Updates on HTPE Propellant Service Life

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ABSTRACT

ATK Tactical Systems Company has continued the development and characterization of both reduced smoke and aluminized propellants based on a hydroxyl-terminated polyether (HTPE) polymer binder. Excellent ten-year aging results have been obtained and are reported here. Service life test results for gas generation, stabilizer depletion and mechanical and ballistic property stability for HTPE propellants are equal to or superior to those of the current successfully deployed minimum smoke propellants in TOW and Hellfire motors. Therefore, HTPE propellants are also projected to meet tactical motor service life requirements as extreme as those actually experienced for TOW and Hellfire motors now deployed around the world.

INTRODUCTION

This paper contains a summary and analysis of the aging behavior for HTPE propellants containing terethane-polyethylene glycol (TPEG) polymer manufactured at Allegany Ballistics Laboratory (ABL) by ATK. Aging data have previously been presented in papers published in 1997[1], 1998[2] and 2004[3]. A recent comprehensive CPIA review of HTPE propellant technology was published in 2003[4]. The CPIA technology review included insensitive munitions test results for 5- and 10-inch diameter analog motors as well as for Sidewinder, ESSM (with steel or composite cases), HP-RAM and Standard Missile 21-inch diameter motors. Motors containing HTPE-based propellants have demonstrated the ability to meet the IM test criteria or provide significant improvements in IM response for most applications. HTPE propellant also passed the six-inch diameter zero card gap test demonstrating that it is a non-detonable propellant for motors with webs up through six inches.

Service life of HTPE propellants has been measured using three criteria: gas generation, stabilizer concentration, and mechanical properties. Burn rate is also measured to confirm the consistency of the propellant burn rate during the aging process. Measurements of these properties for periods of time up to ten years at various temperatures were all used to measure and project HTPE propellant service life. The aging data were compared to that obtained on currently-deployed minimum smoke propellants, which have been demonstrated to have a service life of at least ten years under tactical motor storage conditions. It was reasoned that if the HTPE propellants age as well as or better than fielded minimum smoke propellants, then it can be reliably concluded that motors containing HTPE propellants will also have service lives of at least ten years at tactical storage conditions.

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DISCUSSION OF RESULTS

The service life of HTPE propellants is confidently projected to meet the service life requirements of a tactical rocket motor. This projection is based on measurements of three parameters: gas generation, stabilizer depletion and mechanical property stability. The propellant properties are measured at various times and temperatures and the results are evaluated. These data are compared to comparable data for a tactical minimum smoke propellant. Stabilizer depletion calculations are also made for HTPE and minimum smoke propellants using worst-case aging conditions for a typical tactical motor. The stability of propellant burn rate is also confirmed during the aging process.

The HTPE propellant aging properties were compared to those of minimum smoke propellants because of the similarity of their binder compositions and their identical aging mechanisms. Both propellant types have a binder consisting of a crosslinked polyurethane polymer plasticized with a nitrate ester and stabilized with N-methyl-p-nitroaniline (MNA).

The primary aging mechanism for both HTPE and minimum smoke propellants is the evolution of nitrogen oxide (NO), nitrogen gas (N_2), and carbon dioxide (CO_2). Gases are generated from the degradation of the nitrate ester plasticizer (BuNENA for HTPE propellants, NG for minimum smoke propellants) and their interactions with the urethane crosslinks. The evolution of these gases can cause a propellant to soften and eventually fail by swelling or cracking. Nitrogen gas is only slightly soluble in HTPE propellant; it tends to be the primary cause of grain cracking. The CO_2 is quite soluble, and therefore causes less damage. The NO_x, as discussed below, reacts with the MNA stabilizer (or in the absence of MNA, with the urethane crosslinks in the propellant). It is therefore instructive to examine the evolution of these gases to track the aging process. A comparison of gas generation in minimum smoke and HTPE propellants is presented below in Section 1.

Damage from the evolution of NO gases from the degradation of the nitrate ester plasticizer is controlled by the MNA stabilizer, which reacts with the nitrogen oxide before it can attack the urethane linkages in the propellant binder. Therefore, it is useful to measure the decrease in MNA concentration as it reacts with NO. The decrease in MNA concentration is only an indicator parameter, however, since it is the physical phenomena of mechanical property degradation and cracking that ultimately cause a propellant to fail in the aging process. A comparison of MNA depletion in minimum smoke and HTPE propellants is presented below in Section 2.

The result of the reaction of NO with urethane crosslinks in the propellant is a degradation of mechanical properties. Therefore, it is important to track mechanical properties as a propellant ages. A comparison of propellant mechanical properties in minimum smoke and HTPE propellants is presented below in Section 3.

In each of these three areas of testing, the HTPE propellant aged at least as well as the minimum smoke propellants that have a proven service life of ten years or more at tactical motor storage and deployment conditions. Therefore, it is concluded that the service life of the HTPE propellants (reduced smoke and aluminized) will be at least as long as the ten years the minimum smoke propellants are designed to be stored at tactical motor storage conditions.

1. <u>Gas Generation of HTPE Propellant</u>

Gas generation measurements were performed on a reduced smoke HTPE propellant at 158°F, and these results are compared to those for minimum smoke propellant in Figures 1 and 2. For minimum smoke propellants, experience has shown that the initial gasses generated by the propellant will be absorbed into the binder and will not detract from propellant quality. As the MNA stabilizer depletes, more gas is generated (primarily CO_2 and NO), and the ability of the propellant to absorb the gas will eventually be exceeded, causing propellant grains to swell or crack. The three individual gases are normalized to account for differences in the ability of the propellant binder to absorb them. For minimum smoke propellants, as long as the total normalized quantity of gas ($N_2 + CO_2/50 + NO/2$) remains below 100×10^{-3} cc/gram of propellant in 30 days at 158°F, the service life will exceed ten years at tactical motor storage conditions[5].

