

CHANGES IN THE MECHANICAL PROPERTIES OF ENERGETIC MATERIALS WITH AGING

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The mechanical properties of energetic materials were studied as a function of actual age and accelerated aging produced by heat treatment at elevated temperatures for several months. All measurements were made in uniaxial compression at one or more of three temperatures, i.e. -45, 25 and 65 C at strain rates between 1 and 10/sec. For TNT that was in the stockpile for up to 40 years no change in the compressive properties were found. Single base nitrocellulose propellants that were subjected to 65 C for 18 months also gave no change in the compressive strength. In addition, the compressive strength of a plastic bonded explosive, PAX2A, were not changed after six months at 60 C and 12 months at 50 C. In contrast, after six months at 70 C the compressive strength and modulus of octol were reduced by up to about 40%. The compressive strengths of double and triple base nitrocellulose propellants were also decreased by 50 to 70% by the same heat treatment given to the single base propellants. These changes for octol and the propellants are a function of measurement temperature. Other changes in most of these material were observed and are also discussed. Probable reasons for the changes in mechanical properties are presented.

INTRODUCTION

Changes in performance and safety characteristics of explosive and propellant formulations with aging are a continuous concern. For example, the degradation of nitrocellulose with time is well known and there are very active surveillance programs to monitor the properties of nitrocellulose base propellants with aging. In addition, there have been programs to determine if the properties of explosive fills have

changed with time in the field.¹ Changes with aging of plastic bonded explosives (PBX's) and TNT based explosives properties are also of considerable interest. The effect of thermal conditioning at elevated temperatures to simulate aging on the properties of PBX 9501 have been and continue to be the object of studies and changes with this type of treatment have been found.^{2,3} Similar studies have been made for LX-14.^{4,5,6} The stability of the properties of one of the newest PBX's,

PAX 2A, developed recently by the Army is also of interest⁷ The composition of PAX 2A is similar to that of PBX 9501 since it has the same explosive and plastizer but a different polymer.^{2,7} The stability of TNT and the TNT based explosive octol are also of interest. Therefore, the aging of both PAX2A and octol were studied experimentally. Because TNT has been in the stockpile for many years it was possible to obtain data as a function of actual age. The work reported here on mechanical property aging is part of more general studies to determine if several properties of PAX 2A, TNT and octol change with aging.^{1,8} However, rather than wait many years before initiating the study of aging, the work with PAX2A and octol was done by accelerating the aging processes by conditioning samples at elevated temperatures but shorter periods.

Some gun propellants have compositions similar to those of plastic bonded explosives.⁹ Therefore, it is appropriate to present results on the effect of the same type of accelerated aging on the mechanical properties of some of these materials.^{9,10}

EXPERIMENTAL

Stress-strain data in uniaxial compression were obtained using an MTS servo-hydraulic system operated at a constant strain rate of 1.0/sec for PAX 2A, octol and TNT, while the strain rate for the propellant samples was approximately 10/sec. All samples were in the form of cylinders. The samples of PAX 2A and octol were 1.90 cm in length and diameter and the samples of TNT were 1.27 cm in length and diameter. The propellant samples had length to diameter ratios between one

and two. The end faces of all samples and the loading platens were lubricated to minimize frictional effects between the samples and the platens. Samples were conditioned at temperatures between -45, 25 and 65 C for at least two hours before mechanical measurements and were then compressed along the cylinder axis to obtain engineering stress and engineering strain. In most cases three samples of PAX2A and TNT were measured at each condition, four or in most cases five samples of octol were measured at each condition and between three and nine propellant samples were measure for each condition.

Samples of PAX2A were prepared by pressing at 71 C to the approximate size and then machining to final dimensions. Samples of octol were prepared by casting into molds six inches in length and one inch in diameter, and then cutting and machining to the final dimensions. Samples of TNT were obtained by sectioning shells which were brought in from the stockpile, cutting and then machining to the final dimensions. Precautions were taken to insure that the cylinder end faces of all these samples were flat and parallel. In contrast, the propellant samples were cut from propellant grains containing perforations. The densities of all PAX2A and octol samples were measured and were in a narrow range close to the maximum theoretical (zero porosity) density. A range of densities was obtained for the TNT samples. The densities of the propellant samples were not determined. The densities of PAX2A and octol before and after thermal conditioning but before deformation were determined by weighing in air and measuring the dimensions. The densities after

deformation of PAX2A were determined by weighing in air and in water. The water density was corrected to the measurement temperature.

