ISSN:1983 7402 ITA, 24 a 27 de setembro de 2013

Ageing Assessment of Energetic Materials: A Brief Review

Rodrigo Roversi Rapozo, Koshun Iha, José Atílio Fritz Fidel Rocco
Instituto Tecnológico de Aeronáutica, Praça Eduardo Gomes nº. 50, São José dos Campos, São Paulo.

Abstract **— Product Life Cycle and Personnel Safety are of utmost importance for military ordnance employment. In this aspect, all components must be constantly assessed during the life cycle, leading to risk reduction for production, operational use and demilitarization. For the energetic materials presented in ordnance subsystems such propellants, pyrotechnics and explosives, the assessment of the aging characteristics must be performed during the development of the item. The present work was intended to briefly review some aspects identified on literature and standards regarding to ageing causes, effects and how it has been assessed.**

Key-Words **— Energetic materials, life cycle, ageing.**

I. INTRODUCTION

Among many materials classified as *energetic materials*, one should detach the propellants and explosives, which provide high pressures and temperatures during combustion. Such materials are designed to maximize the energy density against specific boundary conditions, as mechanical sensitivities, production requirements, physical properties and combustion characteristics [1]. The high temperature combustion products are converted in diverse types of mechanical responses.

Regarding military ordnances, the *product life cycle* and *personnel safety* are of utmost importance.

Assuming some specific military ordnance as a system, all subsystems, its components and elements must be constantly evaluated during its life cycle, leading to risk reduction for production, operational use and demilitarization. Therefore, subsystems and components such propellants, pyrotechnics and explosives should have its ageing characteristics assessed during development and certification of the final product [2]. Herewith, the term *ageing* is taken as the evolution of properties and characteristics along the *service life*, by means of physical or chemical transformations.

Material Vulnerability

In terms of weapon systems, as a tactical missile, the major subsystems containing energetic materials are Rocket Motors, preferable Solid Rocket Motors (SRM) and Warheads (WH).

Rodrigo R. Rapozo, rapozorrr@copac.aer.mil.br. Tel +55-12-39421016, extension 235, Fax +55-12-39421016. Koshun Iha. koshun@ ita.cta.br, Tel +55-12-39476852, Fax +55-12-39475845. José A. F. F. Rocco, friz@ita.br. +55-12-39475918, Fax +55-12-39475845.

For a SRM, must be highlighted the solid propellant, the pyrogenic or pyrotechnic igniter, including the initiator.

Concerning WH development, shall be assessed the main charge, booster charges and the explosive train components.

For a specific formulation, the material's vulnerability will depend on many factors [3, 4], as presented at Table I.

TABLE I MAJOR VULNERABILITY FACTORS [3].

Binder Matrix	High Explosive	Binder Components
Type	Type	Plasticizer
Ageing Characteristics	Grain Size	Bounding Agent
Oxidation	Grain Shape	Catalyst
Swelling	Crystallization	Antioxidant
Exudation	Specific Surface	Stabilizer
Coating Capability	Purity	Surfactant
Mechanical Properties	Mechanical Properties	Coating Agent

The fabrication process exerts a strong influence on the vulnerability of the energetic material, as depicted on Table II, which compares two types of explosive charges [5].

TABLE II PROCESS EFFECTS ON AN EXPLOSIVE CHARGE [5]

Process Variable	Charge Type	
	Pressed	Cast
Production Rate	Superior	Moderate
Vulnerability	Moderate	Superior
Compatibility	Superior	Superior
Expansion Coefficient	Superior	Moderate
Cost	Moderate	Superior
Demilitarization	Inferior	Moderate

Figure 1 represents the interdependency of types of processes and the crystal properties [3].

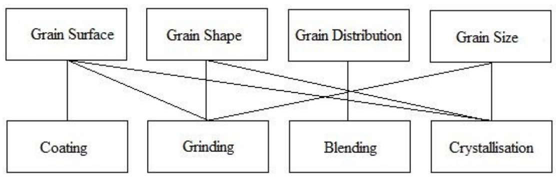

Fig. 1. Interdependency of Processes and Properties.

Ageing of Energetic Materials

The ageing of crystalline and/or polymeric energetic materials may be caused by a sort of factors, including *chemical factors* (decomposition, oxidation, extra cross-linking generation); *physical factors* (humidity, volatiles exudation, plasticizer migration); and *mechanical factors* (thermal cycling induced stress, mechanical shocks, vibration) [6-9].

In mechanical characterization of materials, should be highlighted the *master curve* assessment, in which the stress-strain behavior also includes time and temperature effects [7, 9-10].

