Survey of Solid-Propellant Aging Studies

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Abstract

THE importance of aging studies arises from the assessment of the safe life of the propellant. The objective of the present review is to give a comprehensive picture of the up-to-date knowledge available in the literature on the subject, covering both double-base and composite solid propellants. The present review covers the following topics: 1) failure criteria, 2) estimation of safe life, 3) changes in ballistic and decomposition characteristics, 4) changes in mechanical properties, and 5) mechanism of aging.

Contents

Aging in a broad sense is the "deterioration" of solid propellants during storage, resulting in changes in performance of the solid rocket motors. Two types of aging studies are generally carried out: 1) normal aging, and 2) accelerated aging. Accelerated aging of the propellant is an attempt to reduce the time scale by storing the propellant at eleveated temperatures so that prediction can be made in shorter times; however, extrapolated information sometimes does not match the changes observed under normal conditions. The aging generally leads to changes in ballistic properties (burning rate, calorimetric value, etc.) and in mechanical properties (modulus, ultimate tensile and compression strength, generation of cracks and voids, etc.). The changes may or may not be within the specified tolerance limit and may either lead to smooth functioning of the roket motor with changed performance or to motor failure. The latter category is known as "failure criteria."

Failure Criteria

The general approach to understand failure criteria is the representation of the failure in a geometrical form of a "failure surface" that separates the conditions for safe and unsafe mechanical states. Propellant failure characterization is generally done by using the failure envelope developed by Smith and Stedry[1] for rubbers, where the temperature dependence of mechanical properties is represented by the Williams, Landal, and Ferry (WLF) equation.[1] Multiaxial creep data with superimposed hydrostatic pressures are needed to complete the determination of the failure surface.[1]

Failure estimates are made from constant strain-rate tests under uniaxial and multiaxial conditions. Propellant generally experiences a multiaxial stress field in the combustion chamber, and therefore uniaxial tensile tests can lead to gross inaccuracies. In multiaxial characterization, generally strip tension and the strip biaxial tests are employed. Kelly[1] analyzed the mechanism of tensile failure in a solid propellant by studying effects such as the nature of binder backbone, polarity, crosslink density, and filler fraction. Polyurethane (PU), CTPB, and PBAN-based NH_4ClO_4 (AP) propellants were used to develop the temperature-dependent failure envelope. The data were normalized to fit a master curve based on crosslink density and filler fraction shifts. Hazelton[2] determined the failure properties of a PU/AP propellant at different strain rates and pressures in large motor firing. Tensile properties were found to improve with rapid straining and superimposed pressure.

Estimation of Safe Life

Boyars[3] defined the "safe storage life" as the time during storage, the "safe use life" as the time up to which the propellant can still function without undue hazard, and the "useful life" as the time during which it meets the required ballistic properties. According to Volk,[4] safe life can be divided into two categories: 1) chemical safe life, which is determined by the occurrence of chemical reactions during storage; and 2) physico-mechanical safe life, which is determined by cracking of the grain, decomposition of the material, and diffusion of plasticizers, etc. He estimated safe life for double-base propellants from the following parameters: 1) time for the appearance of the liquid droplets; and 2) time for the autocatalytic decomposition, where the rate suddenly increases. Frey[5] determined safe life for double- and single-base propellants by measuring 1) the heat of decomposition, and 2) appearance of the brown vapors.

In composite solid propellants, the safe life is generally determined from changes in mechanical properties. In special cases, e.g. ballistic missiles, estimation of aging as characterized by ballistic properties is desirable.

Changes in Ballistic and Decomposition Characterisitcs

Volk[6] studied the effect of different burning rate ($\dot{r}$) moderators on the storage stability of double-base propellant. He observed that lead salts postpone the inception of autocatalytic decomposition, whereas copper salts accelerate the same. He further observed that the addition of small amounts of ethylcentralite gave better aging characteristics.

