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Aging of Pentaerythritol Tetranitrate (PETN)

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Aging of Pentaerythritol Tetranitrate (PETN)

1) Key Points	2
2) What is Pentaerythritol Tetranitrate (PETN)?	3
3) What is Known About the Stability of PETN	5
a) Particle Size/Morphology	5
b) Thermal Decomposition	7
c) Moisture	10
d) Phase Transitions	10
e) Crystal Structure	11
f) Purity	11
g) Occlusions	12
h) Chemical Incompatibility	13
i) Biological Activity	14
4) Drivers That Affect Stability	15
a) Temperature	15
b) Radiation	16
c) Stress	18
d) Residual Solvents	19
e) Impurities	19
5) Processes That Are Involved in Change	20
a) Sublimation and Recrystallization	20
b) Surface Diffusion	21
6) How Change is Assessed	21
a) Threshold Test Fire	22
b) Particle Size Distribution	23
c) Specific Surface Area (So)	24
d) Thermal Analysis	24
e) Chemical Analysis	25
f) Powder Compact Specific Surface Area and Density	25
7) Factors Relevant to Stabilizing Particle Size Growth	26
a) Crystal Morphology, Particle Size Distribution and Powder Surface Area	26
b) Crystal Density and Internal Defects	27
c) Powder Compact Density and Density Gradients	27
8) How PETN Powder Surface Area Can Be Stabilized	29
a) Additives	29
b) Surface Agent Treatment	29
c) Heat Treatment	30
9) Acknowledgements	30
10) Acronyms	31
11) References	34

Aging of Pentaerythritol Tetranitrate (PETN)

1) Key Points

Pentaerythritol tetranitrate (PETN) is a relatively sensitive explosive used in many electroexplosive devices as well as in medicine. Of primary interest to LLNL is its use in items such as exploding bridgewire (EBW) detonators and exploding bridge foil initiators (EFI). In these devices the crystalline powder is pressed into a granular, low-density compact that can be initiated by an exploding wire or foil. The long-term stability of this pressed compact is of interest to weapon stockpile lifetime prediction studies. Key points about potential aging mechanisms can be summarized as follows:

- There are a number of factors that can contribute to PETN instability. These include particle size, polymorphic phase transitions, crystal structure, impurities, moisture, occlusions, chemical incompatibility and biological (microorganism) action. Of these factors the most important for long-term aging of high surface area powders used in detonators appears to be that of particle size growth.
- There is a great deal of literature on the thermal degradation kinetics of PETN, unfortunately much of it with little bearing on ambient temperature aging during long-term storage. PETN is very stable with respect to thermal decomposition. Low-temperature thermal studies have not revealed evidence of chemical degradation products in archived PETN. Data extrapolated to 30°C predicts a half-life of 12 million years.
- Moisture seems to lower the activation energy for and accelerate the decomposition of PETN.
- External drivers affecting stability include temperature, moisture, radiation fields, and stress, while internal drivers include residual solvents, and impurities. Temperature affects kinetic processes of crystal growth such as adsorption, desorption, and diffusion rates of molecules on the surface of PETN crystals. A low-level radiation field may induce unexpected changes in the chemical makeup of PETN and its homologue impurities. Stress at high pressure points caused by crystalline surface irregularities may cause a decrease in surface area over time due to smoothing of contact points and sintering. PETN has been found to contain a number of impurities, including homologues, pentaerythryl ethers with a mixture of hydroxyl and nitrate functional groups, and organic salts, that can alter its physical and chemical properties.
- The processes of sublimation/recrystallization and surface diffusion are important processes that can cause changes in PETN crystal morphology, particle size distribution and specific surface area. Sublimation feeds a process called Ostwald ripening, which involves the spontaneous growth of larger crystals from those of smaller size. This process proceeds with age regardless of storage conditions unless the crystals are treated to retard growth. The

coarsening mechanisms include Ostwald ripening, “sintering”, and surface diffusion. The latter has not been experimentally observed, but a molecular modeling approach has attempted to investigate this phenomenon theoretically.

- Threshold test fire, particle size distribution, specific surface area, thermal analysis, chemical analysis, powder compact specific surface area and density are approaches that have been used in the attempt to assess changes attributable to aging of PETN, with varying results. The biggest problem lies in the aging mechanism itself, which likely influences small changes in morphology, both internal and external, and particle size distribution changes on a scale too small to reliably monitor. Other aspects, such as subtle changes in density profiles within pressed powder compacts, may be beyond the capability of current technology to assess. Crystal growth significant enough to affect the PETN particle size distribution is expected to impact detonator performance.
- Factors relevant to stabilizing particle size growth include crystal morphology, powder surface area and particle size distribution; crystal density and internal defects; and powder compact density and density gradients.

Several methods have been tried to stabilize the specific surface area of PETN powders against crystal growth: additives, coatings, and heat treatment. Examples of additives are naturally occurring levels or doped quantities of homologues such as dipentaerythritol hexanitrate (DiPEHN) and tripentaerythritol octanitrate (TriPEON). The mechanisms by which additives and heat treatment work are not understood. The following sections are designed to familiarize the reader with some of the available unclassified literature on topics related to aging of the type of PETN typically used in detonators, specifically long-term storage issues. They do not necessarily reflect aging processes of PETN used in plastic bonded explosives (PBXs), which also involve interactions between the explosive and the binder. Note that the section on biological action is included for a sense of completeness since the literature widely explores both *in vitro* and *in vivo* biodegradation pathways of PETN.

2) What is Pentaerythritol Tetranitrate (PETN)?

Pentaerythritol tetranitrate [PETN; $C(CH_2ONO_2)_4$] also known as corpent, pentrite, pentaerythrityl tetranitrate, or rarely and primarily in German as *nitropenta* or *pentrit*, shown in Figure 1, is a very stable, powerful and brisant high explosive (HE) commonly used in many electroexplosive devices. It is also used in medicine for the treatment of cardiovascular-related disorders. It is an organic nitrate ester in the same family of high explosives (i.e. the nitric acid esters of polyalcohols) as nitrocellulose (NC), nitroglycerin (NG), and ethylene glycol dinitrate (EGDN) to name a few. It's used as pressed powder compacts or with small amounts of desensitizing additives when used as boosters and fillings for small caliber projectiles. The principal uses of PETN are in the explosive core of industrial detonating fuses, in the base charge of commercial blasting caps, in industrial boosters, in linear shaped charges, and in commercial and military detonators.

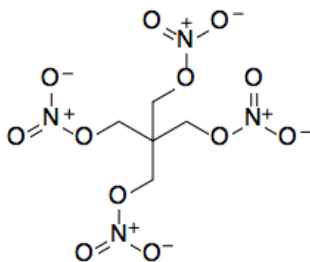


Figure 1. PETN molecule

PETN is used throughout the U.S. stockpile as an energetic material. Of interest is its use in items such as exploding bridgewire (EBW) detonators and exploding bridge foil initiators (EFI)¹. [Varosh 1996] In these devices the crystalline powder is pressed into a granular, low-density compact that can be initiated by an exploding wire or foil respectively. This pellet in turn initiates either a second high-density PETN pressing or a plastic bonded explosive (PBX) pellet that in turn can initiate either a booster or main charge explosive. The long-term stability of the low-density pressed compact or pellet² is of interest to stockpile lifetime prediction studies as the weapons age over time.

PETN is prepared by nitration of pentaerythritol with concentrated nitric acid (98%+), as the standard mixed acid method can create unstable sulfonated by-products. Since PETN is only slightly soluble in nitric acid it precipitates out at the end of nitration. The precipitate is then filtered, washed with water, neutralized and recrystallized from acetone. In some processes the nitric acid is diluted with water after nitration to keep some impurities in solution. [Kaye 1978] It forms colorless crystals that have a melting point around 141°C. The U.S. military specification governing chemical and physical requirements for PETN is MIL-P-387C. Classification 4 is for use in blasting caps and detonators. [Military Specification 1976]

A second recrystallization precipitation is often carried out as a particle-size adjustment process to produce a powder with a desired specific surface area. The process of making high specific surface area³ ($So = 10,000\text{--}20,000 \text{ cm}^2/\text{g}$) powder involves shock recrystallization. PETN is dissolved in acetone in a ratio of ~1:5 respectively and shock precipitated by dropping the solute and solvent into a super-cooled water-alcohol bath at -30°C. Resulting crystals have irregular faces and sizes, with a size distribution usually ranging from 0.5–16 microns (equivalent spherical diameters), with the median ~2 microns in size. The resulting So is high due to the fineness of the crystal size and irregularity of crystal surface and shape. A variety of shapes are formed ranging from spheres to high length-to-width ratio needles. The preferred shape for use in detonators is a tetragonal rod. [Duncan 1972]

¹ EFIs are also called slapper detonators.

² The low-density pressing is also called the initial pressing.

³ Specific surface area is a material property of particulate solids that measures the total surface area per unit of mass, solid or bulk volume, or cross-sectional area. The specific surface area and void structure of pressed PETN are dependent on the particle size distribution, degree of reentrant void formation, particle morphology and density. [Young 2006]

The particle size, shape, and texture of the crystals of PETN precipitated from acetone solutions by the addition of water depend upon many crystallization factors. Among the most important of these are 1) the concentration of PETN in the acetone, 2) both the volume of water and the rate at which the nonsolvent is added, and 3) the amount of agitation of the solution during the precipitation process. All these conditions can be easily controlled because the explosion characteristics of PETN are strong functions of the crystal description. [Dinegar 1985]

3) What is Known About the Stability of PETN

An enormous amount of material has been published on PETN. It's among the most studied explosives from both the experimental and theoretical points of view. A great deal is known about PETN's physical properties, solubility, chemical properties, preparation, detonation characteristics, thermal decomposition, combustion and deflagration-to-detonation transition (DDT) processes, just to name a few areas of interest. [Kaye 1978]

PETN is the least stable of the common military explosives, but retains its properties in storage for longer periods than other nitrate esters such as nitroglycerin or nitrocellulose. PETN is the most chemically stable and least reactive of the explosive nitrate esters. The stability has been attributed to the symmetry of the molecule, [Berlow 1958] although this hypothesis has been disputed based on liquid phase thermal decomposition rates similar to that of other nitrate esters. [Andreev 1961] It is less sensitive than nitroglycerin, but is easily detonated.

While PETN is relatively stable thermally, there are a number of factors that can contribute to instability. These include particle size instability (i.e. growth), temperature- and pressure-driven polymorphic transformations, crystalline instabilities, impurities, occlusions, chemical incompatibilities and even the effects of biological activity. In addition, degree of confinement, purity and crystal size are all known to influence degradation rates. Of these factors the most important for long-term aging, probably the most studied and least understood, appears to be that of particle size growth of the kind seen in high surface area crystalline powders used in detonators.

