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Qualification of Magnesium/Teflon/Viton Pyrotechnic Composition Used in Rocket Motors Ignition System

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ABSTRACT: The application of fluoropolymers in high-energy-release pyrotechnic compositions is common in the space and defense areas. Pyrotechnic compositions of magnesium/Teflon/Viton are widely used in military flares and pyrogen igniters for igniting the solid propellant of a rocket motor. Pyrotechnic components are considered high-risk products as they may cause catastrophic accidents if initiated or ignited inadvertently. To reduce the hazards involved in the handling, storage and transportation of these devices, the magnesium/Teflon/Viton composition was subjected to various sensitivity tests, DSC and had its stability and compatibility tested with other materials. This composition obtained satisfactory results in all the tests, which qualifies it as safe for production, handling, use, storage and transportation.

KEYWORDS: MTV, Pyrotechnic, Rocket motor, Safety.

INTRODUCTION

Pyrotechnic compositions are mechanical mixtures of different components that combust to produce special effects such as heat, light, smoke or sound (Agrawal 2010). The compositions including magnesium are widely known by the pyrotechnics community for their efficiency and performance. Teflon (Fig. 1) is a polymer with highly-polarized flourine atoms (fluoropolymer) and, when mixed with magnesium, a highly energetic material is formed with application in flares and propulsion systems of rocket motors (Göçmez *et al.* 1999).

The application of the magnesium and Teflon compositions in propulsive systems is due to the quantity of heat produced by the oxidation of the magnesium by the gaseous fluorine released by the Teflon (Yong and Smit 1991). The combustion reaction for this composition can be simplified by the equation (Peretz 1982):

$$a\mathrm{Mg} + [\text{-}\ \mathrm{C_2F_4}\text{-}] \rightarrow 2\mathrm{MgF_2} + (a-2)\mathrm{Mg} + 2\mathrm{C} \quad (1)$$

To facilitate the processing, the magnesium and Teflon mixture is coated with another fluoropolymer, Viton (Fig. 2), which acts as a binder increasing the homogeneity of the mixture, the conception of the final product (pellets or granules), and protects the magnesium against oxidation from humidity during the storage period.

The magnesium/Teflon/Viton pyrotechnic composition (MTV) has good technical features for application in ignition systems because during combustion hot solid and liquid particles and condensable gaseous products are released, enhancing the energy transfer to the solid propellant surface (Göçmez *et al.* 1999).

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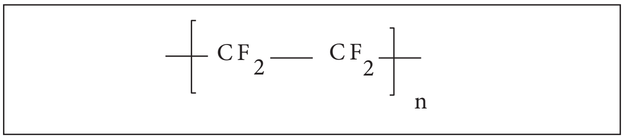

Figure 1. Teflon (polytetrafluoroethylene or PTFE).

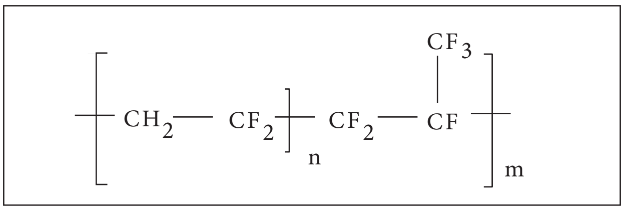

Figure 2. Viton (vinilydene fluoride/hexafluoropropylene copolymer).

However, pyrotechnic devices and rocket propellants have a potential for catastrophic accidents in case of an inadvertent initiation or ignition. In 1985, the US Army experienced an accident with the Pershing II missile, when a rocket motor made of Kevlar auto-ignited, killing three people. The auto-ignition of the motor was attributed to electrostatic discharge throughout the motor in cold and dry weather (Mellor and Boggs 1987).

Events like this made the global aerospace industry to evolve with respect to safety. In 2007, the *Agência Espacial Brasileira* (AEB) prepared the General Regulation of Space Safety, containing requirements to be applied in space activities that characterize Brazil as a launcher state to protect people, propriety and environment against potentially dangerous systems. The Regulation states that, to prevent potentially dangerous systems from activating unexpectedly by hardware failure or human error, barriers should be introduced. These barriers are referred as interception devices (AEB 2007).

The US military standard MIL-STD-1901A of 1992 states that only pyrotechnic compositions qualified by another standard, MIL-STD-1751A, now replaced by the North Atlantic Treaty Organization (NATO) standard AOP-7 (Edition 2) — Manual of Data Requirements and Tests for the Qualification of Explosive Materials for Military Use, may be used in a rocket motor ignition system without interruption (MIL-STD-1901A), that is, these compositions can be used after the interception device.

The AOP-7 standard provides mandatory tests that provide data to evaluate the performance and the safety of energetic materials, including pyrotechnic compositions. The mandatory tests to qualify these compositions are sensitivity to impact, to friction and to electrostatic discharge, stability, thermal analysis and compatibility. The explosive hexogene (RDX) is used as a comparative for the sensitivity tests.