The results for samples subjected to accelerated aging by conditioning at elevated temperatures, the aged samples, are compared to control samples from the same lot and measured under the same conditions. The aged samples of PAX2A were held in air at 60 C for 6 months or at 50 C for 12 months while the aged samples of octol were held in air at 70 C and relative humidity of 30% for six months. Control samples were held at ambient temperature in air for 6 or more months. Because the results for the two groups of aged samples of PAX2A are very similar, only the samples held at 60 C for six months are discussed here. There were also two groups of aged and control samples of octol produced by difference manufacturers. These two groups of samples also gave similar results and so

only one group is discussed here. The propellant samples were held at 65 C for varying time periods between one and eighteen months.

As noted above three aged samples of PAX2A, four or five aged samples of octol, and the same number of control samples were compressed at each of three temperatures, -45, 25 and 65 C. In addition, a few samples of the aged and control groups of each explosive formulation were measured at intermediate temperatures. While most measurements were at a strain rate of 1.0/sec., a few aged and control samples were compressed at a strain rate of 0.001/sec. All of the TNT samples were compressed at 25 C and the propellant samples were compressed at -45 and 23 C.

The main components of the energetic materials considered here are given in Table 1.

TABLE 1. PRINCIPAL COMPONENTS OF ENERGETIC MATERIALS STUDIED

PAX2A	HMX - 85%; BDNPA/F - 9%; CAB - 6%
Octol	HMX - 75%; TNT - 25%
NACO	NC - 93.61%; Ethyl Centralite - 1.15
M26	NC - 66.1%; NG - 25.8%; Ethyl Centralite - 6.35%
M30	NC - 27.61%; NG - 22.67%; NQ - 47.96%; Ethyl Centralite - 1.49%

HMX - Cyclotetramethylene Tetranitramine; BDNPA/F - Bis(2,2-Dinitropropyl)Acetal/Formal; CAB - Cellulose Acetate Butyrate; TNT - Trinitrotoluene; - NC Nitrocellulose; NG - Nitroglycerine; NQ - Nitroguanidine.

RESULTS

The stress-strain curves in uniaxial compression for all of the energetic materials considered here are as follows:

With increasing strain from zero, the stress initially increases linearly with strain and Young's modulus is obtained from the slope of this linear portion of the curve. With further increases in the strain the stress curves over and passes through a maximum. The maximum stress, the compressive strength, is taken as a measure of the failure stress and the strain at the maximum is taken as a measure of the failure strain. For further increases in strain the stress decreases continuously. In most cases the stress decreases gradually in this region of the stress-strain curve due to work or strain

softening. However, in some cases the stress decreases abruptly due to cracking and fracture. This abrupt decrease of the stress occurs primarily at lower temperatures and or higher strain rates.

Changes in the initial part of the stress-strain curve with aging, i.e changes in the compressive strength, Young's modulus and the failure strain are the primarily focus of this paper. In addition, changes in the work softening region are discussed for PAX2A and octol. Changes in the brittleness are also discussed.

PAX 2A and Octol

TABLE 2. PERCENTAGE CHANGES OF PAX2A AND OCTOL MECHANICAL PROPERTIES AFTER ACCELERATED AGING

Measurement	-45 C	25 C	65 C
Temperature			
<u>PAX2A</u>			
Compressive Strength	Unchanged*	Unchanged	Unchanged
Young's Modulus	-10%*	15	14.
Strain at maximum Stress	16%*	-5%	-17%
<u>Octol</u>			
Compressive Strength	-38%	-36%	-8%
Young's Modulus	-44%	-18%	-26%
Strain at Maximum Stress	13%	Unchanged	16%
Damage Modulus	-38%	-63%	-70%

* Below the ductile to brittle transition temperature, which is about -30 C for PAX2A for a strain rate of 1.0/sec., the mechanical properties of interest here are extremely variable from sample to sample. Therefore, the values given at -45 C are very tentative because of this variability and because the number of samples available for measurements at each temperature was limited.