Speaking about ageing assessment of energetic materials and its implications for transport, storage and operational use, a necessary tool is the accelerated ageing [8-9, 11-12].

The basic theory employs chemical kinetics and the Arrhenius equation for the reaction rate constant, k [13]:

$$d(A_1/A_0)/dt = k = Zexp(-Ea/RT) \, . \qquad (1)$$

Equation (1) shows an example which the dominant reaction is a pseudo-first order type [14-15], what is applicable for many High Explosives [13], as is the case of the Hexanitrostilbene (HNS) [11]. It also represents the variation of the property A, from an initial condition A_0 to a final condition A_1. The parameter Z is the Arrhenius coefficient, Ea is the activation energy, R is the gas universal constant and T is the temperature which the reaction occurs.

It might be obvious that (1) concerns to a specific temperature. The *accelerated ageing factor* [12] k_{10} is therefore obtained by taking the temperature variation:

$$k_{10} = k(T_1)/k(T_0) = exp[-Ea/R(1/T_1-1/T_0)] \, . \qquad (2)$$

The time-temperature relationship for the first order reaction type must be defined as explicated in [12]:

$$A = t(T)k(T) \, . \qquad (3a)$$
$$k(T_1)/k(T_0) = exp[-Ea/R(1/T_1-1/T_0)] = t(T_1)/t(T_0) \, . \qquad (3b)$$
$$t(T_1) = t(T_0)exp[-Ea/R(1/T_1-1/T_0)] \, . \qquad (3c)$$

For explosives with an Activation Energy around 0.7 eV, Table 3 presents a scenario which the reference storage temperature is 21°C [11].

TABLE III TIME-TEMPERATURE EQUIVALENCY [11]

Temperature (°C)	Duration (days)	Equivalent duration (years)
71	70	10.59
84	28	10.00
96	14	10.48
108	7	10.47
111	6	10.60

For accelerated ageing, the notion of acceleration factor is also employed [11]; respecting the properties of the materials, once performed the characterization of the transformation temperature events [15-17].

Regarding SRM propellants, the kinetics chemistry is governed by a series of higher order reactions. For example, propellants containing either nitrocellulose (NC) or hydroxyl-terminated polybutadiene (HTPB) a two-step kinetics mechanism are observed from 10°C to 120°C [11, 18-19]. This implies on considering two reaction rate constants, and a reaction shifting mechanism starting at some *shifting temperature* ($T_{S)}$ and at a corresponding *shifting time* (t_S). For evaluation of both constants, a reference temperature must be assumed (Tref).

The necessary steps for proceeding with the two-step analysis were dictated in [12].

Cumulative Damage

Recalling the effects of the formulation on accelerated ageing (4) brings an innovative parameter, named as *accumulated ageing index*, AAI [20]:

$$AAI = 100[(\varepsilon_t/\varepsilon_0-1)-(E_t/E_0-1)] \, . \qquad (4)$$

Equation (4) defines AAI by performing a comparison between the *strain at break*, ε and the *initial elastic modulus*, E from the non-aged (ε_0, E_0) and aged (ε_τ, E_t) specimens. If AAI is zero, it means no ageing effects; otherwise, if its value is highly negative, it means that the ageing is severe.

This parameter has been shown as an interesting quality assessment tool, allowing evaluation of formulation variations and procedural changes as well [20]. Examples are the effects of the changing of an oxidizer supplier, the increasing in bounding agent concentration, and the results of adding this agent in the beginning of the mixing process.

Statistical cumulative ageing analysis also plays a significant role in ageing assessment for *service life prediction* [9-10] although still today the focus of this analysis is the propellant grain structural behavior. There are considered the effects of: *thermal loads*; *acceleration loads; vibration loads (transportation, handling* and *captive carriage*); *cure shrinkage* and *pressurization loads* [7, 9-10]. Also the adhesive bonding properties between propellant, liner and thermal protections have been investigated [6, 21-22].

In terms of performance prediction during energetic materials, a great work effort has been taken by gathering data from thermal characterization and further extrapolation on internal ballistic simulation models allied with field test results [16, 23-24].

International Standards

Recalling the standardization on the ageing assessment subject, should be cited the STANAGs 4147 [25], 4170 [26], and the already referenced STANAGs 4581 [18] and 4582 [19]. A very important one, still under preparation by NATO technical authorities, is the STANAG 4666 [27], regarding *Polymer Bonded eXplosives* (PBX).

