX, and PETN. The relative electrostatic discharge sensitivity of the explosive is tested with an apparatus, whereby variable capacitive resistances and loading voltages generate different spark energies. The electric discharge was determined which is needed to initiate a decomposition or an explosion. The lowest value for an initialization was found for the following nitramine, with an energy of 0.15 J, which is in the range of secondary explosives such as pentarethritol tetranitrate (PETN) and RDX.



Energetic organic peroxides are simple, strong and sensitive. 1,4-Dimethyl-2,3,5,6-tetraoxabicyclo [2.2.1] heptane and several similar alkyl-derivatives were synthesized and crystal structures of the compounds were determined and their energetic properties including sensitivities towards impact, friction and electrostatic discharge [113]. Their thermal behavior was determined and compared to tricetone triperoxide (TATP). The enthalpies of formation and the resulting explosive properties were calculated. The ESD values of compounds 1-6 are in the range of 0.1-0.2 J. Note that the respective value for TATP is 0.16 J. All obtained compounds are found to be highly energetic and sensitive toward mechanical stimuli such as friction and impact.

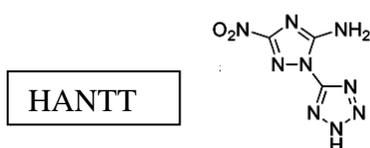


Bian et al., reported the unique and facile synthesis of 7-nitro-4-oxo-4,8-dihydro- [1,2,4] triazolo[5,1-d] [1,2,3,5] tetrazine 2-oxide (HBCM) and proposed a mechanism for its formation [114]. Due to the hygroscopicity of HBCM it was transformed it into salts. The energetic salts of HBCM were characterized. The densities of the salts ranged in between 1.77 to 1.97 g cm<sup>-3</sup>. Most of the energetic salts obtained decomposed above 230 °C and tended to be insensitive to friction, impact, and electrostatic discharge which was reported only qualitatively (+/-). Theoretical performance calculations for the energetic salts provided detonation pressures and velocities within the ranges of 25.2 to 39.5 GPa and 7856 to 9069 m s<sup>-1</sup>, respectively. The hydroxylammonium salt exhibited high density (1.97 g cm<sup>-3</sup>), acceptable decomposition temperature (T<sub>d</sub>= 197 °C), low sensitivities, and excellent detonation velocity (9069 m s<sup>-1</sup>) and pressure (39.5 GPa), all of which suggests that it has some potential to be used as a high-energy-density material.

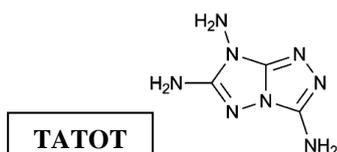


4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole was synthesized starting from readily available materials via a one-step procedure [115]. The compound consists of two combined aromatic triazole molecules with four amino moieties. It has (i) high temperature stability, (ii) a high heat of formation, (iii) a high density and (iv) no sensitivity towards physical stimuli (impact, friction, and electrostatic discharge). The authors investigated the compound in detail as a potential nitrogen-rich, temperature-stable cation for the synthesis of various energetic ionic derivatives which may be used as environmentally benign explosives. The cation was combined with various oxygen-rich counter-anions such as dinitramide, 5-nitrotetrazole-2-oxide, 5-nitrotetrazolate, nitrate, tetranitrobisimidazole, 5,5'-bitetrazole-1,1'-dioxide, 1,1'-dinitramino-5,5'-bitetrazolate, 5-nitriminotetrazolate, 1-methyl-5-nitriminotetrazolate, perchlorate, picrate and nitroformate. The sensitivities towards impact, friction and electrical discharge were investigated using the BAM standards and a small-scale electrostatic discharge-tester. The ESD measurements show that the compounds have ESD values in the range of 0.03-1.5 J (RDX has 0.2 J). The detonation parameters of the compounds without the inclusion of crystal water were calculated using the EXPLO5 (V6.02) code and the calculated (CBS-4M) values for the enthalpy of formation.

Bian et al., quite recently synthesized and characterized a new family of nitrogen-rich energetic salts of 3-nitro-1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (HANTT) [116] which also comprise guanidinium salt, and 1,5-diamino-tetrazolium. All the energetic salts exhibit excellent thermal stabilities with decomposition temperatures ranging within 264-321°C. They are found to be insensitive to impact, friction and electrostatic discharge. All the salts considered in the work were insensitive to electrostatic discharge with the ESD values above 44 J while the neutral compound, HANT, is relatively insensitive (ESD = 7.04 J).