Nagatomo[7] studied the effect of vacuum on the aging characteristics of PB- and PU-based composite propellants and measured the changes in $\dot{r}$ and weight loss. He did not observe any significant differences in the foregoing parameters under vacuum and atmospheric conditions. Schedlbauer[8] determined the changes in $\dot{r}$ and weight loss during aging of PU- and CTPB-based propellants. There was no significant change in $\dot{r}$ up to a period of two years at 80°C. He observed that the weight loss was more when the extent of crosslinking was more. He attributed this to several factors: evaporation of solvent, moisture, crosslinking agent, etc. Recently, we have observed[9,10] that the change in $\dot{r}$ was attributed to the slow decomposition of the propellant. Furthermore, the change in porosity was found to have no significant effect.[9] Using thermal decomposition (isothermal TG at 230° and 260°C) as a technique, in addition to $\dot{r}$, it was observed that decomposition below the phase transition of AP (i.e., at 230 °C) was related to aging characteristics.[10] Furthermore, it was observed that highly AP-loaded propellants age less than those with less AP.

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Index category: Ablation, Pyrolysis, Thermal Decomposition and Degration (including Refractories).

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Changes in Mechanical Properties

Suzuki and co-workers[11] studied the effect of aging on the mechanical properties of PB, PS, and polyester-based propellants. They observed that the elongation and tensile strength decreased but were restored by drying. Schedlbauer[8] studied the long-term aging of PU and CTPB-based propellants. He found that binders containing less hardener showed less changes in mechanical properties. He further observed that a propellant undergoes shrinkage during aging, resulting in increased density, and that CTPB propellants have better storage stability than PU propellants.

Layton[12] studied accelerated aging of CTPB and PBAN-based propellants. He measured several mechanical properties (P) during the course of aging and found that the change in P can be represented empirically by $P=k \log(t)+C$, where C is a constant representing the value of a mechanical property at the inception of aging and k is the rate constant for gel formation. An Arrhenius dependence for the change in P yielded an E value of 5.5 kcal/mole, which he attributed to the diffusion-controlled processes.

Mechanism of Aging

Double-base propellants yield NO_2 during storage because of the dissociation of the weak RO—NO_2 bond. Generally stabilizers are added to consume NO_2 so that further decomposition of the propellant is hindered. Dykes,[13] Delcampo,[14] and Volk[15] separated the intermediate products formed during the aging of single- and double-base propellants containing such stabilizers as diphenylamine, resorcinol, and ethyl centralite. Using TLC techniques, a number of intermediates were separated such as di-, tri-, and hexa-nitroderivatives of the stabilizers.

Wewerka[16] observed that diffusion of NO_2 into the binder is the rate-controlling step during aging in a model propellant containing RDX and a binder. Hartman and Musso[17] studied the aging characteristics of CMDB propellant and found that the E for aging was 34.4 kcal/mole, which they attributed to the scission of O-N bonds. Frey[5] analyzed the nature of decomposition by using a heat flow calorimeter and calculated the critical diameters both before and during the autocatalytic decomposition. He found that spontaneous ignition would occur only in the region of autocatalysis.

Schedlbauer,[8] Myers,[18] and Layton[12] studied the mechanism of aging of CTPB, HTPB, and PBAN-based propellants. All of them observed that the propellant becomes hard during aging from an increase in the extent of crosslinking. The crosslinking in these polymers can occur via reactive groups or through the double bonds in the polymer backbone. Experiments were conducted to distinguish between the two processes. It was concluded that the crosslinking during aging occurs through the interlacing of double bonds, which involves oxidative attack by the $HClO_4$ formed during AP decomposition.

Conclusions

The mechanism of the aging of double-base propellant has been studied adequately. It involves the generation of NO_2 and its subsequent attack on the propellant, and therefore the compounds which consume NO_2 increase the storage stability. Studies on CMDB propellants have not received much attention; the effects of various small ingredients, which are used to modify the performance on aging require investigation.

Based on information available to the present authors, it is concluded that aging studies on composite propellants have not received adequate attention, particularly from a mechanistic viewpoint. The effects of propellant variables on aging need detailed investigation. In conclusion, a general physical and mathematical model that could predict the aging characteristics of double-base and composite propellants is needed.