3a) Particle Size/Morphology

An aspect of stability, and perhaps one of the most important, is that of crystal size and morphology. Understanding the effect of particle size, shape and surface characteristics on the behavior of a powder has been the goal of many studies. In quality control of a powder, seldom is a given parameter known well enough to predict accurately overall behavior of a powder. Therefore, many particle parameters must be evaluated to determine the influencing factors, including width, length-to-width ratio, volume, surface area, reentrant surface, bulk density, compressibility, surface roughness, pore volume, degree of sphericity, etc., and their relation to extrudability, pressability, firing performance, etc. Determining these things is called powder or particle characterization. [Duncan 1970]

PETN powders used as an initiating explosive typically have high specific surface areas (5000-30,000 cm²/g).⁴ If no steps are taken to stabilize the sample, the surface area decreases due to coarsening mechanisms such as Ostwald ripening,⁵ “sintering” (fusion of crystals at contact points or agglomeration),⁶ and surface diffusion. Internal and external factors affect crystal growth rate and morphology. Internal factors include defects in the crystal structure and external factors include crystallization conditions (temperature, supersaturation) and the existence of impurities. Thermal cycling and doping with certain impurities have been proposed as methods to minimize crystal growth problems arising from sublimation under service conditions. [Pitchimani 2007a]

Modeling efforts have attempted to describe crystal growth mechanisms to predict how powder specific surface area, density, and powder to detonator bridgewire gap change with time and temperature. [Burnham 2006] This includes mimicking crystal shapes using kinetic Monte Carlo (KMC) simulations with an accurate intermolecular potential for PETN [Burnham 2005] and development of a coarse-grained model for PETN crystals to speed up simulations. [Gee 2006] Kinetic Monte Carlo simulations of evaporation from the predominantly exposed (110) surface of PETN crystals show that different surface structures, such as “islands” and “straight step” segments, move in very different ways during evaporation. It has been theoretically shown that that closed surface structures (e.g. islands or convex step edges) evaporate faster than open features (e.g. straight or concave step edges). From Arrhenius plots of step velocities researchers have obtained activation energies for evaporation in excellent agreement with predictions from a model and experimental data. [Zepeda-Ruiz 2008]

Duncan used a model that sought to phenomenologically explain the mechanisms of individual crystal growth. [Duncan 1972] With time PETN reduces its total crystalline energy by adopting its preferred shape, a tetragonal rod. This transformation involves rearrangement of molecules within and on the surface of individual crystals by internal relaxation of molecules, molecular flow at contact points, surface diffusion, and bulk or vapor diffusion. Duncan used Kossel’s crystal model to describe a molecule’s location on the surface of the crystal and as a result its relative likelihood of migration or deposition to describe crystal growth. [Duncan 2002]

⁴ Methods developed for achieving high surface area PETN for detonator applications have included 1) the purification of the starting PETN from hot saturated solutions by chilling prior to its shock reprecipitation in cold alcohol/water (Pantex method); 2) purification by charcoal prior to reprecipitation in cold solution (LLNL method); 3) ball milling; 4) conventional spray and ultrasonic spray of an acetone/PETN solution directly into both a nitrogen atmosphere and into water; 5) using the high speed blades of the Cowles Dissolver to disperse the PETN solution into water; and 6) using an 8-inch Micronizer (English method). [Osborn 1968]

⁵ In Ostwald ripening, many small crystals initially form in a system but slowly disappear except for a few that grow larger at the expense of the small crystals. The smaller crystals provide the source material for the bigger crystals. The growth of large crystals is driven by a thermodynamic driving force to reduce the surface to volume ratio.

⁶ Sintering is governed by two interrelated properties, a change in free energy, which provides the driving force for the process, and kinetics, which provides the mobility of the system to the lower free energy state. Sintering can occur by many mechanisms, including viscous flow, plastic flow, evaporation-condensation, surface diffusion, volume diffusion, and grain-boundary diffusion. Predicting the kinetics of sintering has practical aspects for both process optimization and material lifetime prediction, which involves extrapolation of artificial aging experiments outside the range of calibration. [Burnham 2004]

3b) Thermal Decomposition

PETN is relatively stable toward thermal decomposition although there has been some controversy about its stability. When the NO/NO_x chemiluminescence data of Volltrauer is extrapolated to 30°C, a half-life of 12 million years is predicted. [Volltrauer 1982] PETN has been found to show no signs of decomposition when stored for as long as 18 months at 100°C. In fact analytical and stability tests have indicated the stability of PETN is improved by prolonged heating in water at 100°C. [Berlow 1958] Aubertein found that while untreated crystals of PETN gave an initial high loss of water and acid, twice recrystallized (from acetone) PETN did not decompose significantly when held at 100°C for three weeks. [Aubertein 1954] Chambers et al. did not see evidence of “autocatalytic” type decomposition by-products in archived PETN. [Chambers 2002b] Nevertheless Cooper points out that as PETN is heated, it undergoes thermal decomposition long before the melting point is reached. He therefore concludes PETN’s useful service temperature range is limited, normally not to exceed 70 to 75°C. [Cooper 1996]

The thermal stability of PETN, its degradation mechanisms and reaction by-products have been studied extensively, in most cases in studies using air not inert or nitrogen atmospheres.⁷ Many of these studies have focused on high temperature degradation, which is probably not relevant to answering questions about long-term storage but possibly relevant to understanding the chemistry involved in combustion and the heat treatment of PETN. Such studies often focus on kinetics of thermal decomposition important to understanding initiation processes and detonation phenomena. The thermal decomposition of PETN below its melting point (141.3°C) has been investigated by monitoring product gases by mass spectrometry. [Miller 1982], [Ng 1976] Other studies have assessed the thermal decomposition characteristics of PETN using thermal analytical techniques, specifically thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (see for example [Lee 2002], [Kawamura 1997]), high temperature infrared spectroscopy, pyrolysis gas analysis and hot-stage microscopy (see for example [Makashir 1999]), high temperature gas manometry (see for example [Oxley 2000]), and mass electrospray ionization (ESI) and chemical ionization (CI) Fourier Transform Mass Spectrometry (FTMS) (see for example [Kruppa 2002]).⁸

Anhydrous low-temperature decomposition of PETN is poorly understood. Studies searching for the decomposition products of naturally aged PETN used nuclear magnetic resonance (NMR), high performance liquid chromatography (HPLC),⁹ and mass spectrometry, but did not detect any decomposition products. [Brackett 2005] Because the NMR, HPLC and mass spectrometry experiments did not detect condensed phase decomposition products, it was surmised that the decomposition products might be

⁷ One exception is a flash pyrolysis study that compared reaction products from PETN in simulated air and in argon. [Hiyoshi 2002]

⁸ Other thermal degradation studies like the one-dimensional-time-to-explosion (ODTX) experiments have generated input for the development of multi-step chemical kinetic decomposition models in two- and three-dimensional heat transfer computer codes. These models are then used to predict the times to and locations of the onset of thermal explosion in large explosive charges that cannot be tested directly. [Tarver 2003]

⁹ Or high-pressure liquid chromatography.

gases as is seen with explosives HMX¹⁰ and RDX.¹¹ On the other hand, Duncan found in his study of environmental conditions affecting unstabilized, recrystallized PETN that in each thermally aged sample, pentaerythritol trinitrate (PETriN) was present and the sublimation product contained the greater amount. [Duncan 1972] PETriN appears to be a product of thermal decomposition. [Shepodd 1997]

Kaye has summarized thermal decomposition literature on PETN up to 1978. At that time thermal decomposition kinetics had been studied repeatedly, but there was no general agreement about the decomposition mechanism or values of the Arrhenius parameters. [Kaye 1978] This confusion continues today. According to Dosser, the reports on aging of PETN appear to be consistent regarding the evolution of the principal gaseous products. [Dosser 1989] Nonetheless the activation energies for the decomposition reaction(s) are in disagreement. In addition, the activation energy is not a constant, but changes greatly as the temperature changes. [German 2002] Dosser and Ng [Dosser 1989], [Ng 1976], [Ng 1986] independently attribute this problem to different methods of measurement and methods of sample preparation.

The thermal decomposition mechanism is complex, involving retardation, autocatalysis, product interactions and other complications. Most authors agree that decomposition takes place concurrently with sublimation. [Ng 1976] It has been noted that the dominant degradation process at lower temperature is influenced by numerous side reactions involving recombination of radical products. In general a wider distribution of decomposition products are generated in the high-temperature, solid phase decompositions than in those generated at 20-65°C. [Shepodd 1997] There is general agreement that the first step is the scission of the O-NO₂ bond as a reversible, rate-determining, first-order process. The first decomposition products are relatively reactive. Depending on the conditions, a number of second-order decomposition routes are proposed that involve attack by nitrogen dioxide (NO₂), a strong oxidizer. These subsequent decomposition routes are often referred to as autocatalytic or autooxidation reactions. For PETN at ambient temperature, the possibility for a number of autocatalytic mechanisms exists involving oxidation of the PETN alkoxy radical by NO₂, resulting in the formation of peroxide, nitrate or aldehyde by-products. The PETN alkoxy radical, although less mobile under low-temperature conditions than NO₂, might also be expected to attack PETN, resulting in the formation of polymer-like by-products (e.g. DiPEHN, TriPEON). [Chambers 2002a] A low temperature (40-90°C) chemiluminescence study of PETN measured faint light emitted from the condensed phase due to termination reactions of peroxy radicals. Kinetic analysis led to the result that the formation of peroxy radicals, produced by oxidation of the primary products of nitrate ester bond cleavage, predominates a consecutive series of radical reactions. [Kimura 1989]

It has been proposed that the agent of PETN autocatalysis is not the product NO₂, as is generally believed, [Pickard 1990] but may be the product formaldehyde. [Batten

¹⁰ HMX is a high explosive, also called Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, Cyclotetramethylene tetranitramine, or Octogen. The has been attributed to High Melting eXplosive, His Majesty's explosive, High-velocity Military explosive, or High-Molecular-weight rdX.

¹¹ RDX is a high explosive, also called Hexahydro-1,3,5-trinitro-1,3,5-triazine, Cyclotrimethylene trinitramine, or Hexogen. The acronym has been attributed to Royal Demolition eXplosive, Research Department (composition) X, or Research Department eXplosive.

