

Good nanotechnology in explosives article review example

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The Current State of Research on New Methods and Technologies for the Safety and Reliability of Assessment of Propellants, Explosives and Pyrotechnics¹

Abstract

Materials with high energy have in the past and are still in use for both intensive military and civil purposes. Research and studies have been conducted recently to try establishing and inventing new materials likely to have enhanced high performance and that are less sensitive to heat and shock as compared to existing materials. In future military applications have a threshold to be adjusted to. This paper is mainly focusing on the on the advancements, possible formulations of compounds and applications related to space with respect to stability and safety as well. Its subsidiary focus is the moisture influence on thermal propellants.

Introduction

High energy materials such as propellants, explosives, and pyrotechnics have in the past been used widely for both military and civil purposes and also as applications. Currently, we have got a different variety of materials classified as high energy content materials for different applications. The recently highly used applications such as explosives hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX), 2, 4, 6-trinitrotoluene (TNT) and octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX) were thought to be adequate for all kinds and sought of weapons. With time, the named explosives have explosions considered to be catastrophic and resulting to unintentional disposition of ammunition to the atmosphere and environment. The process

could have happened either through aircrafts, marine vessels or even other locomotives such as trains. The process has resulted to the explosives becoming less attractive. Users of explosives intend to use materials that are of high performance, but less vulnerability. The action is the reason high-performance explosives are still in use today irrespective of the previous studies being against them.

Most explosives and propellants are made of organic materials. These materials readily react with water or water accelerates their decomposition during storage. Water is advised to be used during their storage because if let, they are likely to leak to the environment and are highly hazardous.

Other key areas of likely reactivity other than storage are transportation and production. At normal temperatures, the reactivity is highly exothermic.

The United States (U. S.) in the Department of Energy (DOE) developed and operationalized a policy, Integrated Safety Management System (ISMS). The policy requires implementation of hazard and analysis of controls so as to protect workers and general public who operate within and around a hazardous facility. In this case an explosive and propellant industry. The ISMS is applicable to all the DOE facilities. The application is through; Safety Management System Policy, DOE P 450. 4, Integration of Environment, and (DEAR) DOE Acquisition Regulation clause 48 CFR 970. 5223-1, Health and Safety into Work Planning and Execution. However, no DOE-order or standard currently exists that provides specific guidance for the development of safety basis (SB) documentation for non-nuclear facilities.

Various DOE sites over the years have adopted individual site-specific chemical SB processes and documentation resulting in wide variations across

the DOE complex. The CSTC Phase 1 report, Current Chemical Hazard Characterization Practices in the DOE Complex, summarizes the variations in the DOE complex (CSTC 2003-C). 1

For the sake of providing a common understanding of non-nuclear SB for chemical facilities, this report identifies various steps involved in developing a safety document that includes essential features of the five core steps of the ISMS. The Safety Basis development is a highly interactive process which takes the steps below:

- _ Work and facility description;
- _ Identification of Hazard;
- _ Classification of hazard Facility - industry Process Safety Management
- _ Hazard analysis - qualitative and/or semi quantitative;
- _ Controls identification
- _ Commitments to safety management programs (SMP);
- _ Document and approval process

The non-nuclear process tries to focus on t different methodologies, of course including analysis of hazard from the chemical industry and DOE nuclear facility. Such like approaches can be used to implement each and every step. It also an attempt to describe the demerits and a merit of various methodologies of implementation that are either in use already or could be likely to be used by non-nuclear facilities.