In particular, STANAG 4581 explores specific parameters, among these may be highlighted: solvent content; cross-link density; plasticizer and antioxidant contents; *Uniaxial Tensile Test* (as defined in STANAG 4506, [28]); *Dynamic Mechanical Analysis*, DMA (STANAG 4540, [29]); and Shore A hardness (ASTM D2240-00, [30]). The hot ageing environment considered is the item submission to 60ºC during three to six months [27].

The technical committee responsible to define the new STANAG 4666 has been considering additional methods [27]: filler-binder interface tests; *Shock Sensitivity* (STANAG 4488, [31]); *Electrostatic Discharge*, ESD (STANAG 4490, [32]); *Thermogravimetry* (STANAG 4515, [33]); *Differential Scanning Calorimetry*, DSC (STANAG 4515, [33]); *Thermomechanical Analysis* (TMA) for expansion (STANAG 4525, [34]); *Scanning Electron Microscopy* (SEM); *Fourier Transform Infrared* (FTIR); *Friability* (AOP-7, NAVSEA 8020 [35-36]); *Pressure Vacuum Stability* (STANAG 4556, [27]); *Heat Flow Calorimetry*, HFC (STANAG 4582, [19]); and *Simultaneous Differential Thermal Analysis* (SDTA).

For other specific tests there are standards and manuals to also be considered should be: AOP-7 [35]; NAVSEA 8020 [36]; the STANAGs 4170, 4443, 4487, 4489, and 4491 [26, 38-41].

Insensitive Munitions

The raising concerning over the world on personnel safety and cost savings for weapon systems, *Insensitive Munitions* (IM) have gathered more and more importance in new developments [4, 6, 42]. There are some available standards on this subject, in which must be highlighted STANAG 4439 and AOP-39 [43-44].

Although for a weapons systems have its sensitivity/vulnerability reduced and be classified as IM, it must be assessed in a whole scenario, based on a *threat hazard assessment* report (THA) [4, 6], starting by the nature of the materials, the explosive composition itself, the integrated ammunition, its packaging and the logistic depot or storage conditions[2, 36, 42, 44-46]. On support to that evaluation, the system and its subsystems *fault tree analysis* is a useful tool for determining *vulnerability parameters* to be monitored during the *life cycle* [4].

However, the choose for an IM SRM and/or a WH design will imply on logistics consequences for the weapon system, increasing potential to a differential storage, transportation and handling requirements.

Ageing consequences to *Insensitive High Explosives* (IHE) may be compiled in two major facts: the reduction on the shelf life of the system; and the increasing on response levels due to affected hazard properties [47]. To mitigate risks, development efforts have been directed for the use of materials having improved mechanical properties, solution already proved in leading to lessen ageing effects [3, 48-49].

Despite some already consecrated formulations with some particular high explosives, besides the new developments for energetic binders and additives [1, 15], formulations with inert HTPB binders have been preferred [48-49].

In the context SRM, due to the fact that IM propulsion is a component level dependent the propellant composition, the grain configuration, type of loading (case bonded or cartridge loading) must be developed in combination with case, insulation, adhesives, joints, igniter materials, igniter element-level design and the nozzle fixture [50].

Likewise for high explosives, composite solid propellants formulations have been driven upon to the use of energetic binder, energetic additives and alternatives oxidizers to ammonium perchlorate (AP) [1, 6, 49, 51-52]. Therefore, the consecrated formulations include AP due to higher performance and HTPB due to its better strength, vulnerability and ageing performance levels [1, 6, 8, 20, 22].

II. Final Remarks

The present work performed a briefly review on the assessment of ageing effects on energetic materials, highlighting the concept of *accelerated ageing* and presenting useful tools available for its evaluation. It has also included references for standards and guidelines applicable to this subject and the most current characterization tests to aid in further developments and *life cycle* monitoring.

REFERENCES

[1] N. Kubota. "Propellants and Explosives: Thermochemical Aspects of Combustion", 2nd ed. Wiley-VCH: Weinheim, 2007, pp. 33, 82, 262–264, 287–300.

[2] R. E. Bowen, J. M. Ward, E. A. Daugherty. "The Interrelationships between Qualification, Insensitive Munitions and Hazard Classification Testing of Explosives (High Explosives, Propellants and Pyrotechnics)". Minutes of the 25th Expl. Safety Seminar. USA, vol. 3, p. 374–383, August 1992.

[3] P. Wanninger, "Insensitive Booster Charges", presented at the 2006 IMEMTS, Bristol, UK, 2006.

[4] Y. Guengant, M. Rat, B. Mahe, "Munitions Vulnerability Assessment along their Life Cycle – Methods & Results", presented at the 2006 IMEMTS, Bristol, UK, 2006.