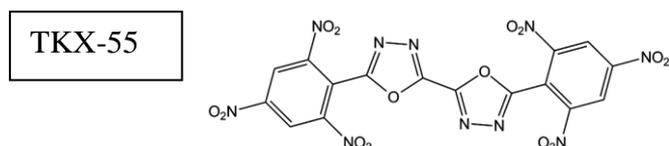


The 3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazolium (TATOT) moiety was incorporated into many ionic, nitrogen-rich materials to form salts having certain advantages such as remarkably high stability towards physical or mechanical stimuli, excellent calculated detonation velocity, and sufficiently low toxicity to be qualified as "green explosives" [117].



Neutral TATOT can be synthesized in a convenient and inexpensive two-step protocol in high yield. To demonstrate the superior properties of TATOT, Klapötke et al., synthesized 13 ionic derivatives and investigated their chemical- and physicochemical properties (e.g., sensitivities towards impact, friction and electrostatic discharge) extensively. Low toxicity was demonstrated for neutral TATOT and its nitrate salt. The ESD value of TATOT was found to be 1.5 J (employing an ESD device of OZM Research). ESD values of other derivatives range between 0.08-1.5 J.

Klapötke et al., in one of their publications reported facile synthesis of a novel, thermally stable explosive 5,5'-bis(2,4,6-trinitro-phenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) [118]. This compound shows outstanding properties (detonation velocity, detonation pressure, sensitivity toward mechanical stimuli, and decomposition temperature). The compound was isolated and characterized. The sensitivity towards impact, friction, and electrostatic discharge was determined. Its electrostatic discharge value is 1.0 J. Note that under the same conditions PYX and HNS have the values of 0.5 and 0.8 J, respectively.

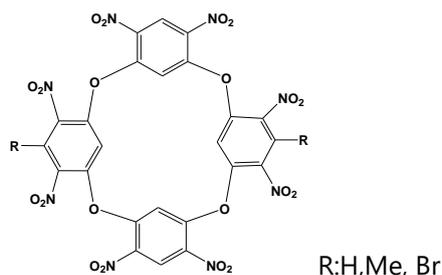


4,6-Diazido-N-(2,4,6-trinitrophenyl)-1,3,5-triazin-2-amine (TNADAzT) and its silver salt (AgTNADAzT) were prepared and characterized by elemental analysis, FTIR, NMR, DSC, AAS and X-ray diffraction for analytical characterization [119]. The sensitivities of TNADAzT and AgTNADAzT were determined and compared with common explosives and MTX-1. The sensitivity of TNADAzT to impact and friction slightly exceeds PETN whereas the sensitivity to electrostatic discharge has been found to be lower than RDX. The sensitivity of AgTNADAzT is on the level of a primary explosives (between PETN and mercury fulminate). The initiation efficiency of AgTNADAzT is higher than 200 mg (acceptor PETN compressed by 64-70 MPa) and therefore excludes it from being used practically as a primary explosive in detonators.

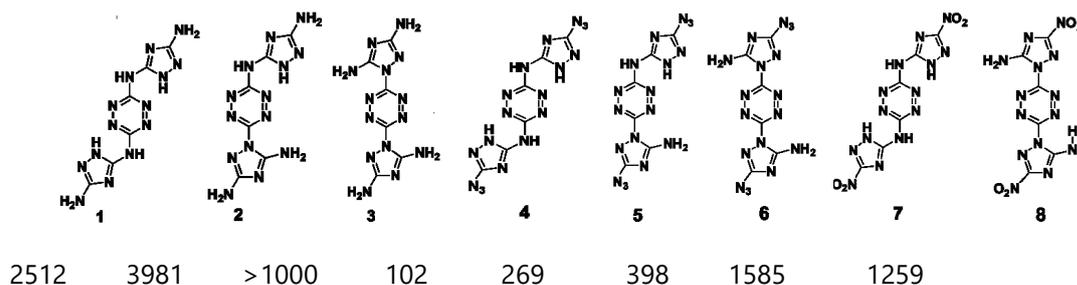
Szimhardt et al., managed the synthesis and characterization of 1-methyl-5H-tetrazole (1, MTZ) from 1,5H-tetrazole and methyl iodide [120]. This neutral ligand was evaluated for its usage as energetic transition metal complexes. The formation of complexes is possible with the large number of possible combinations: (i) metal, (ii) ligand, and (iii) anion. A series of 31 new complexes employing MTZ as the ligand was prepared in order to tune their optical properties (beside their sensitivity values) by using seven different metals ( $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Ag^+$ ) and six different anions (chloride, nitrate, perchlorate, cyanodinitromethanide, picrate, and styphnate). Thus, tailoring of the energetic properties of the desired molecule toward e.g., suitable laser-ignitable materials or primary explosives is possible. The compounds obtained were characterized and the sensitivities toward external stimuli (impact, friction and electrostatic discharge) were determined