TABLE 3. OTHER CHANGES IN PAX2A AND OCTOL AFTER ACCELERATED AGING

PAX2A

Very small decreases in average dimensions and weights $< 0.5\%$

No change in average density within 0.5%

Change of color from white to pale yellow

Decreased stress at 65 C in the work softening strain range

Increased cracking after deformation at 65 C in the work softening strain range

Greater decrease in density due to deformation at 65 C into the work softening strain range

Lower work/volume required for deformation at 65 C into the work softening strain range

No change in the ductile to brittle transition temperature

Octol

Small decrease in average weight, less than 0.6%

Small increase in average volume $\sim 1\%$

Small decrease in average density $\sim 1.5\%$

Change of color from tan to brown

In Table 2 the average percentage changes in the compressive strength, Young's modulus and the failure strain are given as a function of the temperature of compression for PAX2A and octol for the accelerated aging conditions given above. The results of this table indicate significant difference

in the effect of aging on the given properties of PAX2A and octol. There is no change in the compressive strength of PAX2A at all three temperatures within experimental uncertainty, but a decrease in the compressive strength of octol at all temperatures. The results of Table 2 also indicate an increase in

Young's modulus for PAX2A at the two higher temperatures, but a decrease in the modulus at all three temperatures for octol.

In addition to the results given in Table 2 after accelerated aging, several other properties of PAX2A and octol were monitored with and without aging and the results are summarized in Table 3. Of particular interest are changes in the work softening region. For PAX2A at 65 C measuring temperature there is a significant decrease in the stress in the work-softening region. In addition, at this temperature there is an increase in cracking, a larger density decrease due to deformation and a decrease in the work/volume to deform to a strain in the work-softening region. For octol at all temperatures of measurement straight lines can be fitted to the stress-strain curves in most of the work softening-region. Since the decrease of stress with increasing strain is due to strain induced damage, the slope of this line is taken as a damage modulus, D , and the percentage changes with aging are given in Table 2. Very significant decreases in D are observed. The stress-strain curves for PAX2A have continuous curvature in the work softening region so that a damage modulus as in the case of octol cannot be clearly defined. However, these results for both PAX2A and octol suggest greater strain induced damage in the aged material.

The densities are also of interest. For PAX2A there are small decreases in weight and dimension of less than or of the order of 0.5%. These changes are such that there is no change in average density within an experimental error of about 0.3%. In contrast, for octol small decreases in weight and small increases in dimensions were found, thus giving decreases in densities of the order of 1%

to 1.5%. There are also changes in color of both explosives that indicate that chemical changes have taken place with accelerated aging. These color changes were observed on both external surfaces and on fracture surfaces, thus indicating changes throughout the volume. However, the density of chemical species which are required to produce these color changes are most probably much smaller than the other percentage changes observed here.

Propellants

In Table 4, the compressive strengths of a single base, a double base and a triple base nitrocellulose propellants are given at a measuring temperatures of -45 C and 23 C as a function of accelerated aging time at 65 C.⁹ Within the spread of the data at -45 C there is no change in the compressive strength of the single base propellant, but very significant decreases in the compressive strengths of the double and triple base propellants. One other single base and two other triple base propellants gave similar results to those of Table 4 at -45 C.⁹ Although the compressive strengths of the single base propellants did not change with aging, the nature of the failure did exhibit change. With increasing strain before the accelerated aging the stress decreased gradually after the maximum stress and then abruptly fractured only at large strains. Failure was in the form of cracking but not fracture. In contrast, after 18 months of accelerated aging the stress decreased abruptly at or near the maximum stress and the samples fractured. The stress as a function of strain for the double and triple base propellants at -45 C decreased in a moderately abrupt fashion after the maximum stress before aging, but decreased more abruptly after 18 months aging. Thus all three types of

propellants became more brittle after 18 months of accelerated aging. The rather large experimental spread of some of the data of Table 4 at -45 C was found for propellants and also plastic bonded explosives when the failure is brittle (See comment at bottom of Table 3).

The compressive strengths measured at 23 C as a function of aging time are

also given in Table 4. The results suggest a small decrease in the compressive strength of the triple base propellant, no change in the double base propellant, and either no change or possibly a small increase in the strength of the single base propellant. One other single base propellant gave similar results at 23 C.