[5] P. Wanninger, "Insensitive Ammunition for the Artilhery", presented at the 2006 IMEMTS, Bristol, UK, 2006.

[6] J. P. Sutton, O. Bibalrz. "Rocket Propulsion Technology", 7th ed, John Wiley & Sons: New York, 2001, p.458–493.

[7] G. Herder, F. P. Weterings, W. P. C. de Klerk. "Mechanical Analysis on Rocket Propellants". J. Th. An. and Cal., vol. 72, p.921–929, 2003.

[8] K. M. Ide, S. Y. Ho. "Fracture Behavior of Accelerated Aged Solid Rocket Propellants". J. Mat. Sc. 34, p. 4209–4218. 1999.

[9] North Atlantic Treaty Organization. "Structural Assessment of Solid Propellants Grains", AGARD-AR-350. Brussels, 1997, pp.4-1–4-18.

[10] T. H. Duerr, B. P. Marsh, "Solid Propellant Grain Structural Design and Service Life Analysis" in *Tactical Missile Propulsion*, ed. 1. G. E. Jensen, B. H. Prescott, S. O. Leisch, J. G. Laurent, and D. W. Netzer, AIAA: Virginia, 1996, p. 114–135.

[11] B. T. Neyer, L. Cox, T. Stoutenborough, R. Tomasoski, "HNS-IV Explosive Properties and Characterization Tests", 39th JPC, AIAA 2003-5138, p.1–6, July 2003.

[12] M. A. Bohn, "Prediction of equivalent time-temperature loads for accelerated ageing to simulate preset in-storage ageing and time-temperature profile loads", Proc. of the 40th Int. Conf. of ICT on Energetic Materials - Characterization, Modelling, Validation German, p.78-1–78-28, June 2009.

[13] P. W. Cooper. "Explosives Engineering", 1st ed. Wiley-VCH:

Weinheim, 1996, p.81–88.

[14] J. Andrade et al. “Safe Shelf Life of Single-Base Propellants”. Quim. Nova, vol. 31, No. 3, p. 569-573, 2008. Available from <http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422008000300020&lng=en&nrm=iso>. Access on 21 Jan. 2013.

[15] J. S. Lee, C. K. Hsu. “Thermal properties and shelf life of HMX-HTPB based plastic-bonded explosives”. Therm. Acta, N^o. 392-393, p. 153–156, 2002.

[16] B. Roduit, C. Borgeat, B. Berger, P. Folly, B. Alonso, and J. N. Aesbischer, “The prediction of Thermal Stability of Self-Reactive Chemicals From milligrams to tons”, J. Th. An. and Cal., vol. 80, p.91–102, 2005.

[17] J. Andrade et al. “Study of Thermal Decomposition of a Smokeless Propellant.”. Quim. Nova, vol. 31, No. 2, p. 301–305, 2008. Available from <http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422008000200021&lng=en&nrm=iso>. Access on 21 Jan. 2013.

[18] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Assessment of Ageing Characteristics of Composite Propellants containing Inert Binder”. Belgium. STANAG 4581, December, 2006.

[19] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Nitrocellulose Based Propellants, Stability Test Procedure and Requirements Using Heat Flow Calorimetry”. Belgium. STANAG 4582, March 2007.

[20] M. Kivity, G. Hartman, A. M. Achlama, “Ageing of HTPB Propellant”, 41st AIAA/ASME/SAE/ASEE JPC & Exhibit, AIAA 2005-3802, p.1–6, July 2005.

[21] S. Y. Ho, “Viscoelastic response of solid rocket motor components for service life assessment”, J. Mat. Sc., vol. 32, p.5155-5161, 1997.

[22] S. B. Navale, S. Sriraman, V. S. Wani, M. V. Manohar, S. D. Kakade. “Effects of Additives on Liner Properties of Case-bonded Composite Propellants”. Def. Sc. J., Vol. 54, No. 3, p. 353–359. July 2004.

[23] B. Halls. “MSIAC Engineering Tools and Databases”, presented at the 44th Annual Gun & Missile Systems Conference & Exhibition, Kansas City, USA, 2009.

[24] L. T. De Luca et al. “Burning of Nano-Aluminized Composite Rocket Propellants”. Comb., Expl., and Shock Waves, vol. 41, No. 6, p. 680–692, 2005.

[25] Standardization Agreement of North Atlantic Treaty Organization. “Chemical Compatibility of Ammunition Components with Explosives (Non-Nuclear Applications)”. Belgium. STANAG 4147, June 2001.

[26] Standardization Agreement of North Atlantic Treaty Organization. “Principles and Methodology for the Qualification of Explosives Materials for Military Use”. Belgium. STANAG 4170, February 2008.