according to the standard methods. These complexes have been characterized in laser ignition experiments and as new primary explosives. As an outline, in the work a large number of compounds with sensitivities ranging from insensitive to very sensitive were synthesized to give a wide range of new materials for different possible applications.

The work by Zhang et al., describes 14,16,34,36,54,56,74,76- octanitro - 2,4,6,8-tetraoxa-1,3,5,7(1,3)-tetrabenzenacyclooctaphane (a novel, thermally stable explosive) and its derivatives [121]. These compounds show outstanding properties. From the calculated standard molar enthalpies of formation (CBS-4M) and densities, the Chapman-Jouguet detonation properties were predicted using the EXPLO5 V6.01 thermochemical computer code. The sensitivities towards friction, impact, and electrostatic discharge were determined. The ESD values were found to be 1.0 J.



Shlomovich et al., described a series of nitrogen-rich "green" Energetic Materials (EMs), (on the basis of 3,5-diamino-1,2,4-triazole (DAT) and 1,2,4,5-tetrazine building blocks) some having improved sensitivity, thermostability, and very low toxicity [122]. They developed reaction conditions under which some specific isomers could be prepared. On evaluating these compounds (1-8 are shown below together with their ESD values in mJ) for their energetic properties, the authors have found that N5,N5'-(1,2,4,5-tetrazine-3,6-diyl)-bis(1H-1,2,4-triazole-3,5-diamine) (**1**) has very high thermostability (onset of decomposition temperature at 357 °C). It is also insensitive to impact ( $Im > 98$  J), friction ( $> 360$  N) and electrostatic discharge (2512 mJ). A detonation velocity (VOD) of  $8180 \text{ m s}^{-1}$  was calculated for compound 1. In combination with oxidants, compound 1 can generate 1225 L of gases (per kg of energetic mixture of an oxidant and compound 1), which makes this material a potent component in various solid propellants and a very good candidate for a broad range of other civil and defense applications that require the use of "green" and insensitive EMs.



## 7. Safety

More recently, work on test methods for electrostatic ignition hazards avoidance, has commenced. Meanwhile the European Committee for Electrotechnical Standardization (CENELEC) has been active issuing a code of practice for avoidance of electrostatic hazards, as well as various test methods. The paper by Smallwood examines some areas in which new test methods are needed or are currently being developed by IEC TC101 for the world market [63].

Static electricity development is one of the main causes of accidental explosion of explosives. Raha et al., in their study deal with the development of static electric charge resulting from compression of single crystals of explosives including pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT), *N*-2,4,6-tetranitro-*N*-methyl

aniline (tetryl) and cyclotrimethylene trinitroamine (RDX) [123]. It has been revealed that the charge developed on PETN and TNT was "true piezoelectric", whereas on tetryl and RDX, it was tensorial piezoelectric in nature. Measurement of the dielectric constant, piezoelectric coefficient, and compressibility of these explosive crystals revealed the anisotropic character of these crystals. It has been observed that the static field developed under the laboratory experimental conditions, when extrapolated to the condition of detonation, exhibits an inverse relationship with the figure of insensitivity of the respective high explosives.

In the article of Kao and Duh, a dust explosion was considered and concluded where the bulked brush discharging was the possible ignition source for the successive dust explosions [124]. Also, the TNT equivalent and the consequences of the explosion were calculated and compared with the recorded situations.

In the process industries fires and explosions result in serious hazards. Instead of expensive methods such as suppression and venting, ideally, to avoid fire or explosion would be the best option which may be accomplished by either removing the explosible fuel/oxidant mixture, or the ignition source. Usually, one of the most overlooked but preventable ignition sources is electrostatic discharge. To evaluate the potential for ignition of a fuel/oxidant admixture, firstly one has to determine its minimum ESD ignition energy. Once the initiation thresholds is identified, one can evaluate the likelihood of electrostatic charging and storage, which could result in an electrostatic discharge. However, identifying this threshold level can be problematic.