As can be seen in Figure 1, the quantity of gas generated by the minimum smoke propellant is significantly less than the criterion of 100×10^{-3} cc/gram in 30 days, and therefore this propellant has an acceptable service life based on gas generation. The HTPE propellant generated about one-half the normalized gas per gram of propellant that the minimum smoke propellant generated.

As can be seen in Figure 2, the HTPE propellant generated approximately the same amount of normalized gas that the minimum smoke propellant generated when compared on the basis of gas generated per gram of binder. The difference between gas generated per gram of propellant and gas generated per gram of binder can be accounted for by the fact that the minimum smoke propellant was formulated with 35% binder, and the HTPE was formulated with 19% binder.

Therefore, based on gas generation, it is concluded that the service life of HTPE propellant would be comparable to the ten years in a tactical motor storage environment and would meet or exceed that of currently deployed minimum smoke propellants.

Figure 1. Gas Generation of HTPE and Minimum Smoke Propellants per Gram of Propellant

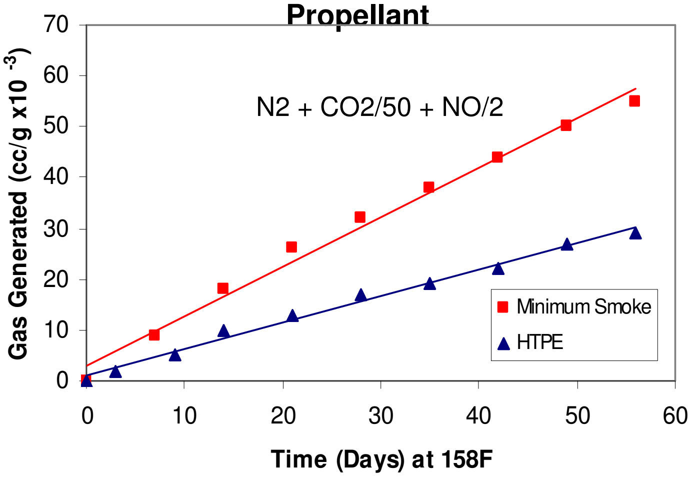
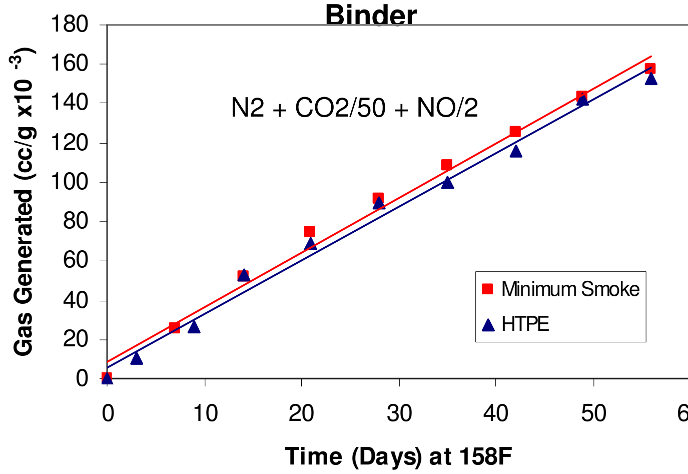


Figure 2. Gas Generation of HTPE and Minimum Smoke Propellants per Gram of Binder



2. Stabilizer Depletion in HTPE Propellant

The service life stabilizers in both HTPE and minimum smoke propellants are MNA and 2-NDPA. It was determined previously[5] for other crosslinked double base (XLDB) propellants that, at high temperatures (≥140°F), the propellant service life will eventually end due to excessive gas generation and grain cracking after the MNA concentration goes below 0.10%. Therefore, a second method for predicting service life is to measure the MNA depletion rate at various temperatures, calculate the temperature sensitivity (Arrhenius activation energy) for the depletion rate, and then calculate the time for depletion of MNA from the starting concentration to the 0.10% concentration at any constant service life temperature or temperature cycle.

Blocks of aluminized and reduced smoke propellants were aged at various temperatures to measure MNA stabilizer depletion rates as well as the stability of mechanical properties and burn rate. Figure 3 is a plot of MNA concentration versus time at four temperatures for aluminized HTPE propellant. There was no measurable decrease in MNA content at 77°F during the three years of this particular study. Figure 4 is a plot of MNA concentration versus time for a reduced smoke HTPE propellant. Note that the reduced smoke propellant was formulated with a slightly lower initial MNA content than the aluminized HTPE propellant shown in Figure 3. The reduced smoke propellant has been aging for eleven years and has shown a small but measurable decrease in stabilizer concentration during that time at 77°F.

The stabilizer depletion rates at various temperatures are shown in Table 1. The MNA stabilizer concentration in aluminized propellant decreases more slowly than in the reduced smoke propellant. Since the binder chemistry in the two propellants is identical, this difference in MNA depletion rate suggests that the aluminum may have a stabilizing effect on the HTPE propellant. The blocks of aluminized propellant that were aged for twelve weeks at 155°F or three years at 120°F still had mechanical and ballistic properties which indicated they would be completely serviceable as described in Section 3 of this paper.