The MTV composition produced by the *Instituto de Aeronáutica e Espaço* (IAE) is used on the space vehicles developed by the Brazilian Space Program. The qualification of this pyrotechnic composition will increase personnel and patrimonial safety and reduce the costs of launch operations by providing physical-chemical data of this specific formulation.

Therefore, this study has the objective of certifying that the MTV pyrotechnic composition is safe for fabrication, handling, use, storage, and transportation, thereby meeting the safety requirements for launching space vehicles.

MATERIALS AND METHODS

MATERIALS

For the MTV pyrotechnic composition, Merch KGaA magnesium powder was used with purity higher than 97% and grain size less than 0.21 mm; Teflon 850A® (PTFE) of DuPont™with grain size less than 0.42 mm; Viton B® (68% fluorine) of DuPont™ in pellets; and Acetone P.A. of Synth with minimum purity of 99.5%.

The RDX used was produced by SNPE Poudres et Explosifs, Groupe SNPE, France, class 5, with 97% of grain size less than 0.044 mm.

MTV COMPOSITION MANUFACTURE

The preparation of the MTV composition (58% magnesium and 38% Teflon) started with the complete dissolution of 4% Viton in acetone inside a proper recipient. A low-molecular-weight ketone swelled and vulcanized the Viton, creating a lacquer. The magnesium powder and the Teflon were added to the Viton lacquer and manually homogenized until the acetone completely evaporated. The mixture was passed through a sieve to classify the grain size less than 0.71 mm and was kiln-dried to remove traces of acetone.

IMPACT SENSITIVITY

The German Bundesanstalt fur Materialprufung (BAM) fall hammer is used to submit solid and liquid substances to an impact force that may cause detonation of the energetic material. The test set consists of two steel cylinders, one over another, and both cylinders are held together by a steel ring, as shown in Fig. 3 (AOP-7). A 20-mm^3 sample is placed between the two steel cylinders, and the test set is positioned at the base of the fall hammer. The weight is fixed at a chosen height and, guided by guide rails, the weight is released. The aim of the test is to estimate the energy that corresponds to a 50% probability of reaction. The reaction can be defined as flash, sparks, noise or explosion. The Bruceton analysis is used to evaluate the results in accordance with the French standard NF T70-500.

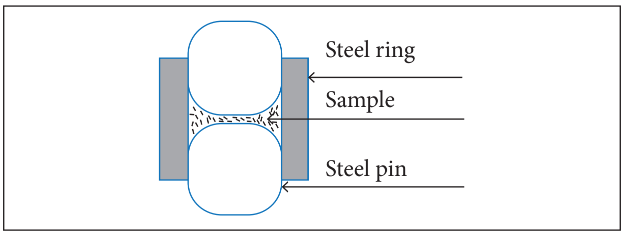

Figure 3. BAM impact test set.

FRICTION SENSITIVITY

The BAM friction tester is used to measure the response of energetic materials to a friction stimulus generated by two porous porcelain surfaces. A 10-mm^3 sample is placed in a porcelain plate attached to the sample table. The porcelain pin placed on the lever arm descends to come in contact with the sample, as shown in Fig. 4. Weights are set at different distances on the lever arm to adjust the force applied on the sample. An electric motor moves the table back and forth causing friction of the sample with the porcelain pin. The aim of the test is to estimate the energy in Newtons that corresponds to a 50% probability of reaction. A positive result is evidenced by gas liberation, sparks or noise. The Bruceton analysis is used to evaluate the results in accordance with the French standard NF T70-503.

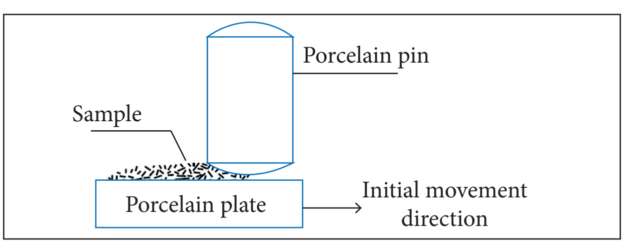

Figure 4. BAM friction test set.

ELECTROSTATIC DISCHARGE SENSITIVITY

This test determines the energy limit needed to ignite an explosive by electrostatic stimulus of various intensities. The test is run in an Energetic Materials Test Unit (Fig. 5), integrated to a Test Unit of 5 kV (Fig. 6) of the Electrostatic Discharge Sensitivity (ESD) Tester ESD-100 (Equatorial Sistemas). The initial energy is 0.25 J, charged by a capacitor of 0.02 μF connected to a discharge circuit charged with 5 kV. The gap between the upper electrode (needle) and the metal sample holder is fixed at 0.018 mm. A sample of 30 mg is put inside a Teflon washer placed on the top of the grounded sample holder, and a mylar sheet (insulating material) is placed on the top of the washer to confine the powder. The needle is charged and manually moved down to the adjusted gap, piercing the mylar sheet and discharging into the material. A positive reaction is defined as a flash, spark, burn or noise. No reaction in 20 out of 20 trials is a pass (AOP-7).