An ASTM standard has been developed but, for this test standard to be effective, it must reflect the true hazard potentials observed. Some important points that need to be considered in order to increase the utility of any minimum ignition energy standard are:

- 1) discharge geometry, 2) duration of the discharge and 3) calculation of the energy of the discharge. This paper by Dahn and Dastidar discusses the importance of these factors when evaluating the least amount of energy required to initiate an explosion [125].

The current ASTM standard for minimum ignition energy (MIE) determination is an adequate approach for evaluating the explosibility hazards posed by electrostatic discharges. However, MIE data should be critically reviewed due to the variability in spark discharge circuitry and geometry, dust dispersion apparatus, and energy discharge measurement. It should be noted that performance assurance of the test apparatus should always be obtained by comparing known minimum ignition energies of standard dusts.

Powder energetic materials are highly sensitive to electrostatic discharge ignition. This study by Poper et al., shows that small concentrations of carbon nanotubes (CNT) added to the highly reactive mixture of aluminum and copper oxide (Al+CuO) significantly reduces ESD ignition sensitivity [104]. It has been explained that CNT acts as a conduit for electric energy, bypassing energy buildup and desensitizing the mixture to ESD ignition. The lowest CNT concentration needed to desensitize ignition was obtained to be 3.8 vol.% corresponding to percolation corresponding to an electrical conductivity of 0.04 S/cm. Conversely, CNT added increased Al+CuO thermal ignition sensitivity to a hot wire igniter.

Lyu et al., considered the electrostatic discharge tests of PETN, TNT and PBX-1 (HMX content 95%) [126]. The tests were done through the powder and tablet test methods. The results showed that the antistatic properties of all test samples increased greatly after press-molding. The main reason of the greatly enhanced antistatic property of press-molded explosive could be due to the non-synchronization of electricity and heat during electrostatic discharged, which decreases the force of electric field and makes the heat effect of spark prominent.

Grabarczyk reviewed the contemporary ideas on the risk of ignition of sensitive explosive atmospheres (minimum ignition energy less than 0,1 mJ) by positive electrostatic corona discharge in the streamer phase [127].

Collins et al., synthesized aluminum particles with shell thicknesses ranging from 2.7 to 8.3 nm having a constant diameter of 95 nm [128]. Then, these fuel particles were combined with molybdenum trioxide particles and the electrostatic discharge sensitivity of the mixture was measured. The results showed that ignition delay increased as the alumina shell thickness increased. These results correlated with electrical resistivity measurements of the mixture which increased with alumina concentration. Also, a model was developed using COMSOL for ignition of a single Al particle. It was obtained that the ignition delay in the model was consistent with the experimental results which suggests that the primary ESD ignition mechanism is joule heating. They have reached a conclusion that alumina retards energy buildup within the particle so that thicker alumina shells result in occurrence of longer ignition delay times. The results also have revealed that the current flow through the particle is a controlling parameter for the ignition. Thus, a thicker shell increases the resistance and therefore lowers the amount of current flowing through the aluminum core.

Yu et al., studied the response regulations of electrostatic discharge conditions for firing device materials of an electric explosive device (EED) [129]. Also, its damages under an electrostatic environment were studied. The ESD process for discharge models under different high static voltage conditions was simulated and analyzed by the ESD models originated from Institute of Electrical and Electronic Engineers (IEEE) standard and Sandia laboratory standard. Energy values produced by discharge were determined and compared and analyzed with those of physical form transformation property of firing materials in a typical EED. The damage situation of ESD to a typical EED was predicted. The results have revealed that the peak discharge current increases with increasing the initial electrostatic voltage, while the other parameters of current waveform unchanges. The temperature of bridge wire in a typical firing device (consisting of Ni-Cr bridge wire having a diameter of 40  $\mu\text{m}$  and lead styphnate), can reach the melting point of tin solder. Whereas, in Sandia laboratory standard ESD model, the temperature in the bridge wire can rise to the melting point of tin solder at 20 kV, then the decomposition and ignition of the explosive at 25 kV and the melting point of bridge wire at 50 kV occurs.

As a useful method of preventing dust explosions, nitrogen ( $\text{N}_2$ ), an incombustible gas, has been applied to an explosive atmosphere. This paper by Choi and coworkers is a report that quantitatively determines whether the minimum ignition energy of powder depends on the nitrogen (or oxygen) concentration in the air [130]. The powders used in this experiment were lycopodium, four kinds of polymer powders, and toner. Hartman vertical-tube apparatus and six sample powders were used in this study. The results showed that the minimum ignition energies of all of the powders used in this study increased with increased amounts of  $\text{N}_2$  in the air. However, the effects were different in all of the sample powders. They suggested that the  $\text{N}_2$  concentration of 84 % (or above) prevents dust explosions due to electrostatic discharges in the industrial process with the sample powders used in this experiment.