TABLE 4. THE COMPRESSIVE STRENGTH OF PROPELLANTS IN MPa AFTER ACCELERATED AGING FOR SEVERAL PERIODS

Measured At -45 C			
Aging Period Months	Single Base NACO	Double Base M26	Triple Base M30
0	217 +/-17	239 +/-41	234 +/-32
6	232 +/-18	154 +/-44	172 +/-47
12	201 +/-12	76 +/-21	177 +/-23
18	230 +/-32	70 +/-18	109 +/-44
Measured At 23 C			
0	117 +/-1	61 +/-10	82 +/-5
18	134 +/-14	70 +/-4	59 +/-6

Between 5 and 9 samples were measured at each aging period for each propellant at -45 C and 3 samples were measured at each aging period for each propellant at 23 C. The +/- is the standard deviation of the measurements in each case.

TNT

Measurements of the compressive mechanical properties of samples of TNT taken from shells that had been in the stockpile for 20, 30 and 40 years indicates no statistically significant change of the compressive strength with age. The same is true for Young's

modulus and the failure strain. In addition, the mode of failure did not appear to change with age. Over 100 samples were measured and these were taken from a number of shells of three different diameters. The average compressive strength of all samples measured is 13.6 +/- 2.3 Mpa. This number can be compared with the

average compressive strength of 12.8 +/- 1.2 Mpa for a group of TNT samples prepared for laboratory studies. This latter group of samples was measured within one year of preparation.

DISCUSSION

A discussion of each energetic material or group of materials is followed by a brief discussion of the relative stability of the various materials against changes with age.

PAX2A

The compressive strength of PAX2A was found to be stable for the temperatures and time periods of accelerated aging and the conditions of measurement used in this study (see Table 2). However, Young's modulus was found to increase somewhat (~15 %) and the failure strain was found to decrease somewhat for the two higher temperatures of Table 2. For no change in the compressive strength but an increase in Young's modulus, there must be a decrease in the failure strain as observed if there are no other significant changes in the shape of the stress-strain curve in this region. Because there is an increase in the modulus but no change in the compressive strength, the proportionality between the compressive strength and the modulus found previously is not valid for these experimental conditions.¹² The increase in the modulus may be due to a segregation of plasticizer with aging. A more complete discussion of the properties of PAX2A with this accelerated aging is given elsewhere.^{12,13}

The most significant changes in the mechanical properties of PAX2A due to this aging occur in the work softening

region of the strain-strain curve at higher temperatures, e.g. 65 C. There is a marked decrease of the stress at strains in this region and so a smaller work/volume to deform the material in this region. Thus, for a constant energy of deformation, e.g., by impact, the final strain and so the degree of cracking (see below) will be greater in the aged material than non-aged material at 65 C. There also is a greater density decrease due to deformation of the aged material than the non-aged material for equal amounts of strain into this region of the stress-strain curve. This density decrease is accompanied by increased cracking in the aged samples. This increased cracking and so larger density decrease can be attributed to thermally activated crack growth in the aged material which does not occur in the non-aged material.^{12,13} The crack growth in the non-aged or reference samples was found to be approximately independent of temperature while the additional crack growth in the aged samples increases with temperature such that the additional crack growth is not observed at 25 C but is observed at 65 C. There are other differences in the properties of this additional crack growth at higher temperatures and this whole matter is discussed in greater detail elsewhere.¹² The increased cracking in the aged samples could be associated with clusters of defects, e.g., clusters of plasticizer molecules, formed during the aging process.

Because the kinetics and associated parameters are not established, the stability under other conditions of aging can not be determined at this time. However, because there are two aging periods at two temperatures, it is possible to obtain an activation energy by assuming first order kinetics. In this manner a activation energy of about 0.6

ev is obtained. This value is close to the value obtained using first order kinetics for PBX 9501.³ Since both materials have HMX and BDNPA/F, the similarity of activation energies suggest that it is associated with one or both of these components. This activation energy may then be associated with the diffusion of NO₂ molecules as proposed for PBX 9501.³

Octol

In contrast to the results for PAX2A, for octol both the compressive strength and Young's modulus are decreased and the failure strain is either increased or not changed for all three measurement temperatures after accelerated aging (Table 2). However, the octol samples were aged at 70 C and so 10 C higher than the highest temperature for PAX2A sample aging. This difference is discussed further below.