Nanotechnology is the convergence of engineering resulting to structures, devices, and systems development with novel functional properties with sizes ranging from1 and 100 nm. Nowadays, particles are being

manufactured on a nano-metered scale so that the novel properties gained can be used in many ways. In general, the reaction rate of nanoscale materials is larger than those of micron scales several orders of magnitude and much larger surface area can significantly change combustion behavior. Because of the behavior of extremely fine particles, such as nanometer-sized particles, the combustion process is largely kinetically controlled rather than diffusion controlled as in standard sized powders. For example, conventional Al-based propellants are inefficient due to incomplete combustion. The incomplete combustion is because combustion product Al_2O_3 condenses on the Al particle during combustion ultimately stopping the process prior to completion. In addition to molecular structure, the microstructure of a material is a key determinant of the properties of the material. Controlling structures at the micron and nano levels is, therefore, essential to new discoveries. One of the emerging principal areas of investigation that integrates chemistry and materials science is Nanotechnology (Qian et al., 2003). Nano-sized aluminium powders can successfully replace the micron-sized Al powder in pyrotechnics that will increase the combustion efficiency and reduce agglomeration of the combustion products due to complete combustion. Two stages of oxidation are observed at temperatures in the range of 500–740°C for the nano Al powder and precursor micron-Al powder. The mass gain for the first oxidation stage of the nanopowder is 3.5 times more which is higher than that of the micron-sized powder. A decrease of the activation energy for Al oxidation has been found for the nano powder when compared to that of the precursor aluminium powder. For the activated nano-sized powder, the major part of aluminium is oxidized below 740°C

with the formation of γ - Al_2O_3 . On the other hand, for the micron-size powder, the major part of aluminium is oxidized in the range of 740–1000°C with pre-dominant formation of γ - Al_2O_3 (Pivkina et al., 2004). Nanopowders have more aluminium oxide content than micron powders. The difference is because the surface area to volume ratio increases dramatically as particle diameter decreases the size of the oxide shell. As particle size is reduced, the active aluminium content is decreased such that a trade-off may exist between the benefits of working on the nanoscale and the diminished purity of the Al particle. Although the reactivity of the particle may not be strongly influenced by the thickness of the oxide shell, the increased Al_2O_3 content of nanopowders may significantly influence the microstructure and macroscopic properties of combustion synthesized materials. Incorporating nanoscale Al particles is also shown to promote a complete reaction at high reaction rates (Granier et al., 2004). With nano-sized aluminium (nAl) particles, the specific surface area increases creating easier ignition and increased burn rates. When a pile of nAl powder is ignited in the open atmosphere, a flame front spreads across the surface of the substance. In contrast, ignition and flame spread cannot easily be obtained with micron-sized aluminium powder. Increasing particle size decreases the propagation velocity and widens the fingers. The decreased propagation velocity is due to the lower specific surface area of the particles. Because of this decreased propagation velocity, the fingers have more time to diffuse laterally creating wider fingers. Furthermore, the higher thermal conductivity of larger particle beds is likely an aid in the lateral diffusion of the flame (Malchi et al., 2007). Recently great attention has been focused on solid propellant formulations

containing ultra-fine energetic particles. The focus is particularly on nanoparticles, because of its advantages such as a significant increase in propellant burning rates, shorter ignition delays and shorter agglomerates burning times. Nanoparticles can enhance the linear burning rate of aluminized solid propellants by 100% or even more. The post-burning analysis shows the better combustion efficiency of nano-sized particles in comparison with micron sized aluminized propellants (Galfetti et al., 2007). Because of the higher surface area and close mixing of reactants, nano energetic systems have reaction rates that are several orders of magnitude faster than systems comprised of micron scale reactants. However, the safe and efficient processing of these nanopowders is still not optimal. So many works had been carried out to study the effects of the particle size from micron to nano size for the various characteristics. Especially, the explosive properties of the particles in various sizes have been carried out. In this paper, an overall view of the explosive properties of the fireworks chemicals and their safety parameters have been collected and discussed. The information will be used by the researchers who are working in the areas of the powder's hazardous (explosive) properties. Ying Huang et al., conducted a study on the combustion of bimodal nano/micron sized aluminium particles with air. The researchers found that flame speed was positively affected by increasing the mass fraction of nanoparticles in the fuel formulation. At low percentages of nanoparticles in the fuel formulation, the flame exhibited a separated spatial structure with a wider flame regime and at higher nanoparticle loadings, overlapping flame configurations were observed (Ying, 2007). Luman et al. had developed the solid propellants which contained