Small-scale safety and thermal (SSST) testing are the first steps in establishing safe handling procedures for explosives. In order to understand the response of homemade or improvised explosives (HMEs) to SSST testing better, 16 HME materials were compared to three standard military explosives [131]. The testing study included impact, friction, electrostatic discharge and thermal behavior. The testing matrix was designed to address problems encountered with powder mixtures, liquid suspensions, immiscible liquids, partially wetted solids, and reactive materials. All testing materials and/or precursors came from the same batch were handled, pretreated, and mixed by standardized procedures. Some general trends observed for each series. The ESD - IHD test usually found the materials less sensitive than the average.

The work by Wei et al., considered three kinds of monitoring methods, which include the field strength monitoring and Faraday cylinder charge quantity monitoring and induced current integral charge quantity monitoring for safely and accurately monitor the risk of combustion and explosion of explosives and propellant powders caused by electrostatic discharge [132]. The corresponding testing devices were established. In the study, the contrast testing study on the accuracy of the electrostatic field monitoring data which were obtained by different methods and the reliability of the electrostatic monitoring was performed by the way of substitute material. The safety of the monitoring system was evaluated. The results showed that when powder pile height in storage bin was 200 mm, the field strength monitored by powder pile surface was 2160 kV,

which was only 1/7 of the field strength of 14709 kV in base of powder pile. Whereas, when powder pile height was 100 mm, the field strength data of powder pile surface was 20 times of the calibration data, thus it cannot achieve accurate and reliable monitoring of electrostatic discharge risk. On the other hand, the monitoring data of Faraday cylinder charge quantity monitoring and induced current integral charge quantity monitoring methods are accurate and reliable monitoring of the electrostatic field, but the Faraday cylinder charge quantity monitoring system itself exists the risk of electrostatic discharge. Whereas induced current integral charge quantity monitoring system exhibits good safety.

Puszynski et al., used several additives such as polyvinyl butyral (PVB), polyvinylpyrrolidone (PVP), and ethyl cellulose (Ethocel™) to improve the flowability and safe pressing of copper(I) 5-nitrotetrazolate (DBX-1), which is a green replacement for lead azide [133]. However, DBX-1 is an extremely sensitive primary explosive, particularly when dry. DBX-1 has shown some loadability issues when tested in contractor manufacturing facilities; particularly, it exhibits a tendency to stick on the loading scoops and punches, which could cause some production delays as well as accidents due to charge buildup on the tooling. Those properties are important for pressing the material into small-volume detonators. Sensitivity tests such as ball drop impact, Bundesanstalt für Materialprüfung (BAM) friction, and electrostatic discharge along with compatibility testings were performed. Also, some performance testings in M55 stab detonators were conducted. For comparison, all testings were done on both uncoated DBX-1 (control sample) and DBX-1 coated with various additives.

It has been observed that DBX-1 with PVB additive effectively increases the flowability of the material while not adversely affecting its performance in M55 detonators. The safety of the DBX-1 material also appears to be significantly improved by the coating process. The pressure required to initiate the explosive during pressing increased twofold relative to the uncoated sample. However, it seems an optimization is still needed for loading the detonators. They have planned additional future studies focusing on finding some effective storage solvents for DBX-1, which will not degrade the coating layer.

Today a large number of electrical products and electrostatic sensitive ammunition have been used in weapons systems. As the modernization of weapons and equipment continues, electrostatic discharge hazards become increasingly serious. Thus, the electrostatic discharge sensitivity of these equipment, electrical products and agents are to be investigated. In the article by Yang et al., the electrostatic hazards of the electro-explosive devices and some protective measures have been presented and discussed [134].

It is known that Zr powder is a promising high energy fuel/additive for rocket propellants, because of its high volumetric heat of oxidation. However, the application of Zr powder is restricted by its ultra-high electrostatic discharge sensitivity. Thus, it poses great hazards for handling, transportation and utilization of this material. Qin et al., has shown that Zr particles can be uniformly encapsulated by thin layers of the polymer by performing molecular layer deposition of polyimide using 1,2,4,5-benzenetetracarboxylic anhydride and ethylenediamine as the precursors [135]. By adjusting the number of deposition cycle, the thicknesses of the encapsulation layers can be precisely controlled. Afterwards, high temperature annealing converts the polymer layer into a carbon coating. By varying the thickness of the polyimide or carbon coating, electrostatic discharge sensitivity of the Zr powder can be tuned in a wide range, thus its uncontrolled ignition hazard can be virtually prevented.