Figure 3. MNA Depletion in Aluminized HTPE Propellant

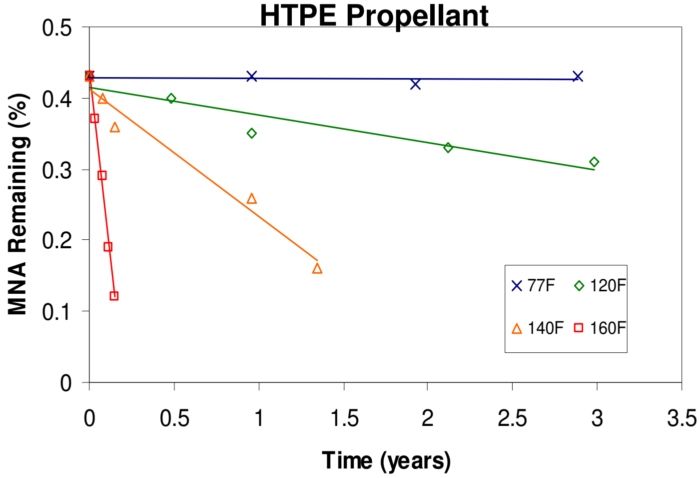


Figure 4. MNA Depletion in Reduced Smoke HTPE Propellant

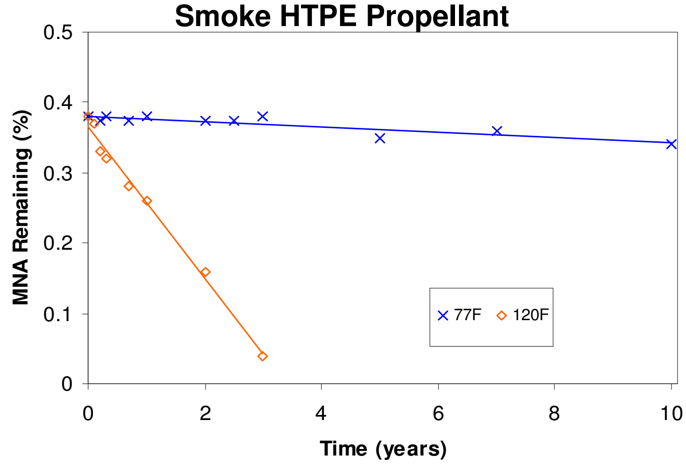


Table 1 - MNA Depletion Rates for HTPE Propellants		
Temperature, °F	**MNA Depletion Rate, %/day x 10^{-3}**	
Propellant Type	**Reduced Smoke**	**Aluminized**
77	0.0067	<0.01
120	0.29	0.16
140	--	0.62
155	3.39	2.38
160	--	2.9
165	--	5.5

Figures 5, 6 and 7 compare MNA stabilizer depletion in aluminized HTPE propellants to the depletion in minimum smoke propellant at 165, 155 and 120°F. As can be seen in the plots, the stabilizer depletes at a slower rate in HTPE propellant than in minimum smoke propellant probably as a result of the higher stability of the BuNENA plasticizer in HTPE propellant compared to NG/BTTN plasticizers in minimum smoke propellants.

Based on the MNA depletion rates at various temperatures, an Arrhenius activation energy of 26 to 29 kcal/mole was calculated for both HTPE propellants (see Figure 8). This value is the same as the activation energy for MNA depletion in minimum smoke propellants, which supports the conclusion that the minimum smoke propellant and the two HTPE propellants are aging by the same mechanism and their service lives can be compared. Note that the individual points used to calculate activation energy for both aluminized and reduced smoke HPTE propellants exhibit a linear relationship linking log MNA and T^{-1} between the temperatures of 76°F (for reduced smoke) or 120°F (for aluminized) and 165°F.

Figure 5. MNA Depletion for Aluminized HTPE and Minimum Smoke Propellants at 165°F

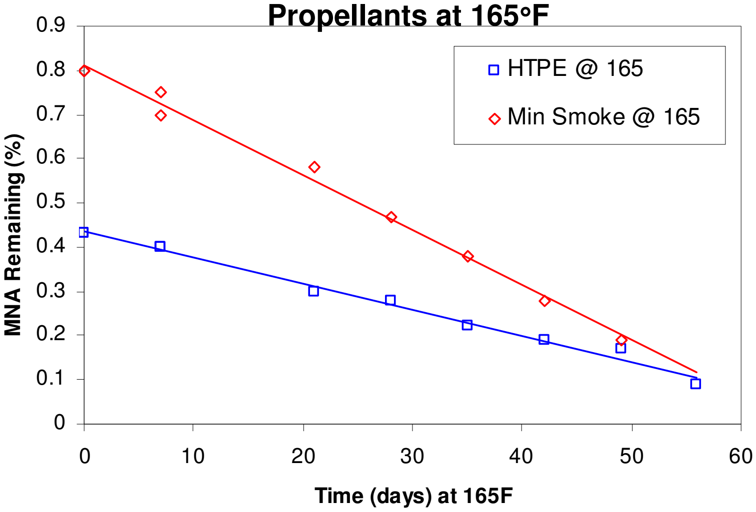
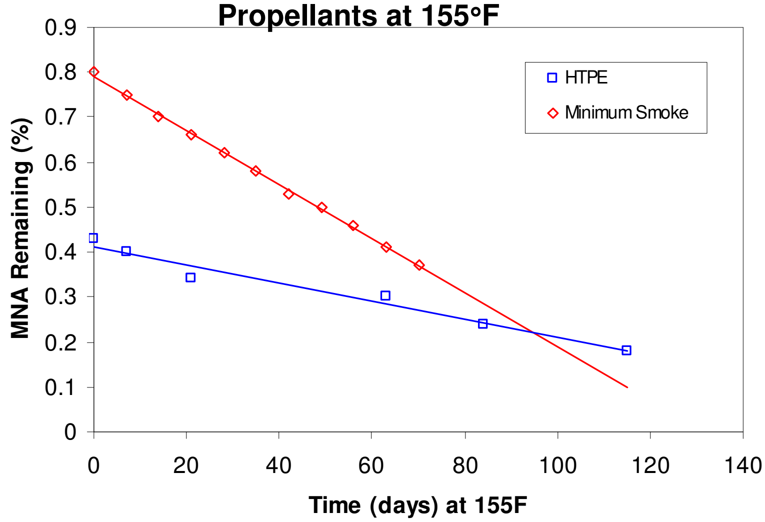
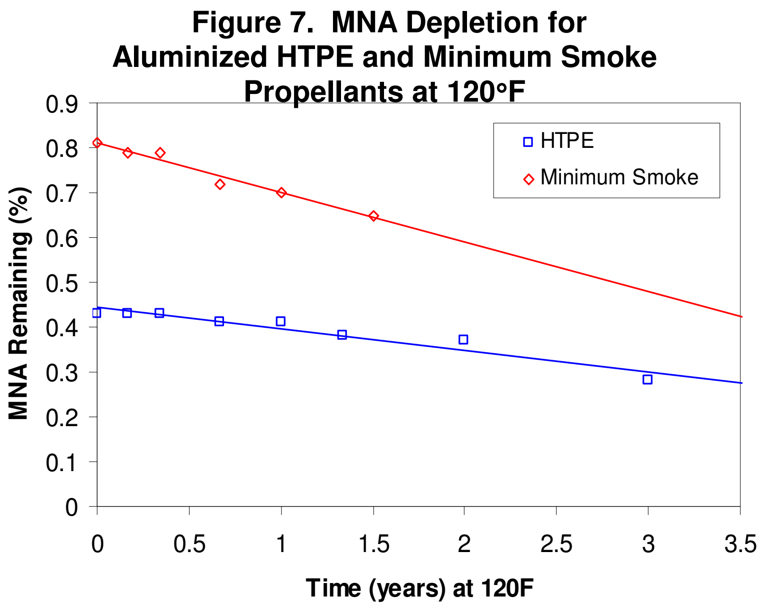
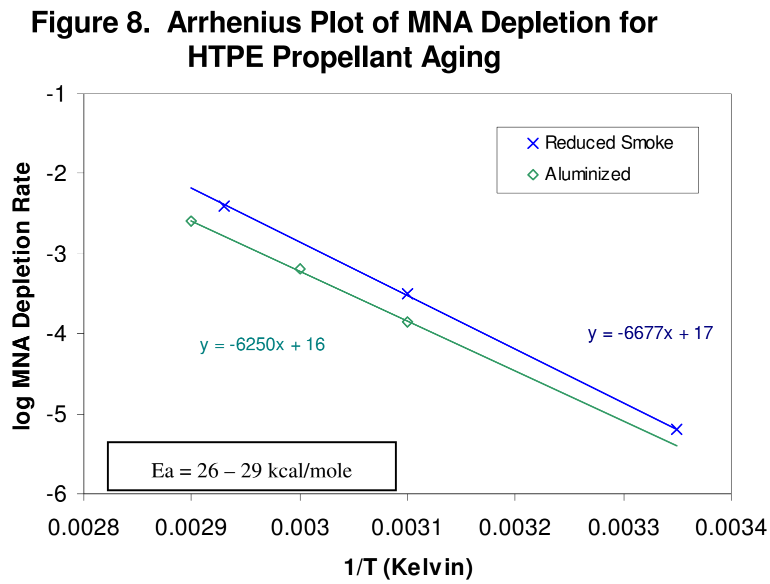