nano-sized particles. It was found that the addition of nano-sized aluminium particles could enhance the propellant burning rate and also exhibited improved impact sensitivity (Luman et al., 2007). Bingyou Jiang et al. examined the explosive characteristics of aluminium nanopowder and compared it with micron size. The result showed that the maximum explosion pressure and its rising rate of 100 nm aluminium powder gradually increased with increasing concentration of aluminium-powder. The conclusion was that the aluminium-powder explosion of 100 nm would produce more harms (Bingyou et al., 2011). Yanan Gan and Li Qiao had studied the burning characteristics of fuel droplets containing nano and micron sized aluminium particles. It was found that for nano suspensions, particle collision and aggregation were dominated by the random Brownian motion. For micron suspensions, how-ever, they were dominated by fluid motion such as droplet expansion, and surface regression resulting from bubble formation and internal circulation. They concluded that the different characteristics of the particle agglomerates, which were responsible for the different micro explosion behaviors (Gan and Qiao, 2011). Bouillard et al. studied the ignition temperature and the minimal explosive concentration (MEC) about the particle size. It was found that as the size of the particle decreased; minimum ignition temperature (MIT) and minimum ignition energy (MIE) decreased. The finding indicates higher potential inflammation and explosion risks for the use of nanopowders (Bouillard et al., 2010). Volkmat Richter et al. studied the risks of metal powders of nano and micron size. They concluded that the inhalation of these metal powders led to a condition known as 'hard metal lung'. The condition was a recognized

industrial disease in Germany and also led carcinogenic effects on the lung (Richter et al., 2007). Kristen Sanders et al., conducted the hazard identification for Titanium dioxide. Nanoparticles by human-derived of retinal pigment epithelial cells were treated with nanoTiO₂ samples. The results showed that nano-TiO₂ decreased cell viability and increased the generation of reactive oxygen species. LC₅₀ values were correlated with reactivity, particle size, and surface area (Sanders et al., 2012). Toshihiko Myojo et al. had also conducted a risk assessment for the airborne fine and nanoparticles. They exposed aerosolized asbestos-substitutes or nanoparticles aerosols (nickel oxide and titanium dioxide), and examined the biological and pathological effects of these particles on the lungs. They found that particle size played a vital role in the hazard assessment (Myojo et al., 2010). A study was conducted by Hong-Chun et al., for Ti powders with diameters of : 3 μm, 8 μm, 20 μm, 45 μm, 35 nm, 75 nm and 100 nm and Fe powders with diameters of 150 nm, 15 nm, 35 nm and 65 nm for their MIE using a modified version of the 1. 2-L Hartmann apparatus. According to the data obtained from the experimental results, the MIEs for all the nanopowders were less than 1 mJ and indicated that they were extremely combustible (Wu et al., 2009). Azhagurajan et al. conducted an open channel burn test to measure the flame height and width for micron and nano-sized flash powder. The flame parameters were also correlated with the performance of the fireworks crackers. It was observed that as the particle size decreased from 250 nm to 104 nm, the flame height and width also increased. The two latter parameters increased from 63 mm and 65 mm to 100 mm and 95 mm respectively (Azhagurajan et al., 2011a).

Nano technology in fireworks

Thanulingam et al. also conducted the noise level for pyrotechnic mixtures of nano and micron sizes using different oxidizers similar to commercial firecrackers. They found that the effect of particle size in producing sound level varied from one oxidizer to another. If the particles were nano sized, 0.5 g of pyrotechnic mixture was sufficient in producing the optimum sound level whereas the same sound level was produced only by using 1 g of micron sized pyrotechnic mixture. It was expected that as the particle size decreased, the pyrotechnic mixture would be effective in producing sound. The particle size effect can be considered to be the result of reducing the activation energy, because smaller particles require less energy to be heated to the ignition temperature (Thanulingam, 2009). Azhagurajan et al. conducted an experiment on the performance of fireworks using nano powders and analyzing the sound level it produced (Selvakumar et al., 2012; Azhagurajan et al., 2011b). As per Govt. of India notification, the sound level of cracker should not exceed 125 dB (AI) at 4 m distance from the point of bursting. The flash powder composition used in the fireworks industry to manufacture the firecrackers consists of potassium nitrate, aluminium and sulphur in 75 mrange. For this experiment cake bomb, one of the sound emitting crackers being manufactured in the fireworks industry was studied by the researchers.