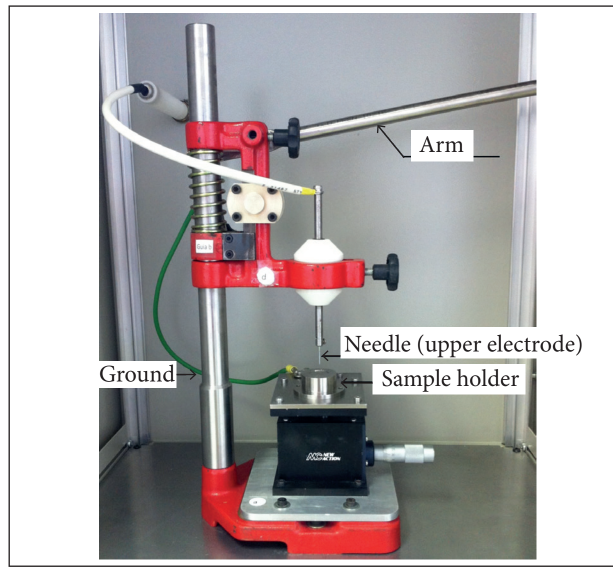

Figure 5. Energetic material test unit.

Figure 6. Test unit of 5 kV.

THERMAL ANALYSIS

The MTV composition was analyzed by the differential scanning calorimeter DSC-7 made by PerkinElmer, at a heating rate of 2 °C/min. Nitrogen gas was purged into the furnace at a rate of 50 mL/min. The temperature range was from 30 °C up to 500 °C, the maximum temperature allowed by this equipment. About 1 mg of sample was placed at a platinum crucible with perforated lid.

VACUUM STABILITY (CONSTANT TEMPERATURE)

The stability test was performed using STABIL Vacuum Stability Tester of OZM Research (Fig. 7), which consists in a heating block and glass tubes with temperature and pressure sensors. A 5-g mass was placed inside the glass tube and closed with a head that contains pressure and temperature transducers. A vacuum was created in the tube until the internal pressure reached values lower than 1 atm. The head is rotated to maintain the internal vacuum, and the tube is placed inside the heating block. The samples were heated at 100 °C for 40 h (AOP-7).

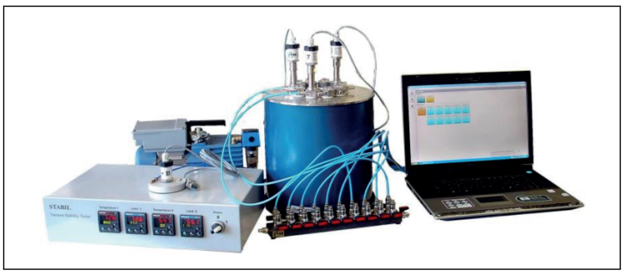

Figure 7. STABIL Vacuum Stability Tester.

COMPATIBILITY

The compatibility of the MTV composition was tested with the alkyl lacquer DOPE LP 453, a resin composed of nitrocellulose, aromatic solvents, alcohols, acetates and additives. This lacquer is used in the assembly of pyrotechnic devices that use the MTV composition as active material. During the assembly and sealing of the pyrotechnic device, the contact between the lacquer and the MTV composition could occur, so it was important to assess the compatibility between the two materials.

The test was conducted with a differential scanning calorimeter DSC-7 made by PerkinElmer, at a heating rate of 2 °C/min. Nitrogen gas was purged into the furnace at a rate of 50 mL/min (STANAG 4147). The temperature range was from 30 °C up to 500 °C, the maximum temperature allowed by this equipment. The samples were analyzed individually and in a mixture with a proportion of 1:1. About 2 mg was placed in a platinum crucible with a perforated lid.

RESULTS AND DISCUSSION

For the MTV pyrotechnic composition to be qualified and considered safe, all the tests must have satisfactory results. For sensitivity tests, the AOP-7 standard requires that RDX be tested contemporaneously with the composition, and the MTV sensitivity levels should not be more sensitive than RDX, which is a military explosive with high stability and low levels of sensitivity.

