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HNS-IV Explosive Properties and Characterization Tests

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Abstract

HNS-IV (2,2', 4,4', 6,6' – Hexanitrostilbene) is a well characterized energetic material that is used in a variety of aerospace, military, and industrial systems. It is an insensitive explosive, and is thermally stable to temperatures of over 200 C. With many modern systems requiring a system life of 20 years, it is important that the explosive be stable during that lifetime, and that there be a method of verifying the stability of the explosive. This paper will discuss the tests typically used to characterize the explosive. It will discuss the theory behind aging studies as well as aging studies performed on bulk powder and several devices containing HNS-IV explosive. The data will show that there is little performance degradation with explosive powder and detonators that have been subjected to accelerated aging. In addition, data is presented showing that a commonly used performance indicator has almost no effect on device performance.

Introduction

HNS-IV Explosive Powder

HNS-IV (2,2', 4,4', 6,6' – Hexanitrostilbene) is a well characterized energetic material that has been the explosive of choice for Exploding Foil Initiators (EFI), also called a slapper detonators, for several decades. HNS is the material of choice for a number of reasons. It is an insensitive explosive that will not inadvertently initiate when exposed to various environments, such as electrostatic discharge, drops, friction, or elevated temperature. In fact, about the only way to initiate the explosive is with a shock wave. However, it is relatively easy to initiate the explosive with the shock wave generated by an EFI.

Because of its high temperature stability, detonators with HNS are useful under extreme temperature ranges. They are used extensively in the oil completion business where down hole temperatures reach well over 200 C. They also function well at liquid nitrogen temperature (-196 C). Detonators using HNS-IV have also been proven to function reliably when subjected to high shock environments produced by penetration of thick walls.

The properties of HNS-IV are governed by the US military standard MIL-E-82903. This standard gives the following prescription. “HNS-IV shall be crash precipitated from HNS-II which was recrystallized from HNS-I conforming to WS 5003. HNS-II must be prepared by recrystallization from an organic solvent system (i.e., Dimethylformamide – DMF certified) by the process approved by the contracting agency. HNS-IV shall be a superfine particle size material with a surface area of 5.0 to 25.0 square meters per gram (m^2/g). HNS-I is a high explosive synthesized by a "one-step" process from trinitrotoluene (TNT).”

PerkinElmer Optoelectronics manufactures HNS-IV according to the military standard process for use in a number of systems. Because the military standard requires several characterization tests that make use of outdated equipment, PerkinElmer developed its own specification, SP0001. This specification has similar requirements to the military standard, but allows for the use of more modern equipment. It also specifies an aging test to ensure that devices made with this HNS continue to meet performance specifications for the device.

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Characterization Tests

Because the manufacturing process for HNS-IV involves a number of steps, various tests are conducted to ensure that the HNS-IV is suitable for the intended application. Both the military specification and the PerkinElmer Optoelectronics specification require a number of characterization tests for each batch of HNS-IV. These tests can be described as wet chemistry (volatile, non-volatile, and conductivity) tests to measure the purity of the HNS, surface area measurement to get an estimate of the HNS-IV particle size, and performance testing of the HNS when built into detonators.

Wet Chemistry Tests

The volatile contamination test consists of weighing a quantity of HNS-IV powder, heating the sample at 100 C for one hour under vacuum, and determining the fractional weight loss. Any volatile substance should be driven off by the temperature and vacuum. Because HNS-IV is hygroscopic, there will always be a small amount of water vapor present in any sample. The amount of weight loss recorded is measurement dependent. If the HNS is spread out and the vacuum is higher, then more moisture will be pulled out. The water vapor should be less than 0.1% of the total weight. If the vapor content is higher than desired, then the powder can be further dried to remove the excess moisture.

The non-volatile measurement consists of dissolving the HNS-IV in a solvent, passing the solution through a filter, and weighing the contamination trapped by the filter. Because the HNS-IV manufacturing process involves passing the dissolved HNS through several very fine filters, there should be almost no solid contamination. The fraction should be less than 0.1% of the total weight. It is typically rather easy to meet this requirement.