Insensitive high explosives based on heterocyclic nuclei

The conventional NC-NG based propellants are more sensitive than high explosive warheds, especially when they stored inside battle-tanks or other

fighting vehicles. So in modern ordnance there is strong requirement for explosives having both good thermal stability impact and shock insensitivity and better explosive performance. The requirement is to reduce the hazards to personnel and material on accidental initiation of a weapon due to environmental stimuli such as rough handling, fragment impact and thermal cook-off. One of the foremost objectives at the stage of the synthesis of new explosives consists in finding the molecules having a good energy capability of optimal safety.

The synthesis of nitrotriazoles as energetic materials and as intermediates to energetic materials has received a great deal of attention in the past 10 years (59). The most studied nitrotriazole explosives, 3-nitro-1, 2, 4-triazole-5-one (NTO). NTO is currently being widely investigated in main charge warhead fillings for insensitive munition. First openly reported as an in 1985, it had obviously been discovered earlier by the French and developed into insensitive PBXs using NTO in conjunction with HMX (63). A useful summary of the structural aspects, chemical and explosives properties and thermal behavior. The synthesis of NTO is straightforward. Semicarbazide hydrochloride condenses directly with formic acid at 100 °C to give 1, 2, 4-triazol-5-one. Nitration of NTO occurs readily with a range of nitration media and conditions, best yields are obtained using those shown below. The crystal density of NTO ~ 1.93 g/cm³, and VOD and detonation pressure are equal to those of RDX. At the same time, it is far less sensitive than RDX and HMX. It is more stable than TNT and RDX, but its sensitivity to ignition is slightly higher than TNT.

A comparison of PBXs based on TATB and NTO further confirms the same

sensitivity levels, while the VOD of the NTO based PBX is slightly higher. The salient feature of NTO as a raw material for PBX is that it may be obtained in particle sizes much larger than TATB i. e. 300–500 μm as against 9–30 μm for TATB, which implies that NTO is suitable for processing by the casting technique also, whereas TATB has to be processed by the coating and pressing techniques (65). The US AF compositon, AFX644 a low vulnerability GP bomb filling, is one example of this class. It is based on TNT and NTO with a performance matching that of TNT. The composition is based on poly-nitratomonomethyl-oxetane (NIMMO)/HMX/NTO/plasticizer, matched the performance goal of equaling composition B, while passing the UN series 7 Transport Test, ranking it as an extremely insensitive detonating substance (EIDS). The composition was not optimal but should prove a suitable candidate for further research. The synthesis and structural characterization of metal salts of NTO i. e. K, Cu and Pb-NTO, reveal that they have special characteristics and may find applications in several fields. Lee et al. (68) reported the preparation of 3-amino-5-nitro-1, 2, 4-triazole by an improved sequence where the dinitrotriazole salt was reduced with hydrazine, giving an almost quantitative conversion. The general interest in ANTA is because of amino-nitroheterocyclic compound as insensitive energetic material. The substituent combination of amino and nitro groups provides the inter and intramolecular hydrogen bonding that may stabilize the molecule and increase in density. The heterocyclic substrate is included to add density compared to the corresponding carbocyclic maA. K. Sikder, N.

Sikder / Journal of Hazardous Materials A112 (2004) 1-15 9 terials and in many cases contribute more to positive heat of formation.