1985] This proposal appears to be supported by earlier work on the thermal decomposition of organic nitrates, which showed that initial addition of nitrogen dioxide retards the scissioning of the O-NO₂ bond. [Phillips 1950] Another study showed that NO₂ retarded the decomposition of another nitrate ester, ethyl nitrate, while nitric oxide (NO) accelerated the reaction. [Levy 1954] In the thermal degradation study of Dosser and Seliskar, PETN showed no reaction with NO₂ at room temperature. [Dosser 1992b] Since the distribution of decomposition products is influenced by the temperature of decomposition, and both NO₂ and NO are formed in relatively large amounts, it is possible that the way their relative abundance changes influences the decomposition of PETN. [Ng 1976]

Dosser studied the thermal stability of a series of PETN samples with various surface areas using isothermal calorimetry and ultraviolet (UV) spectroscopy over the temperature range of 363 to 408 K (~90 to 135°C). [Dosser 1992a] The former method measured isothermal induction times while the latter monitored NO evolution rates. Rate data measured at 383 K (~110°C) were in accord with predictions based on detailed kinetic modeling. Below 383 K, NO evolution data suggested that additional geometric factors might be significant in controlling PETN stability. Time-to-maximum-rate (TMR) of decomposition increased with the surface area. The authors concluded that PETN reactivity is governed by 1) thermally-induced changes in surface area with concurrent production of crystal imperfections at the surface perturbed by differences in stabilizers and 2) residual solvents. Thermal aging would then minimize the surface's free energy, decrease the surface area, and increase the mean particle size of PETN. However below 383 K, thermal microscopy indicated that aging of PETN with high surface area may produce additional crystal imperfections as the mean particle size increases and the surface area degrades. This phenomenon would lead to additional surface-active sites. Therefore the apparent correlation between stability and surface area suggested by the TMR data could be different at lower temperatures.

High temperature decomposition studies have identified gaseous degradation products. Early work showed that the reaction products produced in a closed system at 210°C were NO₂, NO, N₂O, CO₂, CO, H₂, H₂O, H₂CO¹² and unidentified residue. [Rideal 1948] These products were later confirmed by mass spectroscopic analysis of thermally decomposed PETN at 94, 126 and 158°C. [Ng 1976] T-Jump/FTIR¹³ and T-jump/Raman spectroscopies have been used to analyze the gaseous products from PETN that was rapidly heated (2000°C/s nominal) to high set temperatures in the 250 to 500°C range while maintaining a pressure of 5 atm. argon. [Roos 2002] The resulting products produced at 450°C, for example, included CO, NO, H₂, O₂, CO₂, H₂O, N₂, CH₄, HCN, CH₂O, C₂H₂, NO₂, HNCO, and N₂O.¹⁴

Hiskey and coworkers proposed an alternate high temperature (140 to 225°C) decomposition pathway that involves PETN's loss of all four nitro groups and two

¹² In order: nitrogen dioxide, nitric oxide, nitrous oxide, carbon dioxide, carbon monoxide, hydrogen, water and formaldehyde.

¹³ Fourier Transform Infrared (FTIR) (spectroscopy).

¹⁴ In order: carbon monoxide, nitric oxide, hydrogen, oxygen, carbon dioxide, water, nitrogen, methane, hydrogen cyanide, formaldehyde, acetylaldehyde, nitrogen dioxide, isocyanic acid and nitrous oxide.

molecules of formaldehyde to undergo a double ring closure to form a spiral-ketal. [Hiskey 1991] They proposed that this unstable species would then decompose to produce a polymeric residue (polyketo oxetane).

3c) Moisture

Andreev and Kaidymov studied the thermal decomposition of PETN and found it to be greatly affected by the presence of water vapor (and slightly by the presence of oxygen). [Andreev 1961] Addition of water to PETN makes it possible to induce the hydrolytic reaction from the outset. According to Andreev and Kaidymov, judging from the data for the nitrate ester nitroglycerin, nitric acid is formed directly, not the nitrogen oxides. Alternatively, the presence of water has been proposed as promoting a decomposition pathway involving attack of the ester oxygen forming an alcohol end group. [Chambers 2002b] Because this reaction can occur at each nitrate ester group, a stable mono-, di- or trinitrated pentaerythritol can be formed, proceeding sequentially and relatively slowly.¹⁵

In response to an undocumented literature reference that PETN “may be unstable under tropical conditions,” one study compared the decomposition of PETN at 10-degree intervals over the range of 60 - 100°C. [Goosen 1984] The three conditions studied - acidic, recrystallized dry, and recrystallized wet (high humidity) - were considered extreme military storage conditions. Weight loss measurements indicated very little, if any, loss at 60°C and 70°C with a loss of about 5.5% at 100°C after 350 days. No conclusion could be made regarding NO₂ catalysis, but the addition of moisture seemed to lower the activation energy for and accelerate the decomposition of the PETN.

3d) Phase Transitions

Another aspect of stability of importance to PETN is the possibility of a polymorphic phase transition. Blomquist and Ryan first reported the polymorphism of PETN in 1944. [Blomquist 1944] Both of the known ambient pressure crystal structures have been analyzed. [Cady 1975], [Trotter 1963] The common form PETN I¹⁶ is stable to the melting point (141.3°C). The high-temperature phase PETN II melts 0.2°C higher than PETN I. PETN II transforms rapidly to PETN I at temperatures below 130°C. The heat of fusion of PETN I is very dependent on the crystallization technique. Cady noted that it varies from 38 cal/g for well-formed crystals to 32 cal/g for rapidly precipitated fine crystals. Small changes in the X-ray diffraction patterns accompany the changes in heat of fusion. More pronounced changes occur when dipentaerythritol hexanitrate (DiPEHN) or tripentaerythritol octanitrate (TriPEON) homologue impurities are incorporated by solid solution in the crystals. [Cady 1975]

The amount of PETN II that can be quenched to room temperature also depends on the chemical purity of the PETN melt. DiPEHN, TriPEON, and thermal decomposition products stabilize the PETN II phase. PETN II stabilized by impurities trapped in the crystal lattice as a solid solution transforms more slowly to PETN I than

¹⁵ On the other hand rapid heating in the presence of moisture is little different from a dry environment. Relative humidity in the 0-60% range had no effect on the product concentrations in air when T-Jump/FTIR spectroscopy was employed to flash pyrolyze PETN. [Hiyoshi 2002]

¹⁶ PETN I is also referred to as ‘Alpha PETN,’ and PETN II is referred to as ‘Beta PETN.’

does chemically pure PETN II. [Cady 1972] Nevertheless, the existence of the PETN II contaminant is unlikely to be an issue with very long-term storage of PETN powders or granular compacts since it is not thermodynamically stable under ambient conditions.

Other polymorphic conformers of PETN have been observed at high pressure. See for example [Pravica 2006] and [Tschauner 2007] for more information on high-pressure phase transitions of PETN.

3e) Crystal Structure

Molecular arrangements which assume strained lattice positions, asperities where high energy molecules exist, and reentrant cavities where migrating molecules are more efficiently retained are created in the recrystallization process used to produce high surface area powder. All these factors affect the stability of PETN, as each crystal attempts to perfect itself through molecular relation, plastic flow, and surface and bulk diffusion. [Duncan 1972]

PETN molecules can fit into lattice sites as mirror images and in doing so, both molecule and lattice must distort. Such trapped molecules have a high activation energy to reorientation because large cooperative motions of surrounding molecules are required for the transformation. According to Cady, trapped, distorted PETN molecules are probably responsible for the high internal energy of superfine and needle-habit PETN crystals, each with a high activation energy for annealing. [Cady 1972]

PETN is a flexible molecule that can change its geometry via internal rotations about single bonds; there are 12 such bonds in the molecule. [Gruzdkov 2004] The numerous stable conformations of PETN differ in symmetry and dipole moment values. However, the energy expense associated with such rotations could be several kilocalories per mole, making them energetically unfavorable. [Gruzdkov 2000] Prolonged heat treatment could assist in the transformation to more stable conformations and stabilize the crystal lattice.

3f) Purity

Another aspect of PETN stability concerns the role of impurities, especially the naturally occurring homologues often left from the synthesis process. An extensive study of the PETN-DiPEHN-TriPEON phase diagram system has been made by Cady with the goal of providing information on the thermal stability of PETN, particularly with regard to stability of physical properties and chemical decomposition. The system is very complicated in that there are at least two polymorphs of PETN, two of DiPEHN, four of TriPEON and three of the 1:1 DiPEHN-TriPEON addition compound. All the solid phases show evidence of solid solution formation with the other components of the system. In addition, other types of lattice defects influence the physical properties of these phases. [Cady 1972]

The molar heats of fusion and decomposition have been reported for PETN and its commonly found homologues DiPEHN, TriPEON, and tetrapentaerythritol dodecanitrate (TetraPEDN). Both sets of values increase with increasing molecular size, with a larger contribution to the heat of decomposition attributed to the ether group rather than the nitrate group. [Wilson 1970] An estimate of the heat of decomposition gives

insight into relative stability.¹⁷ Thus a small amount of homologue deliberately added to stabilize the surface area of the PETN powder might be more susceptible to preferential degradation. Environmental factors that might not appreciably degrade the PETN could preferentially destroy the less stable homologue, leading to a resumption of crystal growth.¹⁸

The effect of the presence of DiPEHN on the stability of PETN has been studied. According to early studies of these materials, [Berlow 1958] one author stated its presence decreases stability while two others reported improved stability from the presence of very small amounts of DiPEHN. One of these authors (Blomquist) attributed the improved stability to the decreased amount of occluded material trapped in PETN crystallized in the presence of DiPEHN. DiPEHN itself is distinguished from PETN by its lower sensitivity to heat, impact, friction and initiation. Its rate of detonation, brisance, and explosive power are somewhat lower than those of PETN. According to authors cited by Berlow, however, DiPEHN is distinctly less stable than PETN and decomposes far more rapidly at higher temperatures (100°C). Pure DiPEHN melts at 75°C. The other common impurity, TriPEON, is very stable toward heat and moderately sensitive to impact. It melts at 82-84°C.