The conductivity measurement compares the conductivity of HNS in water to a weak salt solution. It is designed to determine ionic content of the HNS-IV. The typical requirement is that the solution has lower conductivity than a 10^{-6} salt solution. The ionic content of the HNS-IV is dominated by the ionic content of the HNS-II starting material. If the starting material is pure, this requirement is easy to meet.

Surface Area

The main difference between the HNS-IV explosive that can be initiated be an EFI and the HNS-II that can not is the much smaller crystal size of the HNS-IV. Since a complete particle size distribution measurement is difficult to obtain, a surface area analysis is usually performed. This measurement consists of determining the quantity of nitrogen gas that is adsorbed onto the surface of the HNS-IV. Since gas adsorption is a surface phenomenon, the quantity of gas adsorbed is directly related to the surface area. Because the surface area of a sample is proportional to the quantity, it is customary to report the Specific Surface Area (SSA), or the surface area divided by the mass of the sample.

The typical dimension of a crystal is related to the surface area by the formula:

$$\text{Dimension} = a/(\rho \cdot \text{SSA})$$

where *a* is a factor that depends on the crystal geometry. For particles that are spherical, the factor is 6. For more needle-like particles, the factor is smaller for the short dimension and bigger for the long dimensions. The density of HNS is approximately 1.74 g/cm^3. If the specific surface area is 10 meters square per gram, a typical measurement, then the typical crystal dimension would be approximately 0.3 micron.

Detonator Performance Tests

Both the military and PerkinElmer specifications require that the HNS-IV be built into detonators and tested to ensure that the threshold meets a specific performance requirement. The military specification requires that the velocity of slapper at threshold be within a narrow range. Since PerkinElmer manufactures both the HNS-IV as well as the detonators, the PerkinElmer specification requires that the detonators meet the required performance specifications. In addition, the PerkinElmer specification also requires that the detonator continues to meet the detonator specification after accelerated aging.

There are two different measures of device performance that are normally required. One measure is detonator output. The output of the device is normally a function of the cavity design and the powder weight, and thus is not expected to vary from lot to lot. This requirement is normally satisfied during qualification by measuring the dent in steel produced by the detonator.

The second performance requirement is initiation threshold. The initiation threshold is dependent on properties of the HNS-IV powder, chip slapper, and manufacturing processes, all of which can vary from lot to lot. Therefore, the initiation threshold is generally measured for each lot of detonators produced. The initiation threshold is determined by conducting a sensitivity test, such as a D-Optimal test to determine the mean firing energy.

ACCELERATED AGING

THEORY

Most energetic devices are required to be able to function reliably a number of years after production. It is common to require that an energetic device function after storage for up to 40 years under various conditions. Because it is not possible to wait to see if the device will work after the required storage time, an accelerated aging test is performed by storing the devices at an elevated temperature.

The theory behind accelerated aging is based on the Arrhenius equation for reaction rates. The chemical reaction rate is dependent on the concentration of the chemical species. For a reaction to occur, the available energy must be above the activation energy for the given reaction. The Boltzman equation gives the probability of any given molecule having the required energy. This probability is given by:

$$\text{Probability (Energy >Ea)} \propto e^{-E_a/kT}$$

where k is Boltzman's constant and T is the temperature in degrees Kelvin. (Sometimes R, the ideal gas constant, is used instead of k. In such a case, the activation energy is the energy required for a mole of the substances to react.) Because at elevated temperatures, there are more molecules with the required energy, reactions proceed faster. The reaction rates for many chemical processes are governed by this same Arrhenius equation:

$$\text{Reaction Rate} \propto e^{-E_a/kT}$$

where E_a is the activation energy of the reaction. The above simple equation assumes that there is one dominant limiting reaction. If there are a number of possible reactions then the simple equation becomes much more complicated.