This research found out that flash-powder mixtures are highly sensitive to shock, friction and electrostatic discharge. Additionally, accidental contaminants sensitize them even to greater extents. As flash-powder mixtures are very easy to initiate, there is a high risk of accidental explosions. It also clearly shows that the reduction of particle size into nanosized explosives displays excellent properties. However safety and health concerns about during handling are also raised. For safe handling of nano powders, the following points should be considered:

- To curb the occupational health hazards, it is strongly advised to wear the personal protective equipment such as dust mask for respiratory protection, leather gloves with long cuffs for hand protection, helmet with mesh for protection against heat or flames for head or face protection, fire-retardant special fabric for body protection and conductive safety shoes for foot protection.
- Avoidance of sources of ignition like, naked flame, exposure to hot surfaces, electrical sparks, electrostatic discharges, chemical decomposition, mechanically induced impact and shock should be ensured.
- Limit the dust concentration by avoiding the release of dust or cloud formation. Also, inert by preventing the ingress of oxygen for closed units.
- Reduce the damaging effects of explosions by adopting constructive explosion protection measures, such as blast-resistant or resistant to explosion shockwaves for explosion isolation and suppression. In the final analysis, the major advantage of using nanosize powders for the

manufacture of pyrotechnic devices is that they are environmental friendly producing less pollution and thereby rendering a cleaner environment.

Nonetheless, the major hazard that exists in using nano size powders is the fire and health hazard. Moreover the cost of the nano size powders is also very high which affects the cost of the firework sproducts. Further research can be carried forward involving safer production methods as large quantities of production can easily overcome these hazards.

Transportation

Transport requirements for the different technologies. It mentions the route the load has to be carried; the vehicles are required to return, so the total demand on transport is twice the

The relative potency of various PAHs is expressed as Benz(a)pyrene (BaP) TEQs, following the suggestions by the ICF-CA. Particle emissions. The transport emissions are based on emission data on CO, NO₂, volatile organic compounds and PAH. It appears that the NEQ-emission is dominated by that of PAH (almost 75%). As emission factors for PAH are derived from a single scientific reference, and calculations of BaP-TEQs are questioned, these results should be used with care. The environmental impact from the preparation, pre-treatment and/or downsizing is limited.

Washout and preparation of a TNT slurry, as in connection to FBC, makes use of a closed

loop of circulating water. A part of the water is used in the slurry and no wastewater is

produced (an environmental hazard related to a possible loss of containment is included

in the hazard analysis, see Duijm (1)). Filters to clean the circulating water need to be

considered as hazardous waste and will be disposed of by incineration in a conventional

hazardous waste incinerator. The amount of this waste stream is negligible compared to,

e. g. the amount of ashes (fly ash) produced in FBC.

The washout and preparation of the TNT slurry uses a fixed facility on the order of 100m²,

which will be included as an indicator for impact on the natural and cultural heritage.

Processing, cleaning, disposal and discharge of waste streams

The main impact of the disposal processes occurs during processing, i. e. detonation or

incineration. Cleaning and disposal of waste streams are often strongly integrated in the

technology and will be included in this section as well. In the following subsections, we

will comment on the impact for each of the environmental issues.

Air pollution

Information about OB and OD has been retrieved from the US-EPA database (Mitchell and Sluggs (9)). In order to obtain the respirable fraction of the dust emission, we use the estimated value of 20% of the total dust emission. The results are presented as NO₂-equivalent only on CO, NO₂ and respirable particulate matter, because for only these substances was information or estimates available for all technologies (except for the MF). For FBC, information on dioxin emission is available. If this is included, it does not change the NEQ results significantly, so we expect that the ranking of the technologies will not be sensitive to the exclusion of PAH and dioxins. Data for CD is based on CO and NO_x-measurements for experiments in the experimental facility at AMA (Markert and Egsgård (16)). The RSP emissions are estimated from the OB/OD data from the US-EPA, assuming a filter efficiency of 95% for RSP. Data for FBC are directly retrieved from the pilot plant experiments. Data for the RK are based on DIN-oven experiments on TNT. The RSP emissions are considered to be equal to those for FBC based on comparable collection efficiencies of the filters. It should be noted that none of the emissions mentioned here would fulfil the emission requirements according to EU-standards, mainly because of emissions of NO_x. However when urea is injected, the NO_x -levels in the flue gas of FBC and the RK will lie within ranges that can be treated using existing denitrification techniques. Weidenhagen (18) claims that mobile incinerator facilities equipped with chemical treatment of the flue gases are able to comply with the emission regulations.