With the improved heat stability of UK PETN, many attempts have been made to duplicate their process in order to produce a PETN powder with high thermal stability. The improvement in stability was thought to be due to the purity of the UK PETN. Therefore the process of double recrystallization and filtration through activated charcoal was employed to remove impurities from PETN prior to shock recrystallization. After thermal treatment, it appeared that the initial specific surface area (So) did not affect the final stabilization level. This may indicate the particle shape is responsible for the final stabilization level and not initial So or purity. [Duncan 1972]

3g) Occlusions

Another issue concerning crystal lattice stability is the presence of occlusions¹⁹ within the crystals. Small pockets of solvents such as acetone have been observed trapped

¹⁷ The larger the heat exchanged, the less stable the molecule. By measuring the amount of heat given off or taken from the surroundings it is possible to determine the overall change in enthalpy of the reaction and thus the degree or level of stability of a compound. The more heat generated or given off by the reaction, the greater the change in enthalpy, and thus the greater the change in energy. In other words when a very unstable compound forms a stable compound, a great amount of heat is released. The change is an indicator of how stable the compound was initially. A big change suggests that the compound was relatively unstable initially and a small change indicates that the compound was relatively stable initially. Much like enthalpy, it is impossible to specify a specific value of stability for a compound. Rather its stability must be compared to a reference. In other words the stability of a compound is relative to other compounds. [Wikipedia 2008a]

¹⁸ On the other hand, it has been shown that the activation energies for thermal decomposition of PETN, DiPEHN and TriPEON are essentially the same (~50 kcal/mole). [Cady 1972] According the DSC studies of Reddy, the thermal stability of PETN is not affected by the presence of DiPEHN, which showed better thermal stability and higher decomposition energy compared to PETN. [Reddy 1992]

¹⁹ Occlusions are foreign materials, liquid or solid, that have been occluded (closed up, blocked off, or adsorbed and retained) within the crystal structure.

in internal voids (solvent inclusions)²⁰ in crystals, a characteristic of superfine crystals. [Rogers 1972] According to Berlow et al., Blomquist found that slow recrystallization produces PETN with a few large occlusions while more rapid crystallization gives crystals with many small occlusions. His work showed that a major cause of instability in PETN is the presence of occluded material in the crystals. [Berlow 1958] It is unclear whether instability is affected by the size of the occlusions. During their PETN solubility study, Roberts and Dinegar found that the addition of water was necessary whether it was miscible with the solvent (acetone, ethyl alcohol, ethyl acetate) or not (benzene) to prohibit the occlusion of solvent as the PETN sample approached dryness. [Roberts 1958]

3h) Chemical Incompatibility

PETN may become destabilized and degrade when in contact with other materials. The chemical stability of PETN when placed in physical contact with microcrystalline metal oxides including MnO₂, CuO, MoO₃, WO₃, Bi₂O₃, SnO₂, and Fe₂O₃ has also been investigated. [Mileham 2008] Samples were placed in a controlled temperature environment at 50°C and checked periodically for the presence of decomposition products using liquid chromatography. PETN proved to be inert over all of the oxides except MoO₃, which showed the relatively rapid evolution of a brown gas over a period of 48 hours. Analysis of the evolved gas indicated that it was primarily NO₂ along with N₂O₄, N₂O, and CO₂.

Another study evaluated the kinetics and products of PETN degradation in the presence of granular iron. [Zhuang 2008] The iron material contained 89.8% metallic iron with a surface layer of various forms of iron oxides. The degradation pathway was proposed to be sequential pseudo first-order kinetics denitration, in which PETN was stepwise reduced to pentaerythritol with the formation of pentaerythritol trinitrate (PETriN) and pentaerythritol dinitrate (PEDN or PEDiN) as intermediates. The short duration of the dip in nitrogen balance indicated that the intermediates degraded quickly. The intermediate pentaerythritol mononitrate (PEMonoN) was not detected; however, the nearly 100% nitrogen mass recovery supported complete denitration. Nitrite (NO₂⁻) was released in each denitration step and was subsequently reduced to ammonium (NH₄⁺) by iron. Nitrate (NO₃⁻) was not detected during the experiment, suggesting that hydrolysis was not involved in PETN degradation. Batch experiments showed that when solid-phase PETN is present, dissolution is the rate-limiting factor for PETN mass removal.

A third study assessed the usefulness of HPLC in combination with chemoluminescence-N-detection (CLND) for the analysis of PETN and its degradation products PETriN, PEDiN and PEMonoN. [Seeling 2006] It was found that quantification is more convenient and sensitivity of this method is about four times higher compared to UV-detection. It was also noted that PETN was surprisingly stable at 37°C in aqueous systems of pH 1.2, 5.5, 6.8 and 7.4, but exhibited dose-dependent degradation after the addition of thioles (thioglycolic acid and cysteine).

²⁰ A type of occlusion is a solvent inclusion, a cavity entrapped in the crystal. Solvent inclusions are linked to lattice imperfections. Most crystals grown in solutions exhibit solvent inclusions with sizes in the range of 1-50 µm.

3i) Biological Activity

Areas of interest with respect to biological activity of PETN are in the fields of medicine, and both bioremediation and phytoremediation of the widespread contamination of the environment caused by the manufacture, disposal and testing of munitions.

Like nitroglycerin, PETN is used at low dosages as a vasodilator in the treatment of angina pectoris, acute myocardial infarction and chronic congestive heart failure, although higher doses cause symptoms such as headaches and convulsions. [Russek 1966], [Arce-Gomez 1980] A medicine for heart disease, *Lentonitrat*, is nearly pure PETN. Metabolism of PETN has been studied in human subjects and rats both *in vivo* and *in vitro*. [Yinon 1990] The metabolic pathways of PETN in humans and laboratory animals can be summarized as the sequential denitration from PETN to pentaerythritol trinitrate to pentaerythritol dinitrate to pentaerythritol mononitrate to pentaerythritol. *In vivo* rat dosing studies indicated that unabsorbed PETN might be further metabolized by intestinal microflora. [King 1984] In contrast to all other anti-ischemic organic nitrates, PETN is able to upregulate enzymes with a strong antioxidative capacity, thereby preventing tolerance and the development of endothelial dysfunction. [Daiber 2008]

A variety of microorganisms (e.g. bacteria, fungi) are able to metabolize explosive compounds in the environment. White and Snape have reviewed known microbial transformations of nitrate esters. [White 1993] In some cases a complete mineralization has been found whereas in others only biotransformation reactions took place producing more or less toxic and/or recalcitrant metabolites. [Gorontzy 1994] There have been some reports of PETN's degradation by bacteria, for example a strain of *Enterobacter cloacae* designated PB2, [Rosser 2001] whose enzyme "PETN reductase" (PETNr) denitrates PETN into trinitrates and then dinitrates [French 1996]. The last compound shown in the pathway, pentaerythritol dinitrate (PEDN or PEDiN), is degraded further to unknown products. The metabolites PEDN, 3-hydroxy-2,2-bis-[(nitrooxy)methyl]propanal, and 2,2-bis-[(nitrooxy)methyl]-propanedial were identified by mass spectrometry and ¹H-nuclear magnetic resonance. [Binks 1996] A similar enzyme ("nitrate ester reductase") was found to be responsible for the nitrate ester degrading activity in *Agrobacterium radiobacter* subgroup B, a bacterium recovered from sewage sludge. [White 1996]

The ability of fungi to produce extracellular enzymes and factors that can degrade complex organic compounds has also sparked research on their use in decontamination of explosives-laden soils and waters. [Gadd 2006] The filamentous white-rot fungus *Phanerochaete chrysosporium* has been shown to hydrolyze the nitrate ester nitroglycerin (glyceryl trinitrate). [Ducrocq 1990] As long as the nitroglycerin extracellular concentration was under the lethal dose, metabolite formation and regioselectivity depend on the nature of the strain used. Composting has been used to treat a wide variety of sludges and soils contaminated with organonitro explosives, including PETN. [Doyle 1993] Fungi are thought to play a vital role in the composting treatment process. In isotopically labeled laboratory-scale compost tests, PETN was mineralized to some extent although highly polar ¹⁴C-compounds were initially found in the composts. These compounds slowly disappeared with the production of ¹⁴CO₂ as the composting process continued. Pilot scale tests in the same study used an aerated static pile with soil spiked

with RDX, HMX, TATB²¹ and PETN mixed with amendments (20:20:10 mixture of horse manure, alfalfa hay and horse feed). Results indicated that RDX, HMX and PETN were reduced below detection limits within 18 days with TATB degrading slower than the other contaminants. Analysis of the final compost indicated there were no persistent degradation byproducts.

One study has shown that the nitroglycerin degradative activities of plant cells are only tenfold less than those reported for bacterial degradation, suggesting that plants may serve a direct degradative function for phytoremediation of sites contaminated by xenobiotic²² organic nitrate esters. [Goel 1997] The intermediates observed, and the timing of their appearance, are consistent with the sequential denitration pathway reported for microbial degradation of nitrate esters. The phytoremediation of the explosives trinitrotoluene (TNT), nitroglycerin (NG), and PETN using *in vitro* plant cultures²³ of *Rheum palmatum*,²⁴ *Saponaria officinalis*,²⁵ and *Populus simonii*²⁶ were also studied. [Vanek 2003] These explosives were degraded to less toxic products and ultimately probably bound to the cell wall or further involved in the metabolism. According to products analysis, PETN was fully degraded after ten days and all four possible products of nitroester enzymatic hydrolysis were identified. The final product pentaerythritol is reportedly utilized as a carbon source.

4) Drivers That Affect Stability

External drivers affecting factors that govern PETN stability include temperature, radiation fields, and stress. Internal drivers include residual solvents and impurities, which include additives, contaminants and coatings. While impurities may instigate or retard (but not prevent) change, the other drivers tend to facilitate change. The processes by which change occurs are discussed in **Section 5**, and the methods by which changes are assessed are discussed in **Section 6**.

4a) Temperature

Temperature affects all the important kinetic processes of crystal growth such as adsorption, desorption, and diffusion rates of molecules on the surface of PETN crystals. Experimental data suggests that at lower temperatures crystals grow to be more spherical (less rod like) with an aspect ratio near unity while elevated temperatures yield needle-like crystals. This contrasting behavior is due to differences in rates of surface diffusion occurring between molecular additions vs. nucleation during crystal growth. [Zepeda-Ruiz 2006]

Duncan's study on the effects of environmental conditions of unstabilized recrystallized PETN found that two conditions influenced thermal aging in the range of

²¹ TATB is the insensitive high explosive 1,3,5-Triamino-2,4,6-trinitrobenzene.

²² Since the C-O-NO₂ linkage is extremely rare in nature, organic nitrate esters like nitroglycerin are considered to be true xenobiotics. A xenobiotic is a chemical which is found in an organism but which is not normally produced or expected to be present in it.

²³ Plant cultures cultivated hydroponically under sterile conditions.

²⁴ Rhubarb.

²⁵ The soapwort "Bouncing Bet."

²⁶ Poplar tree.