The preceding formula gives the reaction rate. To determine the effects of raising the temperature on the reaction rate, it is a simple matter in principle to compute the reaction rate at the accelerated aging test temperature and divide by the reaction rate at the device storage temperature. The relative reaction rate equation or aging factor thus becomes:

$$\text{Relative Reaction Rate} = e^{-E_a/k(1/T_{test} - 1/T_{storage})}$$

If the difference between the test and storage temperatures, $\Delta T = T_{storage} - T_{test}$, is small compared to the storage temperature, then the relative reaction rate can be approximated by the equation:

$$\text{Approximate Relative Reaction Rate} = e^{-E_a \Delta T / kT_{storage}^2}$$

This simple form of the equation is often used to say that the reaction rate doubles for each 5 or 10 degree C increase in temperature. However, this equation is only an approximation, and does not take into account the activation energy for the specific reaction, nor is it accurate for large temperature changes such as those described in this paper.

For HNS-IV degradation, the dominant reaction is assumed to be the interaction of the HNS crystals with residual solvent. A conservative estimate for the activation energy for such a process is 0.7 eV[†]. The normal storage temperature of devices is assumed to be room temperature, or 21 C. Using these factors results in the equivalent aging shown in Table 1.

Table 1: Equivalent Aging Temperature and Duration

Temperature (°C)	Duration (Days)	Equivalent Age (Years)
71	70	10.59
84	28	10.00
96	14	10.48
108	7	10.47
111	6	10.60

The aging tests for this paper were conducted at an aging test temperature of 111 C. This temperature was chosen because previous function and storage testing at this temperature for an HNS-IV single load detonator had indicated that there was no extraneous interaction. The tests could also be completed in a short amount of time. Thus the acceleration factor for this test was

[†] Stanley Caulder, private communication.

645.42. That is, each day stored at 111 C is the equivalent to 645 days (1.7 years) stored at 21 C.

PERFORMANCE REQUIREMENT

The PerkinElmer Optoelectronics HNS-IV specification requires that the detonators made with HNS-IV continue to meet the detonator performance requirements at the end of the design lifetime. For most of the programs, the device lifetime is 10 years. Thus, the standard practice is to perform an accelerated age test to give the equivalent of 10 years. Table 1 shows that a 10 year equivalent age can be obtained by storing the detonators at 111 C for 6 days. After the aging, the initiation threshold of the detonators is measured. The detonators must meet the system performance requirements.

BLUE CHIP DETONATOR

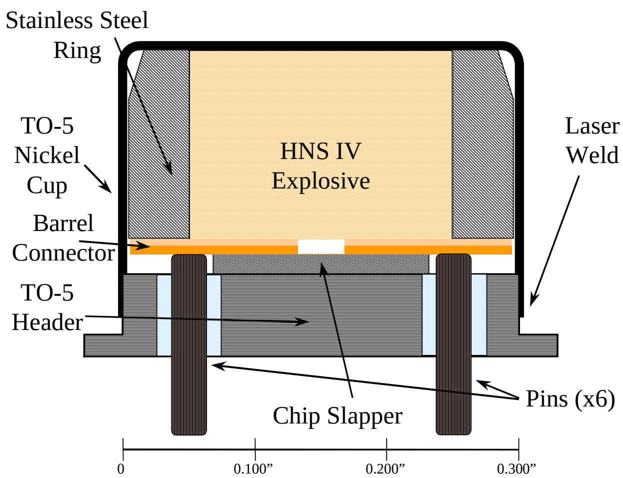

Figure 1: Standard Blue Chip® Detonator

Because the HNS-IV is used mainly in the PerkinElmer Blue Chip Detonators®, the test results reported here were all conducted with those devices. Figure 1 shows a schematic diagram of the detonator. There are different versions of the detonator: two and six pin packages, standard and low energy, and standard and dual load.