Figure 6. MNA Depletion for Aluminized HTPE and Minimum Smoke Propellants at 155°F







Using a 28 kcal/mole activation energy and the fact that the service life at 155°F was greater than twelve weeks it was calculated that the service life at 77°F (time to reach 0.10% MNA) will be 116 years for reduced smoke HTPE propellant and even longer for aluminized HTPE propellant.

Change in MNA content is insignificant in the first few years at 80°F. A change of 0.03% in ten years aging has been measured[6]. Therefore, use of very brief (less than several years) aging at ambient temperature should not be used to calculate an MNA depletion rate or to be used in the calculation of an activation energy as a result of the lack of precision in the measurement of MNA concentration.

Both the aluminized and reduced smoke HTPE propellants were formulated with approximately half the initial MNA content of the minimum smoke propellants because (1) during early development it was observed that the MNA depletion rates in the HTPE propellants were about half that measured in the minimum smoke propellants and (2) a service life comparable to that of minimum smoke propellants would be adequate for HTPE propellants. The time for the MNA to deplete to 0.10% (55 days at 165°F, 115 days at 155°F and six years at 120°F) for both minimum smoke and HTPE propellants is about the same and the activation energies are the same; therefore, based on stabilizer depletion rates it is predicted that the HTPE propellants will have about the same service life as the currently deployed minimum smoke propellant.

3. <u>Mechanical Property Stability of HTPE Propellants</u>

The principal manifestation of aging effects for any solid propellant is the deterioration of mechanical properties in the propellant. Mechanical properties for HTPE propellants were evaluated throughout the aging process to determine the rate of mechanical property changes and the activation energies for the rates of change. Based on this information motor service life can be projected under real-time aging conditions. Thirteen years of aging are now complete.

Reduced smoke HTPE propellants from two 50-gallon mixes were aged at 77, 120 and 155°F and were tested for mechanical properties at 113, 77, -13 and -40°F. Blocks of propellant which were initially 5.5 x 5.5 x 8-inches in size were double-wrapped in aluminum foil and then over-wrapped with polyethylene. These sealed blocks of propellant were therefore aged at their as-manufactured moisture content at all three temperatures.

Figures 9 and 10 are plots of tensile strength and modulus measured at 77°F for the HTPE propellant and minimum smoke propellant (TOW rocket motor) aged for three years at 120°F. As can be seen from the figures, there is a slow decrease in stress but no significant change in modulus with time for the HTPE propellant. The HTPE propellant tensile strength and modulus are more stable than for minimum smoke propellant, indicating that for a process in which service life is dependent upon tensile strength or modulus, the HTPE propellant will have a longer service life than the currently fielded minimum smoke propellant. Figure 11 compares the tensile strength stability for HTPE propellant and minimum smoke propellants aged at 165°F, and again, the HTPE propellant maintains a higher strength than the minimum smoke propellant.

The use of very brief (less than several years) of ambient temperature aging data for HTPE propellants does not give a true picture of how the modulus behaves over longer periods of time. Figure 12 shows the same 120°F aging data previously seen in Figure 10, but with two trend lines (one for all data, one for only the first 250 days) to emphasize the variability in modulus. Note that initial changes in HTPE modulus (within the first 250 days) cannot be extrapolated to later times.