50 to 125°C. One was the type of oven used (circulating vs. static air) and the other was sample configuration (confined by covering vs. open to the atmosphere of the oven). The circulating oven resulted in lower surface area values than the static air oven (i.e. greater crystal growth). Confined samples also showed an appreciable decrease in surface area compared to open samples. This change adheres to Ostwald's ripening theory that in a confined state, equilibrium is reached more rapidly due to the sublimate being retained within the local area, and growth is at the expense of the smaller particles. It was noted that this behavior would also be expected in the confinement of detonators with unstabilized PETN. [Duncan 1972]

Duncan's study went on to observe the effects of temperature above 90°C. In each case the drop in surface area was most rapid at the beginning of the exposure (e.g. 2 hours), leveling off asymptotically over time. As time and temperature increased, crystal size also increased. As duration time in the oven increased with each temperature, crystal agglomeration increased. From these results it was noted that each growth is the result of a sublimation process and that rapid surface area decrease at the onset of aging is primarily due to loss of fine crystals in reentrant surfaces, as well as formation of tightly bonded agglomerates. [Duncan 1972]

An extended pre-aging study was also done on high surface area PETN at 100°C at ambient pressure for 816 hours. After 70 hours of aging, stabilization had occurred in all three batches, which held constant for at least 700 hours. The level of stabilization appeared independent of the starting specific surface area (S_o). [Duncan 1972]

Since different outgassing and decomposition processes apparently occur above and below 110°C, this temperature is used to delineate between low- and high-temperature phenomena. Low-temperature thermal studies are relevant to shelf-life issues. One NO/NO_x analyzer chemiluminescence study found that when "fresh" PETN is first heated, it evolves more NO_x than when held at temperature a few days. The investigators believed this emission was due to desorption of adsorbed NO₂. [Volltrauer 1982] This desorption may initiate autocatalytic²⁷ decomposition.²⁸ [Chambers 2002a]

Kruppa et al. studied the thermal decomposition of PETN that was crash precipitated followed by thermal treatment, and found that vaporization is the predominant process up to the melting point. They also found that the presence of minor impurities from the large-scale synthesis of explosive grade PETN may influence the properties of the material. [Kruppa 2002]

4b) Radiation

Long-term exposure and stability of explosives to radiation may be critical for stockpile stewardship. However, irradiation studies tend to expose the explosive to high doses in a short period of time, not low doses over a long period. As such most probably provide little information on the stability of PETN when stored long-term in a low-level radiation environment.

²⁷ A chemical reaction is said to be autocatalytic if a reaction product is itself the catalyst for that reaction.

²⁸ According to Chambers et al., monitoring of NO₂ is complicated by the fact that a significant amount of it is absorbed onto the PETN powder, and because it is a reactive and polar gas. [Chambers 2002b]

Radiation damage initiates decomposition uniformly within the material by formation of ionized molecules. Unstable ionized molecules then decompose along thermodynamically favored pathways to more stable products. The ranking of explosives susceptibility to radiation damage, as measured by changes in chemistry or performance, is not the same as impact or thermal stability. It reflects the electronic stability of the material and is therefore a fundamental measure of the sensitivity of a molecule to disruption. [Beard 1991]

Irradiation affects thermal decomposition by shortening the induction period to shock initiation and increasing the decomposition rate in the accelerating region. These effects translate into a shorter run distance to detonation under shock initiation conditions. This change has been ascribed to the creation of significant numbers of additional decomposition sites by the radiation. There is some evidence that the decomposition sites may be dislocations or impurities that can act as hot spots. [Dick 1982]

Studies on the effects of ionizing radiation on explosives have included white synchrotron X-ray radiation, higher energy gamma rays, and slow neutrons, fission products, and low- and high-energy X-rays. The synchrotron X-ray radiation experiments of Gieffers et al. showed that PETN rapidly and irreversibly decomposes in the presence of X-ray radiation. The radiation-induced decomposition reaction in PETN was seen to be first-order and nearly pressure independent. [Gieffers 2006] Reaction products that appear red when PETN is pressurized become gaseous at ambient conditions. The authors were unable to determine the reaction products. [Gieffers 2008] It was also found that the decomposition rate varied dramatically depending upon the orientation of the crystalline axes relative to polarized x-ray beam and for differing diffracting conditions (spots) within the same crystalline orientation. The authors suggested that this effect was due to Compton scattering of the polarized x-rays with electron clouds dependent upon their relative orientation. It was suggested that this novel effect might yield valuable insight regarding anisotropic detonation sensitivity in energetic materials such as PETN. [Pravica 2007]

Kaye summarizes studies to 1980 of the radiation-induced changes in explosives (weight loss, gas evolution, mechanical sensitivity, thermal sensitivity and stability, and explosive performance), according to the type of nuclear radiation. This includes alpha particles, neutrons, fission products, reactor radiation (fast and slow neutrons plus gammas), gammas, underground testing, X-rays, electrons and other nuclear radiation. [Kaye 1980] However only a few of the studies discussed by Kaye involved irradiating PETN. None shed light on aging processes of PETN in a long-term low-level radiation field.

Steady state gamma irradiation of any explosive has not been known to trigger rapid reactions, i.e. initiate a detonation. Instead, the effect appears to be a slow decomposition with deterioration in the functional properties of the explosive. For example, a Co^{60} gamma radiation experiment by Avrami et al. showed a decrease in detonation velocity of PETN with exposures greater than 10^7 R. [Kaye 1980] PETN has exhibited weight loss when exposed to high doses of gamma radiation. In Urizar's study on PETN powder in a power reactor, a 5-MR gamma dose caused weight loss of 0.2% and a 240-MR dose caused a 14 % weight loss. A variety of physical and chemical tests

were performed on the irradiated samples. Dosimetry followed by energy deposition calculations revealed that about 90% of the energy deposited was due to the gamma field of the reactor. Although properties such as melting points, phase transition temperatures, and densities were lowered, no significant evidence of sensitization to impact initiation was observed. [Urizar 1962], [Kaye 1980] It was noted in one study that an excess of 10^{16} n/cm² or 10^8 R gammas was required to produce a 10% weight loss in the more sensitive explosives such as PETN and HMX. A 5% weight loss is considered detrimental to the performance of a component containing these explosives. [Kaye 1980]

Miles and Devries conducted an Electron Paramagnetic Resonance (EPR)²⁹ investigation of γ -irradiated PETN. [Miles 1984] Low-temperature irradiation accumulated at least two different radicals. The more stable radical was the NO₂ radical, presumably produced by photon cleavage of the NO₂ groups and/or by radical reactions in excited states resulting in detached NO₂. The spectrum of the more reactive radical was obtained by computer subtraction. The authors proposed decay kinetics for the NO₂ and the unknown highly reactive radical.

Single crystal studies did not result in weight loss in PETN for gamma doses up to 5 MR, but did result in formation and growth of platelets and crack-flaws and yellow discoloration attributed to trapped decomposition gases. It was surmised that flaw development was sensitive to the initial state of the crystal, related to internal strains and imperfections, and that crack growth relieved internal stresses due to accumulation of gaseous decomposition products. Shock initiation of the irradiated samples showed no shock sensitizing effect at doses 0.6 Mrad or less, but an effect above 0.6 Mrad. It has been surmised that the site of a molecule decomposed by a gamma ray could also act as a site for further decomposition in the material after it is shocked. [Dick 1982]

The stability of PETN is decreased by exposure to ultraviolet radiation. The loss of stability resulting from 60 hours exposure is greater than that caused by heating at 105°C for 450 days. [Berlow 1958]

4c) Stress

With PETN powders having many surface irregularities, the contact areas between crystals will be small. This creates high pressure points upon contact which cause plastic flow or internal flow. This results in smoothing of contact points and a decrease in surface area over time. Fusion of crystals (sintering), which is related to surface contact points, also decreases surface area. [Duncan 1972]

Samples of PETN were subjected to ball milling or ultrasonic grinding to assess the roles of surface area and physical attrition. There was no observed change in heat of fusion compared to the original samples, which lead to the conclusion that surface area (i.e. surface energy) is not responsible for observed variations in heat of fusion in various PETN samples. It was also concluded that grinding did not produce significant amounts of stored strain energy in the crystals. [Rogers 1972] This conclusion may extend to the residual strain left due to grain crushing during preparation of pressed pellets.

²⁹ EPR is also known as Electron Spin Resonance (ESR) and Electron Magnetic Resonance (EMR).

4d) Residual Solvents

PETN is insoluble in water but soluble in a variety of organic solvents [Roberts 1958], [Berlow 1958] and particularly in acetone, which is commonly used to recrystallize PETN. [Kaye 1978] Small pockets of solvents such as acetone have been observed trapped in internal voids (occlusions) in crystals, a characteristic of superfine crystals. [Rogers 1972] Over a period of time this residual solvent may change the nature of these voids, which could lead to changes in bulk behavior such as response to initiating insults.

4e) Impurities

PETN often contains a number of impurities that can alter its physical and chemical properties. In studying the thermal decomposition of PETN that was crash precipitated followed by thermal treatment, Kruppa et al. found that the presence of minor impurities from the large-scale synthesis of explosive grade PETN may influence the properties of the material. [Kruppa 2002] Commonly reported impurities in PETN from the synthesis process or sequential thermal decomposition include pentaerythritol, pentaerythritol trinitrate (PETriN), pentaerythritol dinitrate (PEDN or PEDiN), pentaerythritol mononitrate (PEMonoN, or pentaerythritol nitrate), dipentaerythritol hexanitrate (DIPEHN), and tripentaerythritol octanitrate (TriPEON). [Chambers 2002a] Yasuda notes that DIPEHN, for example, can cause a measurable change in the firing characteristics of exploding bridgewire detonators. His work focused on the separation of PETN and PETriN, DIPEHN, and TriPEON by thin layer chromatography (TLC). [Yasuda 1970] Rogers and Dinegar's study on the effect of impurities on the heat of fusion of PETN showed that while 1% by weight TriPEON had no effect, larger amounts had a profound effect, lowering the value. About 1% is considered a degree of impurity expected in "pure" PETN. Of note is that TriPEON is known to form a solid solution with PETN and is not present as a separate phase. [Rogers 1972]

In addition to the homologues in synthesized PETN are other impurities. While the homologues have been synthesized from high purity reagents, TLC indicates numerous satellite impurities present in all the PETN homologues with the exception of ultrapure PETN itself. [Sandoval 1972] Separation and isolation of these contaminants, from a high impurity concentrate, was achieved by liquid chromatography. Infrared spectra of these components suggest these compounds are the various homologues and pentaerythryl ethers with a mixture of hydroxyl and nitrate functional groups.

Klassen et al. identified several organic salts as impurities in PETN. These salts, which include formate, acetate and oxalate, were also found to increase under certain accelerated thermal conditions. [Klassen 2002] According to Chambers et al., the organic salts are probably carried over from synthesis of the pentaerythritol starting material, and are not indicative of a major decomposition pathway. [Chambers 2002b]

Pitchimani et al. studied changes in morphology between the pure PETN and PETN doped with the nitrate salts of iron, calcium, sodium, and zinc. These metal ions were chosen since they are commonly found in tap water, and high surface area PETN is often crash precipitated as a saturated liquor into water. They also carried out studies on the effect of annealing on the morphology of these crystals at the macroscopic and microscopic levels to determine how the different ions modify the crystal. They

concluded that controlling the water-soluble impurities during PETN production may yield powders that do not coarsen over time due to better control of the final morphology. [Pitchimani 2007c]

The effect of additives on the kinetics of thermal decomposition of PETN was studied using high temperature IR spectroscopy. [Makashir 1999] Variation in the absorbency of the NO₂ symmetric stretching vibration was used to monitor decomposition. Evolved gas analysis by IR shows that NO₂, H₂CO are produced in the initial stage of decomposition followed by NO, N₂O, CO₂, HCN and H₂O,³⁰ with the rupture of O-NO₂ bond being the primary step in the thermolysis of PETN. Plots of the fraction decomposed with respect to the original weight of both pure PETN and PETN mixed with 10% carbamate, calcium carbonate and magnesium oxide at 150°C showed that there is an accelerating effect by these additives on the first stage of decomposition of PETN. Similar results were also obtained from TGA-DTA³¹ studies on the effects of these additives.