[27] W. de Klerk, R. Bouma, “Characterization of Aged Polymer Bonded eXplosives – Development of STANAG 4666”, presented at the 2007 IMEMTS, Miami, USA, 2007.

[28] Standardization Agreement of North Atlantic Treaty Organization. “Explosive Materials, Physical/Mechanical Properties Uniaxial Tensile Test”. Belgium. STANAG 4506, March 2000.

[29] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Procedures for Dynamic Mechanical Analysis (DMA) and Determination of Glass Transition Temperature”. Belgium. STANAG 4540, June 2002.

[30] American Society for Testing and Materials.”Standard Test Method for Rubber Property – Durometer Hardness”. USA. ASTM D2240-00, June 1992.

[31] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Shock Sensitivity Tests”. Belgium. STANAG 4488, April 2009.

[32] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Electrostatic Discharge Tests”. Belgium. STANAG 4490, February 2001.

[33] Standardization Agreement of North Atlantic Treaty Organization. “Explosives: Thermal Characterization by Differential Scanning Calorimetry and Thermogravimetric Analysis”. Belgium. STANAG 4515, August 2002.

[34] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Physical/Mechanical Properties, Thermomechanical Analysis for determining the Coefficient of Linear Thermal Expansion (TMA)”. Belgium. STANAG 4525, October 2001.

[35] Standardization Agreement of North Atlantic Treaty Organization. “Manual of Data Requirements and Tests for the Qualification of Explosive Materials for Military Use”. Belgium. AOP-7, June 2003.

[36] Department of Defense. “Ammunition and Explosives Hazard Classification Procedures”. USA. TB 700-2 NAVSEA 8020.8B, January 1998.

[37] Standardization Agreement of North Atlantic Treaty Organization. Explosives: Vacuum Stability Test”. Belgium. STANAG 4556, November 2009.

[38] Standardization Agreement of North Atlantic Treaty Organization. “Explosive, Uniaxial Compressive Test”. Belgium. STANAG 4443, July 1998.

[39] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Friction Sensitivity Tests”. Belgium. STANAG 4487, October 2009.

[40] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Impact Sensitivity Tests”. Belgium. STANAG 4489, September 2009.

[41] Standardization Agreement of North Atlantic Treaty Organization. “Explosives, Thermal Sensitiveness and Explosiveness Tests”. Belgium. STANAG 4491, August 2002.

[42] A. C. Victor. “Insensitive Munitions for Solid Rocket Motors” in *Tactical Missile Propulsion*, ed. 1. G. E. Jensen, B. H. Prescott, S. O. Leisch, J. G. Laurent, and D. W. Netzer, AIAA: Virginia, 1996, p. 273–361.

[43] Standardization Agreement of North Atlantic Treaty Organization. “Policy for Introduction and Assessment of Insensitive Munitions (IM)”. Belgium. STANAG 4439, Rev. 3, March 2010.

[44] Standardization Agreement of North Atlantic Treaty Organization. “Guidance on the Development, Assessment and Testing of Insensitive Munitions (IM)”. Belgium. AOP-39, ed. 3, March 2010.

[45] A. Stanton, “Insensitive Munitions Packaging Options”, presented at the 1st Annual NCRES, MD, USA, 2009.

[46] C. Spyckerelle, C. Songy, G. Eck. “IM Melt Cast Compositions based on NTO”. 2010 IMEMTS, Munick, October 2010.

[47] M. Sharp, “Topics of Interest: Ageing & Cook-off”, presented at 2003 IMEMTS, Orlando, USA, 2003.

[48] A. D. Merran, “Polyurethane Binder Systems for Polymer Bonded Explosives”, DSTO-GD-0492. DSTO: Australia, 2006, p.1–14.

[49] I. J. Lochert, R. M. Dexter, B. L. Hamshere, “Evaluation of Australian RDX in PBXN-109”, DSTO-TN-0440. DSTO: Australia, 2002, p.2–13.

[50] K. Nofer, C. Jones, C. Allen, “Application of IM Technology to the Aerojet/Roxel Rocket Motor for Joint Common Missile”, presented at the 2006 IMEMTS, Bristol, UK, 2006.

[51] C. Nguyen, F. Morin, F. Hiernard, Y. Guengant. “High Performance Aluminized GAP-based Propellants – IM Results”, 2010 IMEMTS, Munich, Germany, October 2010.

[52] Horst, A. W. et al. “Insensitive High Energy Propellants for Advanced Gun Concepts”, ARL-TR-2584. Weapons and Materials Research Institure. Aberdeen, 2001, p. 3–9.