Figure 9. Tensile Strength For HTPE and Minimum Smoke Propellants During Aging at 120°F

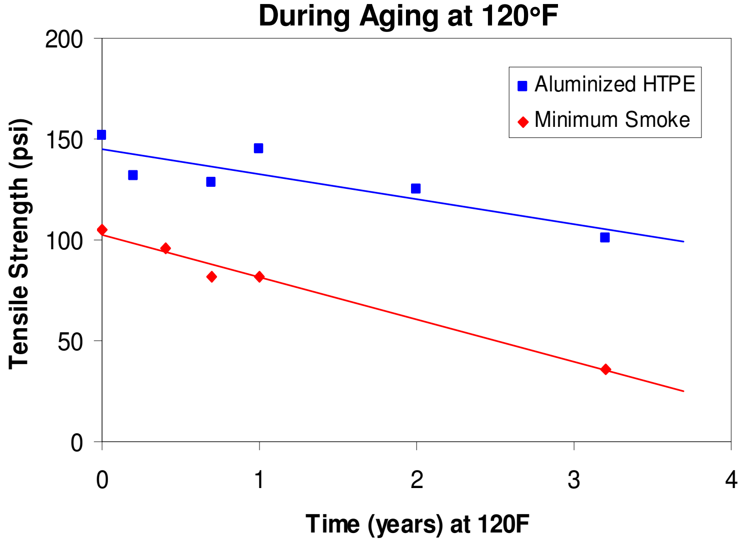


Figure 10. Modulus For HTPE and Minimum Smoke Propellants During Aging at 120°F

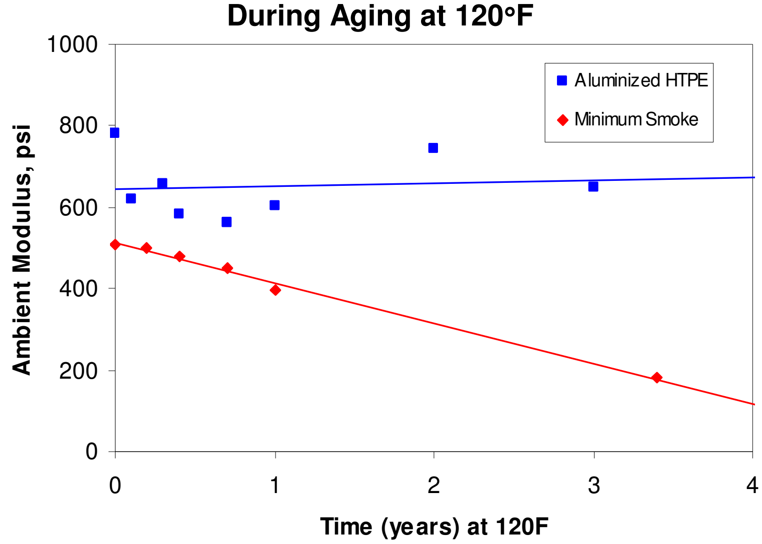


Figure 11. Tensile Strength for HTPE and Minimum Smoke Propellants During Aging at 165°F

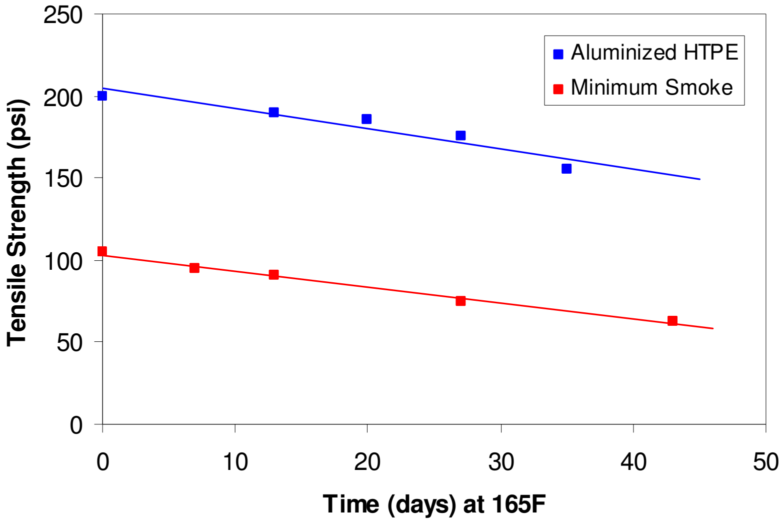
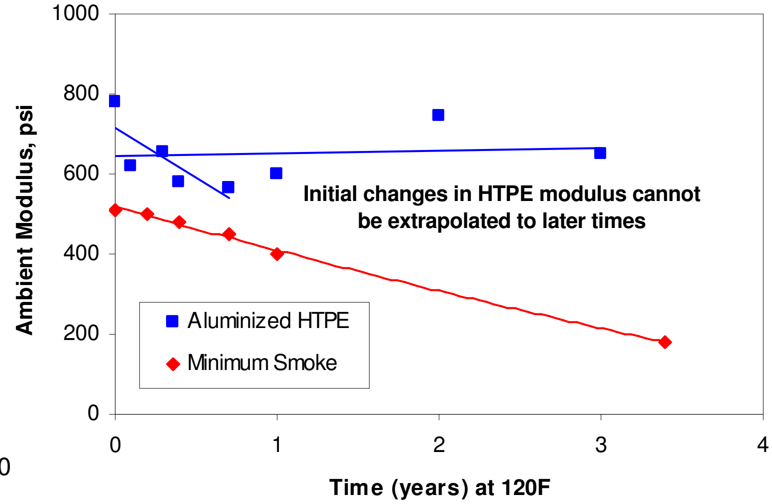


Figure 12. Modulus For HTPE and Minimum Smoke Propellants During Aging at 120°F



Mechanical properties have also been obtained for HTPE propellant aged for ten years at 77°F. Figure 13 shows that the modulus and tensile strength for the HTPE propellant did not change during the ten-year aging period. Initial and final mechanical properties, stabilizer content and burning rate are all shown in Table 2. Tensile strength decreases with time during HTPE propellant accelerated aging as shown in Figure 14. This change appears to be linear unlike the non-linear modulus aging behavior shown in Figure 12. Figure 15 shows strain for a reduced smoke HTPE propellant tested at 113°F. Propellant samples were aged at 77°F, 120°F, and 155°F. Figures 16 and 17 show tensile strength and strain for a reduced smoke HTPE propellant tested at conditions that simulate cold ignition conditions (-13°F, 0.02 in/min crosshead speed to 13.8% strain, then 100 in/min crosshead speed to failure @ 1000 psi). Figure 18 shows strain for a reduced smoke propellant that has been aged for ten years at 77°F and tested at both 77°F (2 inch per minute crosshead speed) and -40°F (0.02 inch per minute crosshead speed).