5) Processes That Are Involved in Change

The processes of sublimation/recrystallization and surface diffusion are important processes that cause change in PETN crystal morphology, particle size distribution and specific surface area.

5a) Sublimation and Recrystallization

As PETN ages with time, changes in its morphology have been attributed to sublimation and recrystallization through sintering, ripening, and other coarsening mechanisms. These changes in morphology lead to a decrease in the surface area, and therefore changes in the overall material performance properties. [Dinegar 1987]

Sublimation and recrystallization play a role in affecting all the variables associated with crystal growth: crystal morphology, powder surface area, particle size distribution, crystal density, powder compact density and density gradients. Sublimation feeds a process called Ostwald ripening, which involves the spontaneous growth of larger crystals from those of smaller size. As the larger crystals grow, the area around them is depleted of smaller crystals. Microscopy has shown that smaller particles disappear and particles fuse. While the formation of smaller crystals is kinetically favored, larger crystals are thermodynamically favored. The smaller crystals nucleate more easily than larger ones, but the larger ones have greater volume to surface area ratio with a lower energy state. This process proceeds with age regardless of storage conditions unless the crystals are treated to retard growth. [Duncan 1972]

Information is available concerning sublimation of PETN over a broad temperature range. Lau et al. reports the sublimation pressure of PETN from room temperature to 109°C. [Lau 2004] The vapor pressure of PETN has been determined over the temperature range of 50 to 98°C. [Crimmins 1969] According to atomic force microscopy (AFM) studies of the activation energy for evaporation of PETN (33.50

³⁰ In order: nitric oxide, nitrous oxide, carbon dioxide, hydrogen cyanide and water.

³¹ Differential thermal analysis (DTA).

kcal/mol),³² sublimation is not significant below 40°C. [Pitchimani 2007b] At room temperature, the vapor pressure of PETN is quite low, in the range of parts per trillion. [Dionne 1986] Cundall et al. also reported the equilibrium vapor pressure, standard enthalpy, entropy and Gibbs energy of sublimation for PETN. [Cundall 1978]

Burnham et al. used atomic force microscopy and thermogravimetric analysis (TGA) evaporation experiments to investigate the process of sublimation. These methods show that PETN molecules are quite mobile on the crystal surface even at temperatures as low as 30°C. Based on this work, calculations suggest that about 2% of the PETN might be expected to recrystallize during a year at this temperature. [Burnham 2005]

Below 130°C PETN sublimates to give crystals of PETN I, the polymorph stable at room temperature. PETN II is the stable polymorph between 130 and 140°C but quickly reverts to PETN I below this temperature range. As the temperature is increased to near the melting point, PETN II crystals are observed in the sublimate. PETN, like many other explosives, decomposes at a finite rate in the solid state as it approaches the melting temperature. Although some PETN decomposition products are gaseous, others are liquids near the melting point and form solutions with PETN, hence catalyzing the decomposition. [Cady 1972]

5b) Surface Diffusion

According to Lin et al., the morphology of a PETN crystal can change through two proposed mechanisms: surface diffusion and sublimation, both of which are believed to occur simultaneously. No experimental observations of surface diffusion have been made, but a molecular modeling approach has attempted to investigate this phenomenon theoretically. [Lin 2007a] Surface diffusion on a PETN crystal was investigated by treating surface diffusion as an activated process in the formalism of transition state theory. In particular, surface diffusion on the (110) and (101) crystal facets (the surfaces most exposed on the PETN crystal) as well as diffusion between the facets was considered. Results show the (110) facet is more thermally active than the (101) facet and the PETN molecule mainly diffuses from (110) to (101) facet. The results are reportedly in good agreement with experimental observations and previous simulations. [Lin 2007b]

6) How Change is Assessed

The following approaches - threshold test fire, particle size distribution, specific surface area, thermal analysis, chemical analysis, powder compact specific surface area and density - have been used in the attempt to assess changes attributable to aging of PETN with varying results. The biggest problem lies in the aging mechanism itself, which likely influences small changes in morphology, both internal and external, and particle size distribution changes on a scale too small to reliably monitor. Other aspects, such as subtle changes in density profiles within pressed powder compacts, may be beyond the capability of current technology to assess.

³² Rate of mass loss measured using TGA with PETN crystals heated from 110-135°C yielded an activation energy of 32.50 kcal/mol. While these two sets of experiments showed similar activation energies at different temperatures, total evaporation rates estimated by extrapolations of the AFM measurements were >300 times faster than from TGA experiments. [Burnham 2005]

6a) Threshold Test Fire

There are two dynamic processes involved in the initiation of an EBW detonator – the bursting of the wire by an electrical signal and initiation of the explosive by the bursting wire. The latter is related to the current at which the wire bursts. It has been shown that this relationship depends only on the properties of the detonator and not the properties of the firing set. Thus the threshold and transmission time of any given EBW detonator are, from the electrical point of view, functions only of burst current. [Tucker 1964]

From the perspective of the PETN pellet in the EBW detonator, it undergoes a deflagration-to-detonation transition (DDT) during initiation. Experiments with pressed granular columns of PETN indicated that upon ignition, early choked flow of the combustion gases prevents the continued propagation of the combustion via a convective heat transfer mechanism and that the propagation of reaction becomes governed by a leading compaction wave which causes ignition through the mechanical formation of hot spots. [Luebecke 1996] More recent studies have indicated that the detonation criterion is not dependent on the rate of deflagration, but on a volume of material that must be burned to create the critical pressure needed at the compaction wave front that occurs before the onset of detonation.³³ [Martin 2006] Modeling of the DDT phenomenon has addressed the effects that the variability in the grain microstructure in PETN explosive powder beds can have on the overall mechanics of DDT. [Sáenz 2008] The variability in the distance to detonation was noted to occur at a wide range of initial powder bed densities, but is higher for low initial bed compactions (i.e. low density). The authors considered it likely that a significant source is the variability in the microstructure in the powder bed. In an example they noted that because the thickness of the compaction wave was on the same scale as the size of a few particles it is reasonable to expect the microstructure to have a significant effect on the mechanics of DDT in explosive powders. This observation is echoed in an experimental study of shock initiation of standard and ultrafine PETN powders. It was found that the sensitivity of the material was dependent on the chemistry, the grain size, the density of the charge, and the nature of the shock itself (long or short duration). [Chakravarty 2002] Earlier work by the same laboratory had shown that short pulse duration shock waves with thickness on the order of a few microns (on the order of typical hot-spot sizes) readily initiated ultrafine PETN ($\sim 1 \mu\text{m}$ grain size), but not conventional PETN ($106 \mu\text{m}$ grain size). [Watson 2000] The investigators noted there is a trade-off between initiation from a short duration intense shock and a longer duration, lower intensity shock. Grain size is important in this case as the grain burning time is the critical factor when looking at the shock duration required.

Tucker carried out an experimental study of the dependence of threshold burst current³⁴ (I_{bth}) of exploding bridgewire detonators upon major detonator parameters. It was found that over the range of parameter values of practical interest, I_{bth} with gold or gold alloy bridgewires and loaded with PETN could be related to bridgewire length and

³³ See also [Gifford 2002] for a discussion of Type I vs. Type II DDT in porous PETN powder.

³⁴ Threshold burst current is defined as the value of burst current that produces 50% firing of a given sample of EBW detonators. Burst current is defined as the current flowing in the bridgewire at the time of peak voltage across the wire, and can be used to define the initiation sensitivity of an EBW detonator.

diameter, explosive specific surface area and density, and firing temperature. Threshold burst current was seen to increase with increasing pellet density. Increasing wire diameter or decreasing wire length generally resulted in an increase in I_{bth} , but the magnitude of the increase depended on the specific surface area of the explosive powder. Small-diameter bridgewires required high specific surface area to minimize I_{bth} . Thus the explosive needs to be matched to the bridgewire and changes in either will affect threshold firing. [Tucker 1968] If the threshold current begins to rise due to aging of either component, then the detonator function time can be affected. Additional explosive characteristics such as purity, particle size distribution, crystal shape and surface properties are also expected to play a lesser role in the initiation phenomenon.

Rogers and Duncan carried out particle characterization of production lots of RR5K-type PETN³⁵ to develop predictive models that would identify those particle characteristics influencing sensitivity and performance. In general, large distributions of shapes and sizes, with the larger particles being needle-like or elongated, led to low threshold burst currents and short transit times. The I_{bth} was also found to be inversely proportional to the temperature at which the units were test fired. [Rogers 1982]

6b) Particle Size Distribution

Crystal growth significant enough to affect the PETN particle size distribution is expected to impact detonator performance. Blackburn and Reithel note that the size of PETN crystals has a pronounced effect on the buildup zone during exploding bridgewire initiation. Comparing two powders with significantly different specific surface areas showed the build-up to detonation both in time and space is shorter for the finer PETN. [Blackburn 1964] Dinegar showed that heating PETN powder causes an increase in sensitivity to detonator bridgewire initiation and an increase in detonator function time, attributable to an increase in transit time.³⁶ In addition, heated PETN was seen to build up to detonation more slowly than unheated material. The effects are attributed to a physical rather than a chemical phenomenon, and are caused by a decrease in the explosive particle specific surface area, i.e. increased particle size. [Dinegar 1987]

The simplest method to determine particle size distribution is sieve analysis, in which powder is separated on sieves of different sizes. The most obvious disadvantage is that the smallest practical sieve size is 20-40 μm , and many particle size distributions involve much smaller sizes than this. A 20- μm sieve is exceedingly fragile, and it is very difficult to get material to pass through it. [Wikipedia 2008b] This method is also not practical for the very small samples of PETN used in detonators.