The apparatus they used in the experiments includes a capacitor bank with capacitance varied in the range from 100 to 10000 pF. The capacitor can be charged to a voltage varied in the range of 100 V to 26 KV. A limiting resistor (with resistance varied from 0 to 100 Kohm) is connected in series with the pin-electrode in order to change the range and sensitivity of the measurement. The uncoated Zr powder has an  $E_{50}$  value less than 1 mJ, approaching the lower detection limit of the apparatus. This value is much lower than the maximum energy that could be dissipated from a human body (8.33 mJ) [78]. Therefore untreated Zr powder is dangerous to handle. By adding a graphite powder (upto 10 wt %) to the metal fuel by mechanical mixing has little effect on improving the electrostatic safety. In comparison, molecular layer disposition (MLD) surface modification is very effective for reducing the ESD sensitivity. The  $E_{50}$  values of the Zr powders fabricated by

100-, 200-, and 400-cycle MLD PI (PI: polyimide) are respectively 36.4, 88.2, and 126.7 mJ. Carbon coatings are even more effective for mitigating the ESD ignition hazard. It has been observed that after high temperature annealing, the  $E_{50}$  values of the carbon nanofilm encapsulated Zr powders are almost doubled. Note that for either MLD PI or carbon coating, the  $E_{50}$  value increases with the increasing thickness of the encapsulation layer. Since the thickness of the PI coating can be precisely controlled by varying the number of MLD cycle, the  $E_{50}$  of the Zr powder can be finely tuned in a wide range from less than 1 to hundreds of mJ.

Although, nanothermites suffer from high electrostatic discharge sensitivity which makes their handling hazardous, they are attracting much attention for energetic applications. Developing safe as well as powerful nanothermites still remains a challenge. In the work of Dai et al., nitrocellulose (NC) was adhered to the surface of Al and  $\text{Bi}_2\text{O}_3$  nanoparticles by a facile electrospray method in order to improve the ESD safety and energy output of Al/ $\text{Bi}_2\text{O}_3$  [136]. The morphological and compositional characterization of Al/ $\text{Bi}_2\text{O}_3$ @NC confirms the NC-coated structure. It was observed that the ESD safety of coated Al/ $\text{Bi}_2\text{O}_3$  was improved. For instance, the Al/ $\text{Bi}_2\text{O}_3$ @NC containing 10 wt% of NC exhibited a ESD ignition threshold to be 81 mJ instead of 1 mJ for the Al/ $\text{Bi}_2\text{O}_3$  without NC. On the other hand, by the addition of NC coating tunable energy output was obtained. Specifically, Al/ $\text{Bi}_2\text{O}_3$ @NC (3 wt%) exhibits remarkable enhancements in pressurization, heat release and combustion reaction, which even outperforms the most widely used primary explosive lead styphnate (LTNR). The enhancements can be attributed to the fact that NC serves as a gas-generating agent to prevent the nanoparticles from sintering to larger particles and enables sufficient combustion.

## 8. Epilogue

The present short review article considers electrostatic discharge, its physics and kinds, ESD sensitivities of certain groups of explosives and some predictive studies. Static or electrostatic discharge may supply enough energy to initiate ignition/detonation in a number of materials under some, most of the time unpredictable, circumstances. Multiple tests, standards and methodologies have been developed to investigate the ignition behavior of various substances exposed to spark. Through the years, effects of electrode materials, electrode shape, discharge duration and some other parameters have been investigated.

Some researches have tried to investigate the effect of ESD energy as a thermal source capable of raising the temperature of a flammable/explosive substances. However, it remains obscure how the spark heats the materials, what portion of the spark energy is being transferred and by which mechanism.

Great deal of effort has been done, at least qualitatively, to correlate sensitivity of certain group of explosives and some properties of them, in order to have certain information in the absence of any experimentation. Although, some of them are quite successful, those predictive approaches most of the time do not reflect the true mechanism of ignition or contributing factors to ignition because most of them suffer from lack of analysis of regression statistics.

On the other hand, experimentally determined and reported ESD sensitivity data are highly influenced by the sampling techniques, types of instrumentation, etc. Therefore, a lots of research still are needed for the perfect understanding of the phenomenon.

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