TEST RESULTS

PARTICLE SIZE TEST RESULTS

As part of the routine lot acceptance testing, a threshold test is performed on each lot of Blue Chip Detonators®. The test data reported here is for both two and six pin devices with standard energy and standard output. In general, most of the two pin detonators were tested with a fireset that has a 0.1 uF capacitor and relatively high inductance, and most of the six pin detonators were tested with a low inductance fireset with a 0.2 uF capacitor. Testing with the other combinations of fire sets and detonators has shown that there is almost no threshold difference between the two and six pin detonators fired with the same fireset. To be able to compare the test results from both firing systems, all data has been normalized by dividing by the average threshold value of the fireset.

Each of these tests was conducted with a sample size of approximately 30. The standard deviation determined is typically 2 to 4% of the mean threshold. With such a sample size and standard deviation, the mean can be estimated to 4%. On average

Figure 2 shows the results of the measurements performed on 40 lots of PerkinElmer Optoelectronics detonators manufactured during the last few years. Each dot on the graph represents the relative threshold of a separate detonator lot. There are a number of detonator lots for most HNS-IV batches, as shown by the multiple results for a number of surface area measurements. The circles on the graph are the average of all detonator lots with the same powder batch. The plot also shows a least square fit to the data. The slope is essentially zero, i.e. there is little to no relationship between surface area and threshold voltage.

The graph shows several things. The first thing to notice is that there is little variation between lots. With this sample size the statistics are such that there is a 4% error for each measurement.

Thus, the overall variation is close to the measurement precision. The variation in these measurements is due to the HNS-IV powder variation, as well as to all variations in chip slapper and detonator manufacturing.

The second point to notice is that there is little variation of mean initiation threshold with the surface area, at least for the range of surface areas studied. Even a factor of two change in the surface area results in at most a few percent change in the mean threshold voltage.