References

[1] Kelly, F.N., "Solid Propellant Mechanical Properties Testing Failure Criteria and Aging," *Advances in Chemistry*, American Chemical Society, Washington, D.C., 1969, Ser. 88.

[2] Hazelton, I.G., "Effect of Rate and Superimposed Pressure on Tensile Properties of Composite Solid Propellants," *High-Speed Testing*, Vol. 5, 1965, pp. 217-228; *Chemical Abstracts*, Vol. 64, No. 11, 1966, p. 15665(d).

[3] Boyars, C., "Surveillance of Solid Propellant Rockets," *ARS Journal*, Vol. 29, Feb. 1959, pp. 148-150.

[4] Volk, F., "Determining the Shelf Life of Solid Propellants," *Propellants and Explosives*, Vol. 1, Aug. 1976, pp. 59-65.

[5] Frey, M., "Measuring the Heat of Decomposition of Propellants," *Chemical Abstracts*, Vol. 82, No. 16, 1975, 100,865(x).

[6] Volk, F., "The Effect of Regression Moderators on the Chemical Stability of Double-Base Solid Propellants," *Third Symposium on Chemical Problems Connected with the Stability of Explosives*, May 28-30, 1970.

[7] Nagatomo, M., "Effects of Space Environments on the Burning Rate of Composite Propellants," *Chemical Abstracts*, Vol. 71, No. 26, 1969, 126,685(m).

[8] Schedlabauer, F., "Report of the Problems of Determining the Life-Time of Composite Solid Propellants and New Research Results," *ICT Jahrestagung*, 1971, pp. 275-303; *Chemical Abstracts*, Vol. 81, No. 8, 1974, p. 10855(h).

[9] Pai-Verneker, V.R., Kishore, K., and Prasad, G., "Effect of Preheating on Burning Rate of Solid Propellants," *AIAA Journal*, Vol. 14, Sept. 1976, pp. 1330-1331.

[10] Kishore, K., Pai-Verneker, V.R., and Prasad, G., "Storage Stability of Solid Rocket Fuels," *Fuel*, Pt. I, Vol. 56, July 1977, pp. 292-294, and Pt. II, Vol. 57, Jan. 1978, pp. 22-24.

[11] Suzuki, K., Omura, I., Iizuka, T., and Harada, T., "Effect of Aging on the Mechanical Properties of Composite Propellants," *Kogyokayaka*, Vol. 30, March 1969, pp. 126-130.

[12] Layton, L.H., "Chemical Aging Effects on Composite Solid Propellants," presented at the AIAA/SAE 11th Propulsion Conference, Anaheim, Calif., Sept. 29-Oct. 1, 1975.

[13] Dykes, H.W.H., "Thin Layer Chromatographic Separation of Diphenylamine and Resorcinols Used as Propellant Stabilizers," *Chemical Abstracts*, Vol. 63, No. 20, 1967, p. 924,834.

[14] Delcampo, P., "Thin Layer Chromatographic Stability Determination of Powder Containing Diphenylamine as a Stabilizer," *Chemical Abstracts*, Vol. 85, No. 12, 1976, p. 804,657.

[15] Volk, F., "Determination of the Life-Times of Gun Propellants Using Thin Layer Chromatography," *Propellants and Explosives*, Vol. 1, 1976, pp. 90-97.

[16] Wewerka, E.M., Laughram, E.D., and Williams, J.M., "Effects of Long-Term Storage at Elevated Temperatures on Small Cylinders of PB 9501," *Chemical Abstracts*, Vol. 86, No. 16, 1977, p. 108,803(d).

[17] Hartman, K.O. and Musso, R.C., "Thermal Decomposition of Nitroglycerine and Its Relation to the Stability of CMDB Propellants," *Chemical Abstracts*, Vol. 78, No. 18, 1973, p. 113,507(z).

[18] Myers, G.E., "Chemical Structural Aging Effects," *Chemical Abstracts*, Vol. 83, No. 10, 1975, p. 82,249(p).