Soil pollution

All incinerator processes lead to some solid waste that needs to be disposed of. The solid waste residue consists of bottom residue and fly ash. It is usually disposed of in a landfill, although some residues can be used in building materials (cement, asphalt). In some countries (e. g. Germany and the Netherlands) solid waste residue from incineration is classified as toxic hazardous waste, due to concern about dioxins (Colombo et al. (13)). Fly ash and other smoke particles will also be the main carrier of PAH. OB and OD lead to deposition of these solids in the near vicinity of the burning or detonation site. This uncontrolled disposal may well be considered as the most important negative environmental impact of OB and OD. We consider uncontrolled disposal a hundred times more serious than controlled disposal. Estimates of the amount of solid waste for OB and OD are taken from the US-EPA data on total dust emissions (0. 36 and 0. 13 kg/kg MEM, respectively, see Mitchell and Sluggs (9)).

Incompletely incinerated waste products from CD, including active coal filters and the like, are considered as hazardous waste that needs to be incinerated using an existing RK.

Final rest products are considered to be about 5% of the MEM. Table 5 presents the solid waste and soil pollution scores for the different technologies.

The future of propulsion and ordnance technology holds many possibilities. Chemical explosives and propellants are likely to enjoy continued incremental improvements in density, energy and stability to the point where future materials are safer and superior.

The future agenda of energetic materials research will almost certainly pose four challenges:

- (1) To development of truly insensitive energetic oxidizer
- (2) An energetic fluorine containing oxidizer
- (3) An insensitive high energy explosive with a density $> 2 \text{ g/cm}^3$ and (4) high energy fuel technology. The first three goals are being promoted worldwide, the fourth is largely a Russian endeavor which has so far yielded an unprecedented morphology of Aluminium hydride as a fuel for propellant applications.

The development of fluorine-laden oxidizers will enable the use of boron-laden fuels. Even in the realm of explosives, there is no reason why a formulation of appropriately encapsulated fuel and oxidizer can not surpass conventional nitro organics in both performance and economy.

The development of CPX 413 has demonstrated the potential in the binder system has proved to be successful. The aim of designing a formulation to meet a specific performance goal while being insensitive has been met. The composition based on an energetic binder, in combination with nitramine, insensitive high explosive and plasticizers, matched the performance goal of equaling composition B, while passing the UN series 7 transport tests, ranking it as an extremely insensitive detonating substance (EIDS). The composition was not optimal but should prove a suitable candidate for further research. Attempts to match Octol performance are under way and early results are up to expectation. The combination of a higher energy binder and the range of energetic fillers now available should make it possible to go even further in designing for function. Whatever impact future

technologies may have on the design of rocket motors and ordnance, chemical propellants and explosives will always have a place in the science of controlled kinetic energy release.

Conclusions

The most prevalent environmental impacts are the emissions of toxic air pollutants, uncontrolled deposition of solid waste and the occupied area. Global and regional air pollution problems and waste water problems are less relevant in the research. With respect to these three main environmental problems, the reference scenarios, OB and OD perform badly. All the new technologies avoid uncontrolled solid waste deposition and excessive area occupation. Air pollution emissions can be reduced considerably, by at least a factor 10 if NO_x-reduction techniques are applied.

Safety issues are relevant for explosive waste disposal. Without proper disposal is when issues such as pollution sets in. some explosive are radioactive and undergo radioactivity. In such processes, stability is acquired since the heavy nuclides tend to disintegrate, in the process the emit energy or harmful rays which are likely to affect the ecosystems in one way or the other. Once the balance is affected, the future generations of living things will have serious problems, both genetically and physically. For all technologies, safety requires permanent attention because the effects are not only short term but long-term as well. Risk can be reduced effectively by transforming explosives into de-sensitized, water-based slurries at an early stage in the disposal process. The effect reduces the possibilities for explosion and fire. On the other hand, activities that require extensive

manual handling of explosives, like CD, remain risky.

Measures should then be taken at possible areas of production, transportation and storage to mitigate the likely risks associated with leakages.

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