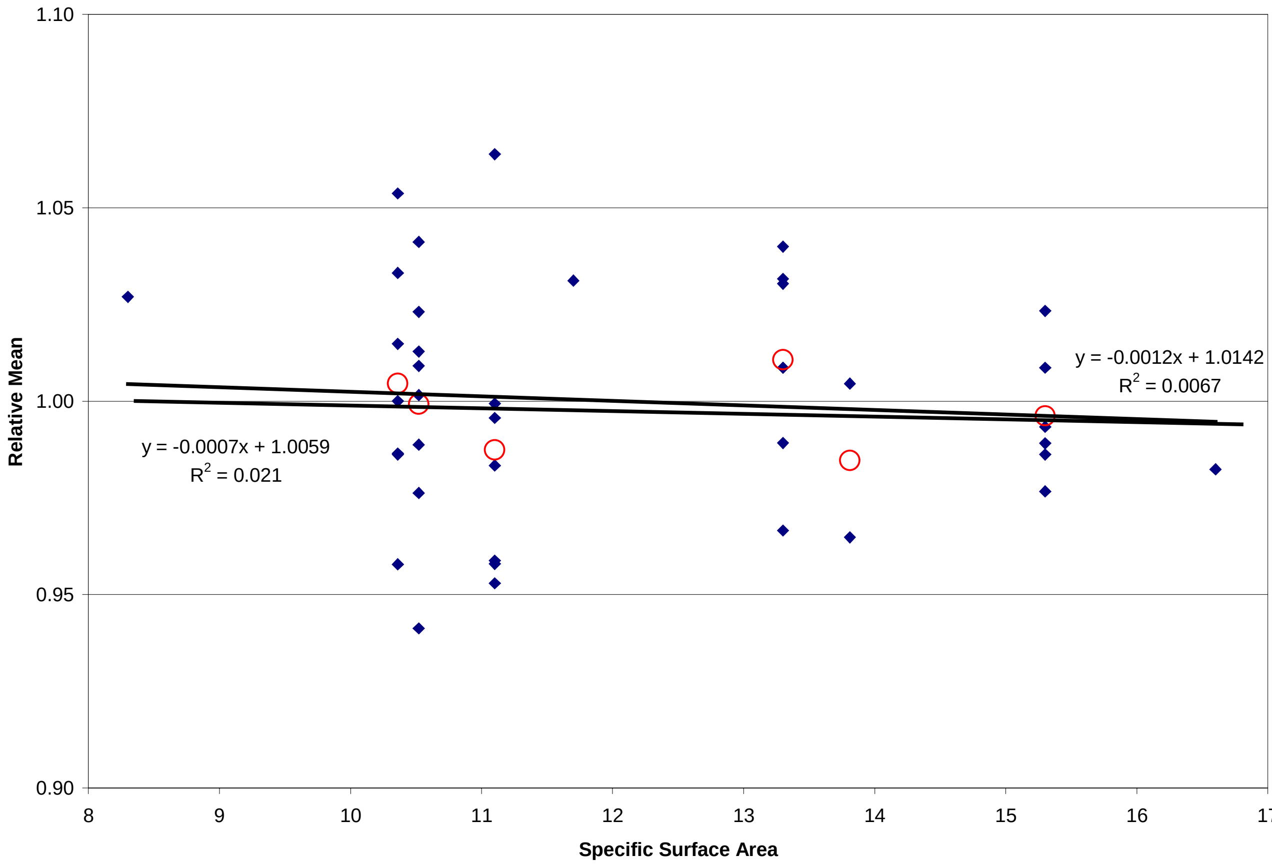

Figure 2: Threshold versus Surface Area

Accelerated Aging Test Results

PerkinElmer Optoelectronics has manufactured 6 batches of HNS-IV for which there is threshold data from both long term aging and from devices that have not experienced aging. Each of these threshold tests were conducted on samples with approximately 30 units. The detonators were aged for 6 to 11 days. The threshold voltage of the aged samples was divided by the threshold voltages of the lot acceptance tests mentioned in the previous section. This data is shown in Figure 3.

The graph also shows the results of testing with a small sample size of approximately 5 for a number of additional days, up to 500 days. The error in threshold determination for such smaller samples is approximately 10%.

The data clearly shows that there is some effect, on the order of 7%, but that there does not seem to be any significant change with time for the PerkinElmer Optoelectronics devices.

Figure 3 also shows data for tests conducted on detonators made with Pantex powder. These tests were also conducted with a different detonator configuration, and a different fireset. The data was normalized the same way by dividing by the threshold voltage of the sample that was not aged. One final note is that the aging test for this powder was conducted at the much lower temperature of 75 C. Unlike the PerkinElmer data, the data from the Pantex sample show a clearly increasing threshold voltage as a function of time.

The Pantex data can be rescaled according to the accelerated aging equation to have the same aging factor. This figure is also shown in Figure 3. The data clearly show that the accelerated aging had a different effect on the PerkinElmer devices than the Pantex devices.