Upon aging, the ambient, low, and high temperature strains for HTPE propellants are either constant or increase slowly as can be seen in Figures 15, 17, and 18. These data support the claim that the service life for low temperature operation and storage, which is dependent upon having adequate strain capability, does not decrease with aging time. The margin of safety actually increases with aging time[6]. This is also true for minimum smoke propellants.

Figure 13. Tensile Strength and Modulus for Reduced Smoke HTPE During Ten Years Ambient Storage

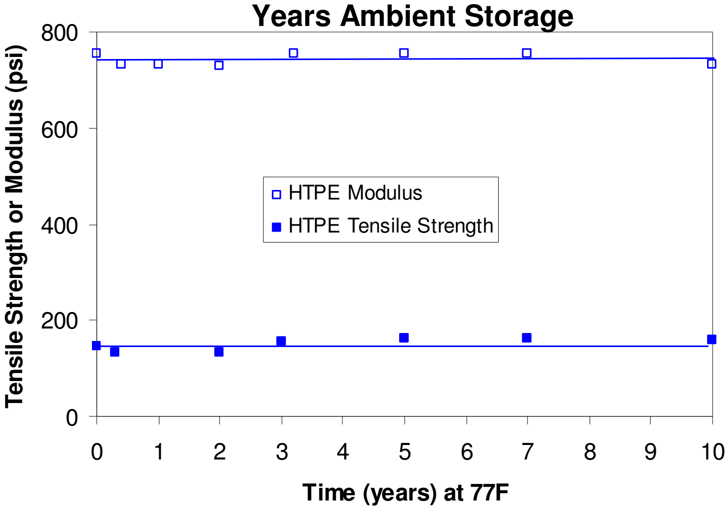


Figure 14. Tensile Strength for Reduced Smoke HTPE During Aging at Three Temperatures

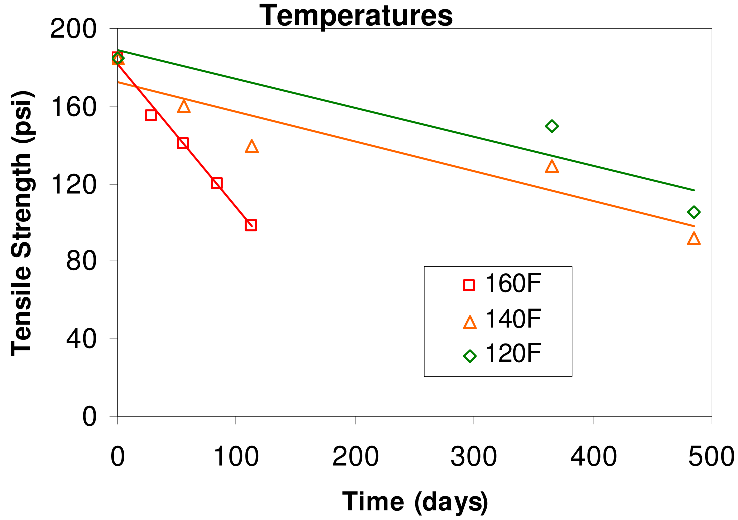


Table 2. Ten Year Aging Data for Reduced Smoke HTPE propellant

Property Average	Initial	10 years
Ambient Stress, psi	152	158
Strain at Max Stress, %	36	42
Modulus, psi	757	737
-40, 0.02 ipm Strain, %	35	36
MNA, %	0.365	0.33
2-NDPA, %	0.24	0.24
Burn Rate at 1000, in/sec	0.xx	+0.01

Figure 15. Strain For A Reduced Smoke HTPE Propellant Tested At 113°F

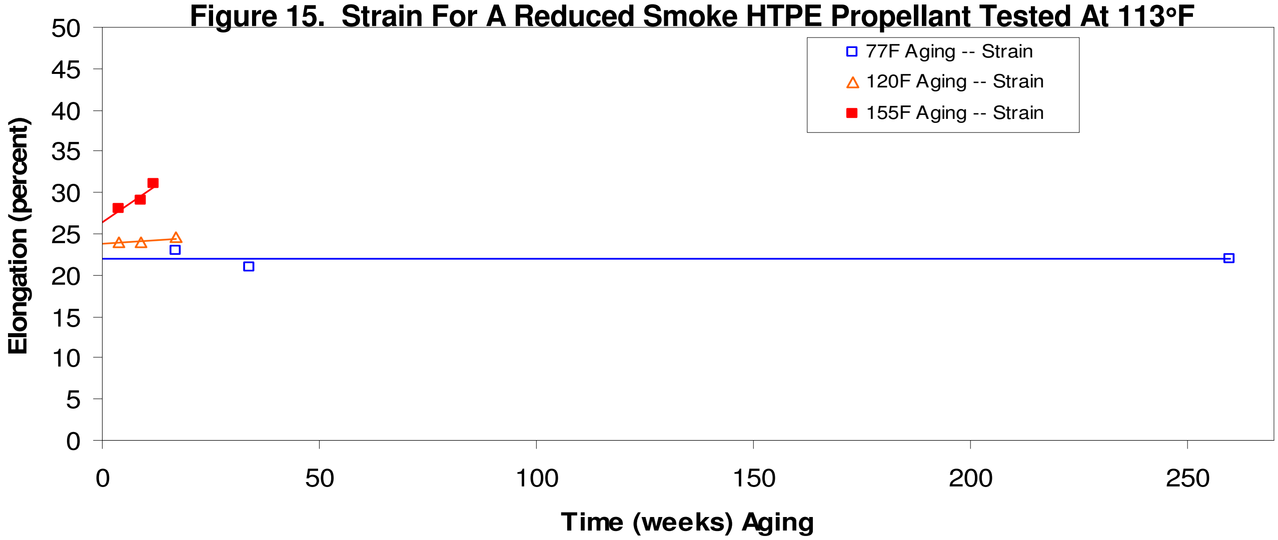


Figure 16. Tensile Strength For A Reduced Smoke HTPE Propellant Tested At –13°F Ignition Simulation (0.0074 in/in/min to 13.8% strain, then 39 in/in/min @ 1000 psi)