A decrease in both the compressive strength and the modulus is expected if the porosity is increased by the aging process.¹⁵ However, if some or all of the porosity is in the form of micro-cracks, calculations indicate that the compressive strength could increase or decrease but the modulus is still decreased.¹⁵ For specific porosity not in the form of micro-cracks calculations indicate that the relationships between the strength, the elastic modulus and porosity are approximately of the form

$$E = E_1 \exp(-\alpha\Delta P) \quad (1)$$

and

$$\sigma = \sigma_1 \exp(-\beta\Delta P) \quad (2)$$

E_1 and σ_1 are Young's modulus and the compressive strength at a porosity P

before aging, E and σ are the values for an increase in porosity ΔP , and α and β are constants. ΔP is taken as the fractional decrease in density. α is not equal to β because the averaging processes are different for the strength and the modulus. Assuming that all of the decreases of E and σ after aging are due to porosity, values of α in the range of 13 to 37 and values of β in the range of about 8 to 30 are obtained for a porosity change of 1.5%. While these values of α and β are large compared to the predictions of calculations, values of this magnitude have been reported for Composition B (39.5% TNT, 59.5 RDX% and 1% Wax) and other materials.¹⁵ Therefore, the changes of E, the modulus, and σ , the compressive strength, at all three measuring temperatures after aging can be attributed to porosity introduced during the aging process. However, the low percentage decrease of the compressive strength at 65 C and so the small value of β suggests that probably the failure process has changed somewhat at this temperature. The ratio of the percentage change of the modulus to the percentage change of the compressive strength is much higher at 65 C than at the other two temperatures. Perhaps the role of porosity in the form of micro-cracks is different at the higher temperature.

TNT and HMX are not expected to have any significant thermal decomposition at 70 C for 6 months. In addition, the measurements given here show that the compressive mechanical properties of TNT are not changed with age up to forty years. This result also suggests that TNT does not significantly decompose during actual storage conditions. However, chemical analysis indicates an increase in the percentage of

HMX in octol after treatment at 70 C for two and four months.¹⁶ Although the percentages of TNT and impurities were not measured, this increase in the percentage of HMX indicates that either the percentage of TNT and or the percentage of impurities has decreased. Therefore, the observed small weight loss could be due to the loss of TNT and or impurities. The effect of these losses on the observed volume expansion and density decrease are not known. Impurities could decompose and cause internal strain. Impurities could also diffuse to the surface and either stay on the surface or escape. Thus the small volume expansion and small density decrease could be associated with impurities. Sublimation of TNT might also take place since the aging temperature of 70 C is close to the melting temperature of TNT at 81 C.

In summary, the decreases of the compressive strength and Young's modulus can be attributed to porosity increases during the accelerated aging. The observed volume expansion and density decrease support this interpretation. A decrease in the percentage of TNT and or impurities and the observed weight decrease indicate that TNT and or impurities were lost during the aging. The porosity increase may be associated with this loss.

Propellants

Before aging the compressive strengths of the single, double and triple base propellants of Table 4 and other single and triple base propellants at -45 C are the same within experimental uncertainty.⁹ It is therefore concluded that the compressive strengths of these propellants at this temperature are determined primarily by the properties of nitrocellulose. In contrast, before

aging at 23 C the double and triple base propellants of Table 4 and other triple base propellants have lower compressive strengths than the single base propellant of Table 4 and other single base propellants.⁹ From these observations it is concluded that the properties of nitrocellulose primarily determine the strength of the single base propellants, but the lower values of strength for the double and triple base propellants at 23 C are due to the plasticizing effect of nitroglycerine. It is also concluded that the addition of a relatively large percentage of solids in the form of nitroguanidine has little or no effect on the compressive strengths at 23 and -45 C.