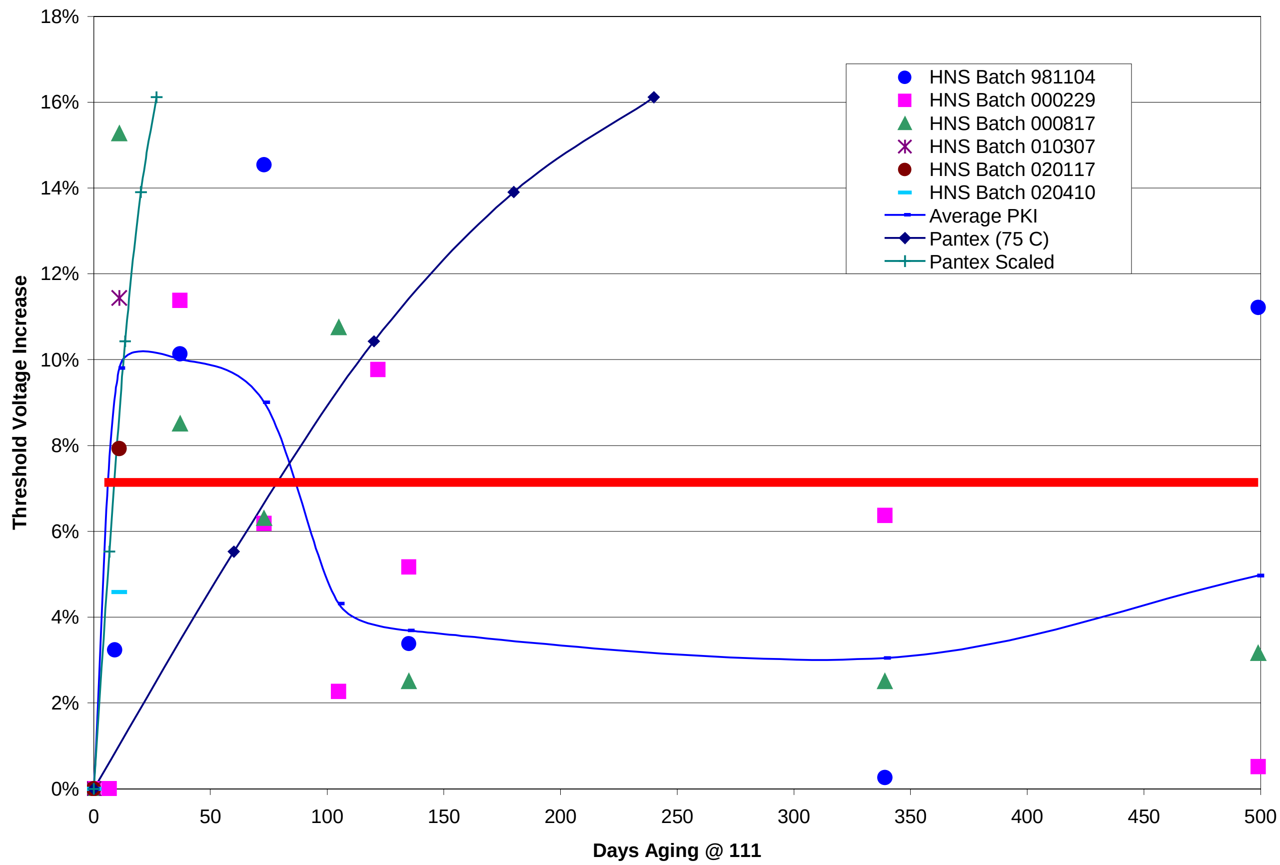

Figure 3: Accelerated Aging

The fact that the "aging" of the PerkinElmer detonators appears to take place within a short period and then stop suggests that there may be other phenomena at work instead of chemical aging according to the Arrhenius equation. In an attempt to determine the cause of the small threshold shift, smaller scale experiments have been conducted by aging bare powder and HNS-IV loaded sleeves. Threshold tests have shown that there is no increase in threshold for either of these samples.

Additional testing has taken place with devices that had the chip slapper part of the detonator removed after aging and replaced by chips that were not aged. These devices showed the same small shift in threshold voltage.

The data show that there is a small increase in threshold voltage of the detonator, but not of the powder, loaded sleeves, or slapper chips. The implication is that there is some interaction within the detonator, possibly between the polyimide of the chip slapper and the HNS that results in a small increase of the threshold.

SUMMARY

Analysis of the results of performance tests conducted on PerkinElmer Blue Chip Detonators® containing HNS-IV show that there is essentially no variation in performance throughout the production history, and as a function of surface area. There is a minimal performance variation of the detonators themselves, but the data suggest that the effect may not be a traditional aging phenomenon, but rather due to the elevated temperature alone.

REFERENCES

Barry T. Neyer, "A D-Optimality-Based Sensitivity Test," Technometrics, Vol 36, pp 61-70, February 1994.