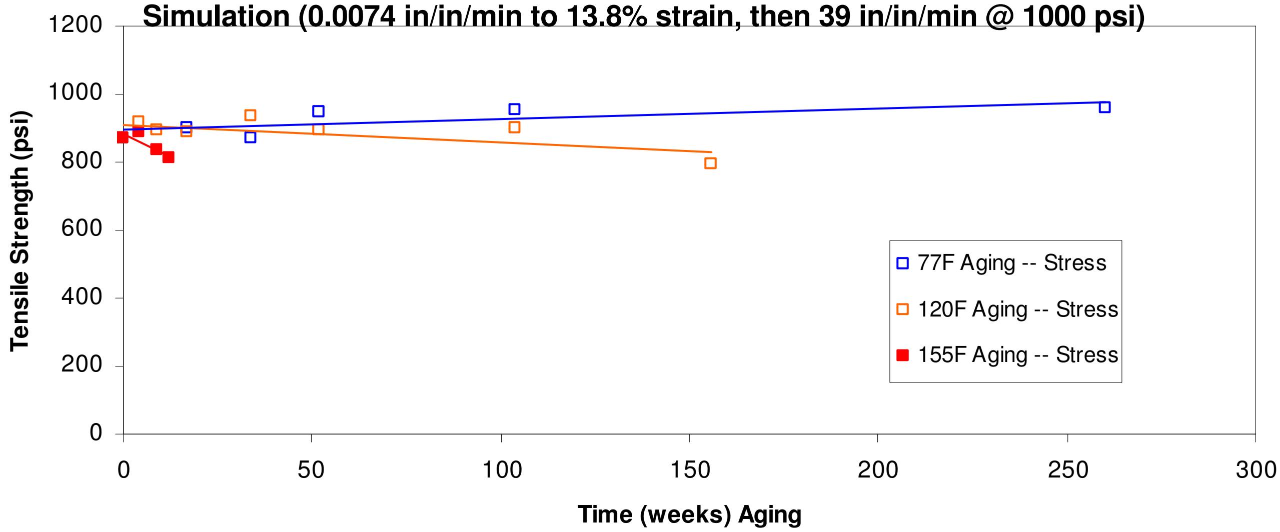


Figure 17. Strain For A Reduced Smoke HTPE Propellant Tested At –13°F Ignition Simulation (0.0074 in/in/min to 13.8% strain, then 39 in/in/min @ 1000 psi)

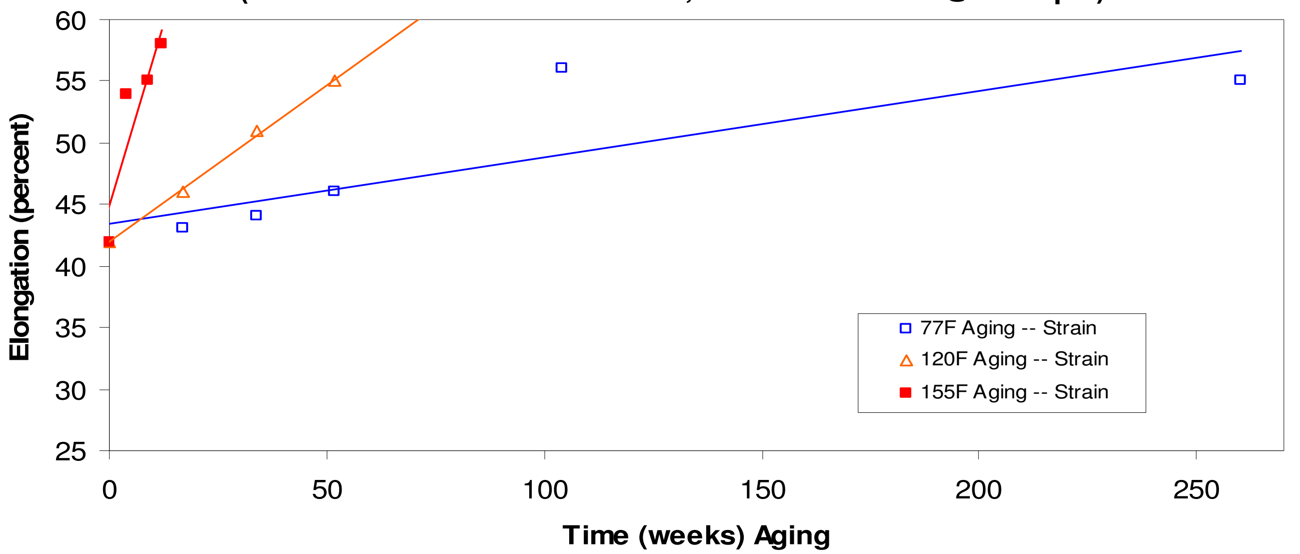


Figure 19 illustrates the stability of casebond tensile strength between HTPE propellant and EPDM motor case insulation. Data are shown for three years aging at 120°F. There is a parallel decrease in casebond tensile strength and bulk propellant strength on storage for three years at 120°F. It is normal at ABL for the casebond specimens to give a lower strength than that measured in bulk propellant. Casebond specimens fail in propellant rather than at the interface between insulation and propellant. Therefore, the strength decrease shown in Figure 19 simply reflects the change in bulk propellant properties.