It is also important to know if these propellants are primarily in a glass or a rubber state at -45 and 23 C as a function of aging time. While measurements have not been made to clearly determine this as a function of aging, some measurements have been made on relatively freshly prepared propellant. A ductile to brittle transition was found to take place in the non-aged triple base propellant (M-30) between 0 and -15 C for a strain rate of 10/sec., the same strain rate as used here.¹⁷ Therefore, it appears that this propellant is in a glass state and a brittle state at -45 C but in rubber state at 23 C before aging. While a glass transition temperature of -57 C was observed for this propellant, this was measured at a much lower strain rate.¹⁷ The glass transition temperature increases with rate. Because of the type of failure and the composition, the double base propellant is most likely also in the glass state at -45 C and in the rubber state at 23 C. For the single base propellant before aging the situation is not clear. At -45 C the failure mode is partly ductile and partly brittle. Therefore, at

this temperature it may be in a transition between the ductile and brittle states and also between the rubber and glass states. At 23 C it should be in the rubber state.

The decomposition of nitrocellulose is auto-catalytic and all nitrocellulose containing propellants have a stabilizer, in these cases, ethyl centralite, to hinder this auto-catalytic action.⁹ The concentration of the stabilizer was found to be significantly decreased with this aging, thus indicating nitrocellulose decomposition. In addition, nitroglycerine decomposes and the products of this decomposition are known to also cause nitrocellulose decomposition.⁹ It is, therefore, concluded that although there was decomposition of nitrocellulose for the aging conditions used in this study this decomposition was not sufficient to affect the compressive strength of the single base propellants (see Table 4). However, with the presence of nitroglycerine in double and triple base propellants and the added nitrocellulose decomposition caused by the decomposition products of nitroglycerine, the compressive strengths at -45 C are significantly decreased (see Table 4). The effect of accelerated aging on the mechanical properties of propellants is discussed in terms of nitrocellulose and nitroglycerine decomposition by Pinto et al.⁹

The decrease of the compressive strengths of the double and triple base propellants at -45 C may be due to the formation of porosity during the aging treatment as discussed above for octol. This porosity may be 'frozen in' during the transition to the glass state and may cause the generation of micro-cracks. Alternately, pockets of molecules or regions of more general damage produced during the decomposition may

be frozen in and cause the generation of micro-cracks. Micro-cracks can decrease the compressive strength and increase the brittleness as observed. In addition, these pockets or regions may not be load supporting and so decrease the applied stress for failure in the same manner as porosity. However, at 23 C these same propellants are in a rubber state. In this state the micro cracks may not exist or are blunted or otherwise changed so that they have little or no effect on the compressive strength. The same argument may be applied to regions of more general damage. Most probably the mechanism of failure at 23 C is significantly different from the mechanism at -45 C. Thus, the compressive strength is either unchanged or only mildly decreased at 23 C although it is strongly decreased at -45C.

By the same analysis it can be deduced that the single base propellants are primarily in a rubber state at -45 C before aging. Thus the state of the disorder produced by decomposition, the amount of decomposition and the failure mechanisms must be such that the compressive strengths at -45 are not reduced. The amount of nitrocellulose decomposition is less in the single base propellants because of the absence of nitroglycerine. The same argument applies to single base propellants at 23 C and thus there is no observed reduction of the compressive strength at this temperature either within the uncertainty of the data. Because the single base propellants become brittle at -45 C after long term aging, there must be sufficient decomposition to change their state from primarily rubber to primarily glass and so brittle without a change in the compressive strength.

The rationale given for the changes in the mechanical properties of single, double and triple base propellants are very speculative and more measurements are highly desirable. Studies of the glass transition temperature, the nitrocellulose molecular weight, Young's modulus, sample weight and dimensions as a function of aging are some of the phenomena that would be very helpful in understanding the observations. Decreases in the molecular weight of the polymer component of a plastic bonded explosive after accelerated aging have been linked to decreases of the compressive strength as measured at 24 C.² There is little or no change of the compressive strengths at 23 C for the propellants studied here. Thus, it appears that decreases in the molecular weight and/or changes in cross-linking of nitrocellulose with aging do not play significant roles in determining the compressive strength at this temperature.

TNT

It was demonstrated that the storage of TNT in shell in stockpiles for up to 40 years does not result in changes in the mechanical properties that were measured. Since the storage temperature and other conditions are not known, these results cannot, however, be easily applied to other storage conditions without knowledge of the decomposition kinetics of TNT and its impurities.

Comparisons of the energetic materials studied.