³⁵ As an aside, the thermal degradation study of Dosser and Seliskar showed that the behavior of samples of RR5K PETN was significantly different from that of other powders studied. [Dosser 1992b]

³⁶ Function time is the time from the start of discharge of the firing capacitor until breakout at the end of the detonator. It is the sum of two values, the time until burst and the transit time, the time from burst until breakout. Transit time is mainly a function of the detonator design, the type, density and length of explosives in the detonator. The transit time is equal to the length of the explosive pressing, divided by the detonation velocity, plus the excess transit time due to buildup of run distance to steady state detonation. Excess transit time is a function of the initiating shock pressure. And initiating shock pressure is a function of burst current. [Cooper 1996]

Other methods include optical counting, electrical counting (e.g. Coulter counter), sedimentation techniques, laser diffraction, and acoustic spectroscopy (aka ultrasound attenuation spectroscopy). [Wikipedia 2008b] Each method has advantages and limitations. The optical method requires a large number of particles to be measured, which today can be done with commercial software reading scanning electron micrographs. It is still impacted by non-representative dispersion of particles within the field of view and the fact that it is a two-dimensional analysis. The sedimentation methods are limited in not being able to measure sub-micron sized particles due to Brownian motion. However, it is possible using the latest generation of commercial laser light scattering instruments to focus the detection and measurement on the submicron-sized fraction of the powder. Nonetheless, instruments that use a flow-through cell for light scattering measurements exhibit a preferential alignment of rod-shaped and platelet particles in the direction of the flow, which precludes a random distribution of orientations.

The biggest problems associated with monitoring changes in particle size distribution are detecting a quantifiable change in aspect ratio as PETN particles grow and monitoring the distribution of sub-micron particles, which would be expected to diminish over time due to Ostwald ripening. Most light scattering instruments rely on the assumption of individual, smooth spherical particles. Complications with real powders include surface roughness, high aspect ratios, agglomeration, a wide variation in particle size, and a large fraction of submicron particles. Some sample preparation steps, such as use of a carrier fluid and sonication meant to deagglomerate and disperse the PETN powders in a liquid medium, may alter the characteristics of the particles in suspension. [Young 2006]

6c) Specific Surface Area (So)

Because of the difficulties encountered in directly measuring the surface area of small particle samples, several methods are in use that indirectly estimate the surface area. Two examples cited by Young are gas flow permeametry using the Fisher sub-sieve sizer (FSSS) and gas adsorption using the Brunauer, Emmet and Teller (BET) methods. The FSSS method measures resistance to flow or permeability, which is related to the compacted bed pore structure and reentrant void characteristics as well as powder surface area. Results are unaffected by particle shape, but surface roughness affects gas flow around each particle and it fails to measure much of the deep surface texture. Packing the bed for FSSS analysis may damage crystals and arbitrarily increase the surface area of the powder. [Young 2006] The BET method has the advantage of measuring the surface of fine structures and deep texture on the particles. However, the results can differ markedly depending on the type of gas adsorbed. [Wikipedia 2008c]

6d) Thermal Analysis

For practical purposes none of these techniques have proven sufficiently sensitive to detecting changes in aging PETN that has not undergone deliberate accelerated thermal degradation. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature ramp. All these methods can be used with materials that decompose at elevated temperature. In differential thermal analysis (DTA), the

temperature difference that develops between a sample and an inert reference material is measured, when both are subjected to identical heat treatments. A DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak can be related to the change in enthalpy. The related technique of differential scanning calorimetry (DSC) relies on differences in energy required to maintain the sample and reference at an identical temperature. Thermogravimetric analysis (TGA) monitors changes in the mass of the specimen on heating. [Bhadeshia 2008] Examples of TGA data for PETN and DiPEHN and other explosives can be found in Zeman's paper. [Zeman 1993] Examples of DSC data for PETN and DiPEHN can be found in Reddy and Rao. [Reddy 1992]

6e) Chemical Analysis

Measuring the content of naturally occurring or doped homologues in aging PETN samples is only meaningful if the original content is known. Analysis for thermal degradation products such as PETriN may not provide useful data about the aging process if detectable changes do not correlate with changes in performance. Surveillance of PETN homologues (DiPEHN, TriPEON, and TetraPEDN) and PETriN in the stockpile is currently carried out using high performance liquid chromatography (HPLC) with ultraviolet detection. Harvey et al. assessed the use of a quadrapole mass spectrometer as the detection system to provide mass clues to the identity of unknown chromatographic peaks. [Harvey 2005] HPLC in combination with chemoluminescence-N-detection (CLND) has also proven useful for the analysis of PETN and its possible biological and chemical degradation products PETriN, pentaerythritol dinitrate (PEDN or PEDiN) and pentaerythritol mononitrate (PEMonoN). [Seeling 2006]

6f) Powder Compact Specific Surface Area and Density

These factors appear to be the least explored yet play an important role in detonator functionality. PETN powder is compacted to 50% of crystal density (~0.88 g/cc) in many exploding bridgewire devices. [Cooper 1996] In general, all exploding wire detonator configurations exhibit a decreased sensitivity with increasing explosive density. [Tucker 1968] For example, Cooper estimates that a 10% increase in density from an initial 0.88 g/cc calculates to an increase in threshold burst current of 32%. [Cooper 1996]

The surface area and compaction properties of PETN are important to performance and aging characteristics of detonators. Removal of the powder from detonators destroys the compact and prevents performance testing, losing the relationship between physical or chemical changes with performance. The relationship between specific surface area and performance properties and how they change with aging are of particular interest. Firing time variation is dependent on a number of factors, including not only the specific surface area, but also the density and density gradient within the compact. The lower the specific surface area, the longer the firing time between current input and explosive event. Edmonds et al. developed a detonator test system based on air permeability measurement of specific surface area that allows in-situ analysis of powder compacts prior to performance testing. These authors note that during aging, specific surface area changes may occur through both surface and bulk effects. Since air

permeametry cannot detect surface changes, a gas adsorption method may be necessary. [Edmonds 2007]

7) Factors Relevant to Stabilizing Particle Size Growth

With time, changes can occur in the PETN crystals driven by the instability mechanisms listed above. Some changes may have counterbalancing or synergistic influences on the performance and initiability of PETN, making it difficult to predict the outcome with single parameter models. These changes occur on the molecular, crystalline and powder compact levels, and include deviations in:

- Crystal morphology, particle size distribution and powder surface area
- Crystal density and internal defects
- Powder compact density and density gradients

7a) Crystal Morphology, Particle Size Distribution and Powder Surface Area

Explosive powders consist of a distribution of crystalline shapes and sizes. According to Rogers and Dinegar, at least three general crystal habits of PETN have been observed: 1) “tetragonal” with apex angles and little evidence of strain, produced by slow recrystallization techniques, 2) “needle” or “hour glass” with reentrant cavities from the ends and/or high aspect ratio, and 3) “superfine,” named after the original Dupont product, consisting of irregular plates. [Rogers 1972] An example of the needle shape with end cavity is shown in Cady’s papers on growth and defects in explosive crystals [Cady 1993] and on the PETN-DiPEHN-TriPEON system. [Cady 1972]

The crystalline size and shape distributions control chemical, mechanical and thermal properties different from the bulk. Because PETN molecules have a high surface mobility, the morphology and surface area can change over time due to surface diffusion and/or sublimation and recrystallization. The rate of recrystallization and aspect ratio³⁷ of the crystals is strongly dependent on the storage temperature. The aspect ratio of the crystals may change with supersaturation of the storage environment. Although the particle size distribution can be measured experimentally, there is little information on the mechanism associated with the commensurate change in powder surface area. [Zepeda-Ruiz 2006]

To study crystalline surface irregularities produced by shock recrystallization, Duncan compared the total surface area to external surface area. The thought was that both surface and volume effects could be important during the aging cycle. Measurements were made by both air-permeability (Fisher Sub-Sieve Sizer, FSSS) and gas adsorption (Perkin-Elmer Adsorptometer, PEA) to compare the external surface area measured by the FSSS with total (external plus internal) surface measured by the PEA.³⁸ [Duncan 2002] Results indicated that volume effects are occurring with the decrease in internal surface area being quite significant in terms of the size of the decrease, and occurring quite early in thermal aging. In other words, in the process of surface diffusion,

³⁷ The aspect ratio of a shape is the ratio of its longer dimension to its shorter dimension.

³⁸ Airflow around individual particles in the FSSS does not include its reentrant surface while physical adsorption of gas measures an area represented by the surface covered by a monolayer of close-packed molecules of gas. Surface area determined by gas adsorption will include a particle’s reentrant surface topology.

reentrant pores and cracks are filled, resulting in a smoother crystal. When all the surface irregularities are eliminated, measured gas adsorption and air-permeability surface areas are seen to become equal. [Duncan 1972]

Interstitial gases and specific surface area play an interacting role in initiation if not the aging process. In small-scale gap tests, Dinegar et al. found that the initiation sensitivity of pressed low-density granular PETN decreases both with an increase in specific surface area and as the gas pressure is increased. [Dinegar 1973] Later work by the same author showed that decreases in PETN surface area correlated with an increase in detonator function time. [Dinegar 1987]

7b) Crystal Density and Internal Defects

Both crystal density and internal defects have been associated with the initiability of PETN. When explosive powders are pressed to near theoretical maximum density (TMD) pellets the phenomenon is known as “dead pressing,” which desensitizes the explosive. Dead pressing is a well-known phenomenon in solid explosives that occurs when all the porosity is compressed out of the explosive resulting in a voidless material. [Muraour 1950] It has been observed that at or near theoretical maximum density (crystal density) that it becomes nearly impossible to induce a detonation. This is because the number of internal defects that serve to create hot spots under shock conditions decreases as crystal perfection is approached. [Dick 1991]

Crystal defects, in particular dislocations, have been observed to play a significant role in crystal growth. Speculations have also been made of their involvement in both slow and rapid decomposition of energetic solids. The properties of a dislocation are in general strongly dependent on its character and whether or not it is formed during growth or induced mechanically at a later stage of growth. Halfpenny and coworkers used transmission X-ray topography to determine the nature of the growth-induced dislocation structure of PETN. Most dislocations observed originated from either inclusions or growth-sector boundaries, both of which are characteristic of growth-induced dislocations. There was no direct evidence of dislocation motion by either glide or climb mechanisms, which the authors attributed to likely solvent-impurity pinning of the dislocations. [Halfpenny 1984]

Shock sensitivity may relate directly to the absolute number of internal voids and defects, which is expected to scale with crystal size, and not just interstitial voids. The effect of particle size on shock sensitivity was determined for PETN, RDX and Tetryl³⁹ in a modified small-scale gap test. The dimensions of this small-scale test were believed to correspond to those typical of explosive components. The shock sensitivity of PETN was seen to increase slightly as particle size is increased, with a larger effect seen for RDX and Tetryl samples. [Scott 1970]

7c) Powder Compact Density and Density Gradients

The density of a packed powder can either increase or decrease due to environmental factors and either way affect detonator performance. Packing density and interstitial voids have been related to changes in performance and initiation

³⁹ Tetryl is a high explosive, also called N-Methyl-N,2,4,6-tetranitrobenzenamine or Tetranitromethylaniline.

characteristics, respectively. Both detonation pressure and detonation velocity are seen to decrease with decreasing packing density for the same lot of material. [Hornig 1970]

Shock initiated energetic material typically demonstrates a characteristic distance for the detonation wave to appear. A plot of the run-to-detonation length⁴⁰ against percent theoretical maximum density (% TMD) shows the commonly observed ‘U-shaped’ plot with an increase in length to both higher and lower densities. [Luebcke 1996] This data indicates that either densification or increase in porosity can lead to a slower turnover to detonation and therefore slower detonator transit times.