Figure 18. Reduced Smoke HTPE Strain During Ten Years Ambient Storage

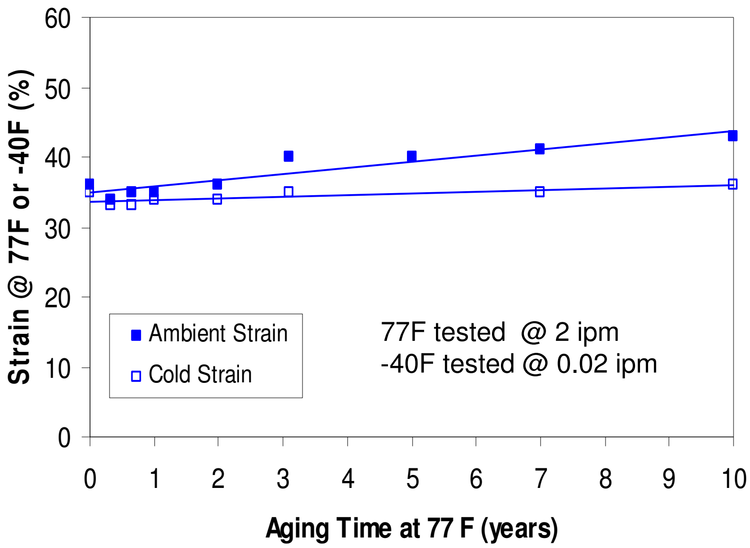


Figure 19. Comparison of HTPE Tensile Strength in Bulk Propellant and in Bond-in-Tension Casebond Samples Aged at 120°F

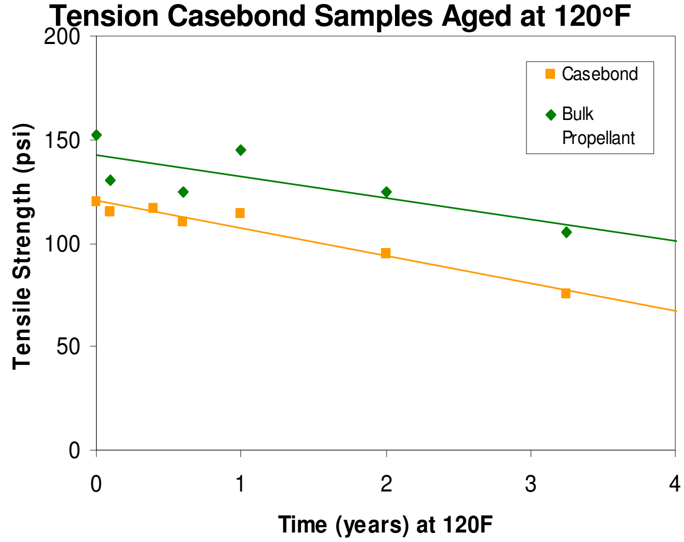
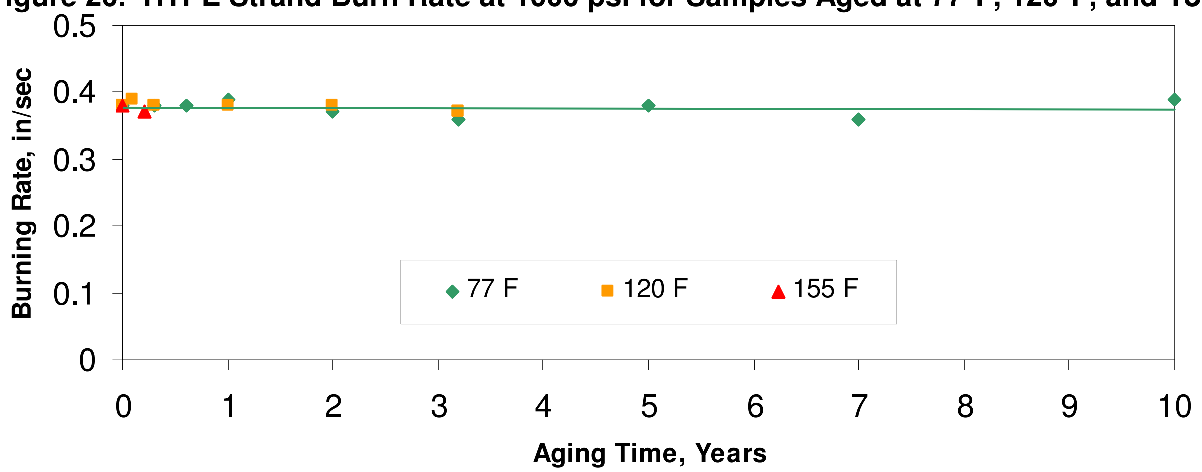


Figure 20 illustrates the stability of burning rate for HTPE propellant. There was no change in strand burning rate at 1000 psi for the ten-year or shorter aging periods. This demonstrates that the particle size of the ammonium perchlorate does not change with aging time in a manner that would tend to change burning rate.

Figure 20. HTPE Strand Burn Rate at 1000 psi for Samples Aged at 77°F, 120°F, and 155°F



4. Other Comments on HTPE Propellants

BuNENA, as is the case with other nitrate esters, may exhibit chemical incompatibility with other chemicals. When formulating an HTPE propellant system, care must be exercised in selection of ingredients to ensure that incompatible chemicals are not inadvertently introduced as stabilizers or contaminants in the raw materials. For example, many types of commercially available ammonium nitrate use anticaking agents or phase stabilizers that accelerate the decomposition of BuNENA.

Because the introduction of an incompatible chemical can affect service life of propellants, ATK routinely tests compatibility among the ingredients used in HTPE propellants. The Modified Taliani test is used to measure compatibility among ingredient combinations that include BuNENA. Differential Scanning Calorimetery (DSC) is used to measure compatibility among ingredient combinations that include AP.

In summary, it is concluded that HTPE propellants are very stable and will easily support a ten-year service life in tactical motors.

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