The temperatures of aging are different for each energetic material or group of materials, i.e. the temperature is unknown but probably in the vicinity of ambient for TNT, the temperatures are 50 and 60 C for PAX2A, 65 C for the propellants, and 70 C for octol. In

addition the kinetics and associated parameters for changes in the mechanical properties during aging are unknown. Therefore, it is not possible to make direct comparisons of the stability of all of these materials and it is also not possible to reliably extrapolate the results of accelerated aging to actual storage conditions. It is highly desirable to make measurement at least at two or more temperatures and a few aging periods so that a measure of the kinetics and associated parameters can be obtained. With this information extrapolations to other conditions, especially long term storage conditions can be much more reliably made.

Neglecting the differences in storage temperature or temperatures of accelerated aging, the compressive strengths of TNT, the single base propellants, and PAX2A appear to be the most stable. TNT is stable for a long time period under actual storage condition. The accelerating aging temperature for the single base propellants was five degrees higher than the highest temperature used for PAX2A and the time periods were longer. Therefore, the single base propellants are at least as stable as PAX2A and may be more stable. The double and triple base propellants are of course less stable than the single base propellants. The compressive strength at -45 C of the double base propellant may be less stable than that of the triple base propellant because the decrease of the compressive strength of the double base propellant is greater than that of the triple base propellant for each aging period of Table 4. However, because of the experimental spread of the data this is not conclusive at this time. With the information available it is not possible to determine the relative stability of the compressive strengths of PAX2A, the

double and triple base propellants and octol. Although the compressive strength of PAX 2A was not changed after accelerated aging for six months while the strengths of the double base and triple base propellants and octol were decreased after this same period of accelerated aging, the aging temperatures were all different. Because of these differences in aging temperatures and because of the lack of knowledge of the kinetic parameters it is not possible to make a meaningful comparison.

SUMMARY

The compressive strength, Young's modulus and the failure strain of TNT were found to be unchanged for storage under stockpile conditions for up to 40 years. The compressive strengths of single base propellants were found to be unchanged after accelerated aging at 65 C for up to 18 months. In addition, the compressive strength of PAX2A was found to be unchanged within experimental uncertainty for a twelve month accelerated aging period at 50 C and a six month accelerated aging period at 60 C. Young's modulus of PAX2A was increased by about 15% and the failure strain was decreased after these same treatments. It is suggested that these later changes may be due to clustering of plasticizer.

The compressive strengths of double and triple base propellants at -45 C and octol at -45, 25 and 65 C were decreased after accelerated aging. The compressive strength of the propellants at 23 C were either unchanged or decreased only slightly. Young's modulus of octol was decreased and the failure strain was either increased or unchanged. The propellants were

subjected to accelerated aging at 65 C for up to 18 months and octol was subjected to accelerated aging at 70 C for six months. The decrease of the compressive strength and Young's modulus of octol can be attributed to increased porosity after aging. This conclusion is supported by observations of small decreases in density and weight and increases in volume after the aging. The decreases in density and weight and the increases in volume are thought to be due to impurity processes since neither of the main components of octol, HMX and TNT, are expected to decompose significantly for the accelerated aging conditions of this work. Loss of TNT is also a probable cause of the weight decrease. The decreased compressive strength of the double and triple base propellants at -45 C may be due to increased porosity and/or regions of disorder produced by nitrocellulose and nitroglycerine decomposition that are effectively not load supporting and are frozen in the glass state at -45 C. Micro-cracks may also play a role in decreasing the compressive strength. The disorder which is frozen in the glass state and which causes a reduction of the compressive strength is not effective in reducing the compressive strength in the rubber state at 23 C.

The brittleness at -45 C of the single double and triple base propellants is increased after accelerated aging. This can be attributed to increased densities of cracks in the aged samples in the glass state. For PAX2A increased cracking in aged samples was observed, but only at the higher temperatures. This increased cracking is attributed to thermally activated crack growth in aged samples which does not take place in non-aged samples.

It is not possible to extrapolate the results of accelerated aging to other condition, e.g. aging at ambient conditions for much longer time periods, because the kinetics are not established. Accelerated aging at a few temperatures and several time periods are probably sufficient to determine the required kinetic parameters.

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