The shock sensitivity of PETN decreases as packing density increases, a trait reportedly common to practically all explosives. [Kaye 1978] This trend implies that aging processes that could densify a pressed pellet could lead to decreased sensitivity to initiation. In threshold firing conditions this could lead to an increase in detonator function time.

It was also found that although smaller particles are less shock sensitive than larger particles, once initiated⁴¹ smaller particles more readily reach a stable high order detonation. This phenomenon may be due to differences in the interstitial voids between large and small crystals pressed to the same density. [Scott 1970] Interstitial voids have been related to the initiation behavior of explosives. The most acceptable theory that explains initiation by mechanical stimuli is the “hot spots” theory. The dynamic action on the material causes strain and stress to appear locally resulting in heating in hot spots, which result in ignition. If the number of voids between grains of explosive is proportional to the number of grains, then the coarse-grained material should have fewer but larger voids than fine-grained explosive at the same density. Experimental results for pressed granular explosive have shown that the volume of fine voids is more efficient in producing chemical reactions than the same volume of coarse voids. This suggests the importance of surface reaction, which may take place at the surface of the void or more likely, at the “surface” of the hot spot produced by shock convergence beyond the void. [Campbell 1961] Thus it may be surmised that crystal growth (e.g. by Ostwald ripening) will change the void volume such that larger voids are formed and the material becomes less sensitive to shock initiation. This in turn leads to a longer run distance to detonation and longer transit times to breakout of the shock wave on the surface of the pressed pellet. Changes in the density gradient within pressed pellets would likewise be expected to affect shock wave transit time. However it does not appear that this phenomenon has been studied.

Interstitial gases and specific surface area play an interacting role in initiation. In small-scale gap tests, Dinegar et al. found that the initiation sensitivity of low-density granular PETN decreases with an increase in specific surface area of pressed explosive with air at atmospheric pressure in the crystal interstices, and decreases as the gas pressure is increased. Substitution of helium, argon, nitrogen and carbon dioxide for air

⁴⁰ Also called “run distance to detonation.”

⁴¹ In low-density pressed explosives, initiation is not the result of uniform shock heating nor is it explained by shock heating of the interstitial gas. [Seay 1961] Initiation seems to depend on the discontinuities and resulting shock interactions. The shock interactions are believed to contribute to spalling, jetting or some combination. [Seay 1963]

for both low and high specific surface material is accompanied by a decrease in explosive sensitivity. Substitution of oxygen sensitized powder compacts with mixtures of oxygen and nitrogen showing sensitivities intermediate to those observed with the pure gases. This effect was also noted with exploding bridgewire initiation under an oxygen high-pressure atmosphere. The greater the molecular complexity of the gas, the greater its desensitizing effects. [Dinegar 1973]

8) How PETN Powder Surface Area Can Be Stabilized

Successful use of PETN in detonators requires use of high surface area powders pressed into powder compacts. A number of stabilization methods have been discussed that are meant to mitigate sublimation of PETN crystals, and therefore crystal growth, under service conditions. These include thermal cycling, doping with higher molecular weight homologues, and the addition of certain impurities during or after crystallization of PETN. [Pitchimani 2007a], [Pitchimani 2008]

8a) Additives

Homologues DiPEHN and TriPEON have been noted in the literature as two naturally occurring impurities in PETN. One study referred to the use of 1% TriPEON additive in the PETN as a “mild binder”. [Campbell 1961] TriPEON has been used to stabilize PETN. [Moore 2004] (See Section 3.f on “Purity” and Section 4.e on “Impurities” for more discussion about the PETN homologues.)

Maiti and coworkers developed a simple working formula to calculate the desorption rate of TriPEON, referred to as “a foreign surface inhibitor,” from the (110) surface of the PETN crystal. [Maiti 2007] They compared the desorption range of a PETN molecule from a “kink” site⁴² on an exposed crystal face with that of TriPEON from the same kink site. They concluded that once all kink sites on the surface are saturated with TriPEON there should be a significant slowdown in the kinetic processes on a PETN surface resulting in surface and morphology stabilization for at least a few years.

8b) Surface Agent Treatment

Polymers such as polysaccharide, binders, and wetting agents can be used to retard sublimation by coating the surface. [Moore 2004], [Osborn 1969], [Osborn 1970] It has been speculated that the presence of certain types of large molecules on the crystal surface should interfere with the surface activity, resulting in less growth and crystal change. [Osborn 1970] As an example study, twenty Micronizer⁴³ runs were made to ascertain the effects of various fluids and wetting agents on the stability of high surface area PETN and to establish the limits for process repeatability. One sample, after being

⁴² The work done to take a molecule away from a “kink” site is half the work necessary to extract it from the bulk. [Mutaftschiev 2001] The kink site is of special importance when evaluating the thermodynamics of a variety of phenomena. This site is also referred to as the “half-crystal position” and energies are evaluated relative to this position for processes such as adsorption, surface diffusion, and sublimation. The term “half-crystal” comes from the fact that the kink site has half the number of neighboring atoms as an atom in the crystal bulk, regardless of the type of crystal lattice. [Wikipedia 2009]

⁴³ A Micronizer is a jet mill employing compressed air or gas to produce particles less than one micron in size.

treated with the wetting agent dodecyl sodium sulfate, stabilized at 7400 cm²/gm after the 300-hr bake at 100°C. [Osborn 1969] A polysaccharide used to wash PETN crystals in a surface area stabilization study is a commercial guar gum sold by Stein-Hall under the designation Jaguar J2S1. [Osborn 1970]

8c) Heat Treatment

Thermal cycling has been proposed as a method to alleviate the sublimation of PETN crystals under service conditions. [Pitchimani 2007a] An example is “heat treated” micronized PETN, prepared by heating recrystallized powder at 212°F (100°C) for 300 hours. It was found that PETN could also be effectively stabilized after 8 hours at 240°F (~116°C). [Osborn 1970], [Osborn 1971]

In Duncan’s study of recrystallized unstabilized PETN, it was noted that preheated material did not lose any appreciable amount of surface area after 586 days of storage. This stability was suggested as possibly due to the fact that surface irregularities were removed during the pre-aging, in that molecular relation, contact points, and surface diffusion had been completed, and additional loss would be due to bulk diffusion. At ambient conditions bulk diffusion is quite slow, so that slight changes in surface area would not be obviously detectable. [Duncan 1972]

Another part of Duncan’s study used coarse and fine (<10 micron) PETN samples sieve cut from the same batch and compared the surface area of each with a sample of the uncut batch after thermal cycling. It was found that the uncut sample maintained a higher surface area than either coarse or fine samples, which attained the same surface area during the first two hours of aging. The stabilization level of the <1 micron sized material was unexpected in that it was significantly lower than that of the original sample. [Duncan 1972]

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10) Acronyms

AFM – atomic force microscopy

BET - Brunauer, Emmet and Teller (gas adsorption method)

Bi₂O₃ – bismuth trioxide

¹⁴C-compounds – molecules with ¹⁴C (or radiocarbon), radioactive isotope of carbon

¹⁴CO₂ – carbon dioxide labeled with ¹⁴C (or radiocarbon), radioactive isotope of carbon

C₂H₂ – acetylene

CH₄ – methane

CI – chemical ionization (spectroscopy)

CLND – chemoluminescence-N-detection

CO – carbon monoxide

CO₂ – carbon dioxide

Co⁶⁰ – Cobalt-60, radioactive isotope of cobalt

CuO – cupric oxide

DDT – detonation-to-deflagration transition

DiPEHN - dipentaerythritol hexanitrate

DSC – differential scanning calorimetry

DTA – differential thermal analysis

EBW – exploding bridgewire (detonator)

EFI – exploding foil initiator

EGDN – ethylene glycol dinitrate

EMR – Electron Magnetic Resonance (spectroscopy)

EPR - Electron Paramagnetic Resonance (spectroscopy)

ESR – Electron Spin Resonance (spectroscopy)

ESI - mass electrospray ionization (spectroscopy)

Fe₂O₃ – ferric oxide [Iron (III) oxide]

FSSS - Fisher sub-sieve sizer (gas flow permeametry method)

FTMS – Fourier Transform Mass Spectrometry

H₂ – hydrogen

H₂CO – formaldehyde

H₂O – water

HCN – hydrogen cyanide

HE – high explosive

HMX - Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, or Cyclotetramethylene tetranitramine, or Octogen (acronym may be from “High Melting explosive”)

HNCO - isocyanic acid

HPLC - High-performance liquid chromatography, or High-pressure liquid chromatography

I_{bth} – threshold burst current

IHE – insensitive high explosive

KMC – kinetic Monte Carlo

LLNL – Lawrence Livermore National Laboratory

MnO_2 – manganese dioxide

MoO_3 – molybdic oxide (molybdenum oxide)

MR – mega-Roentgen (unit of radiation exposure)

Mrad – mega-rad (mega- Radiation Absorbed Dose)

N_2 – nitrogen

NC – nitrocellulose

NG – nitroglycerin

NH_4^+ - ammonium ion

NMR – nuclear magnetic resonance

NO – nitric oxide

NO_x – any one of the oxides of nitrogen

NO_2 – nitrogen dioxide

NO_2^- – nitrite ion

NO_3^- – nitrate ion

N_2O – nitrous oxide

N_2O_4 – dinitrogen tetroxide

O_2 – oxygen

PBX – plastic bonded explosive

PEA – Perkin-Elmer Adsorptometer

PEDN or PEDiN – pentaerythritol dinitrate

PEMonoN – pentaerythritol mononitrate

PETN – pentaerythritol tetranitrate

PETNr – PETN reductase (enzyme)

PETriN – pentaerythritol trinitrate

R – Roentgen (unit of radiation exposure)

RDX - Hexahydro-1,3,5-trinitro-1,3,5-triazine, or Cyclotrimethylene trinitramine, or Hexogen (acronym may be from “Research Department (composition) X”)

SnO₂ – stannic oxide (tin oxide)

So – specific surface area

TATB -1,3,5- Triamino-2,4,6-trinitrobenzene

Tetryl - N-Methyl-N,2,4,6-tetranitrobenzenamine or Tetranitro-methylaniline

TGA – thermogravimetric analysis

TLC – thin layer chromatography

TMD – theoretical maximum density

TMR – time-to-maximum-rate (decomposition)

TNT - trinitrotoluene

TetraPEDN - tetrapentaerythritol dodecanitrate

TriPEON - tripentaerythritol octanitrate

UK – United Kingdom

WO₃ – tungsten oxide

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