IMPACT SENSITIVITY

The results are presented in Table 1. Using the "up and down" Bruceton method with a minimum of 30 tests, we can analyze the data statistically and find, with a 95% confidence level, the energy that causes a 50% probability of a positive result, that is, initiation or detonation, as well as the lower and upper limits. The RDX resulted in a range of initiation energy from 2.5 to 6.3 J with average of 5.0 J. Meyer *et al.* (2007) reported in their book "Explosives" an energy of 7.5 J for RDX, but they did not specify the grain size of the explosive, which has an influence on the sensitivity of the material. The results show that the MTV composition is less sensitive to impact than RDX, since the energy required to initiate the sample is 50 J. Koch (2012) states that large spherical grains, with 2 or 3 mm diameter, may not have a positive reaction at a 50-J energy. The grain size of the sample was less than 0.71 mm, which resulted in nine positive results in 30 trials, confirming the influence of the grain size on the sensitivity of the material.

In this test, the energetic material is subjected to a plastic work, which causes heating and initiation. The strain rate of the material in the edges is greater than in the center, causing an initiation reaction at the edges first (Mellor and Boggs 1987). This was seen when the MTV composition was tested. Positive reactions vary from small black dots at the edges to expulsion of the steel pin from the ring along with noise and sparks.

Table 1. Impact sensitivity results.

Product	Impact sensitivity results (J)
RDX	5.0 (2.5 to 6.3)
MTV	50

FRICTION SENSITIVITY

The results are presented in Table 2. Using once more the Bruceton method with 30 tests and analyzing the data statistically, the RDX tests resulted in a range of initiation energy from 105 to 183 N, with an average of 159 N. Meyer *et al.* (2007) reported an initiation energy level of 120 N but again they do not specify the grain size of the RDX. These results show that the MTV composition is less sensitive to friction than RDX, and the energy necessary to initiate the composition is greater than 353 N. Materials that contain PTFE are not susceptible to ignition by friction due to the low friction coefficient of the PTFE (m = 0.04). There is no reaction up to 360-N friction forces with the BAM apparatus (Koch 2012).

Friction is the hardest stimulus to eliminate, because it is present at handling, at manufacture and at the storage of the energetic material. Friction is found in sliding, rotation and scrape movements (Mellor and Boggs 1987), which often happens during the preparation of the composition and the assembly of pyrotechnic devices.

Table 2. Friction sensitivity results.

Product	Friction sensitivity results (N)
RDX	159 (105 to 183)
MTV	> 353

ESD SENSITIVITY

The results are presented in Table 3. As we can see in the tests results, the MTV composition is about ten times less sensitive to ESD than RDX. Low ESD sensitivity materials are in a range from 12.5 mJ to 12.5 J (TM 9-1300-214), therefore, both samples can be considered low ESD sensitive. The threshold energy is found with no positive results at 20 consecutive trials.

The Teflon on the composition justifies the low ESD sensitivity of the MTV composition. The Teflon has high dielectric strength, in other words, it is considered an insulating material. The hazard of initiation by ESD arises when the energetic material becomes charged to a potential where the breakdown of the material occurs, or when changes at the grounding allow the discharge of the existing charge. The discharge process reduces the material resistance, which increases the electric current passing through. This process can create an arc and can also establish discharge paths followed by the catastrophic initiation of the material (Mellor and Boggs 1987). Therefore, the use of insulating material in pyrotechnic compositions decreases the hazard of initiation due to ESD.

Table 3. ESD sensitivity results.

Product	ESD threshold energy (mJ)
RDX	22
MTV	250

THERMAL ANALYSIS

This analysis is conducted to characterize the thermal decomposition behavior of the MTV composition. This characterization will be used afterwards to analyze the compatibility of the composition with other materials that it might come in contact with.

Figure 8 presents the DSC curve for the MTV composition. A small endothermic peak is identified at 340 °C and indicates the fusion point of the polymeric material in the mixture, because the Teflon fusion point is about 335 °C. The complete decomposition of the MTV composition at this heating rate occurs at temperatures above 500 °C, since there is no register of any exothermic event in the present curve.

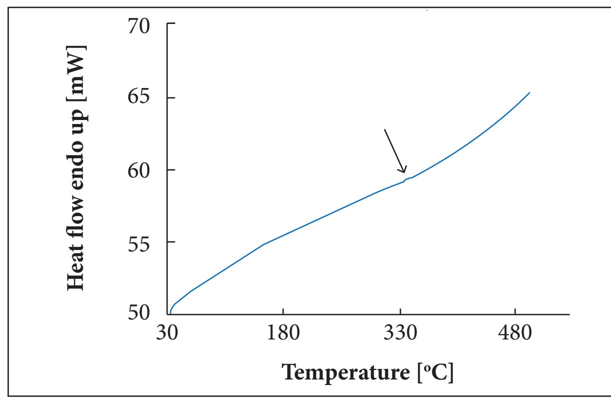

Figure 8. DSC curve of MTV composition — heating rate of 2 °C/min under nitrogen atmosphere from 30 to 500 °C.

VACUUM STABILITY (CONSTANT TEMPERATURE)

The gas volume released by the MTV composition after 40 h at 100 °C was of 0.61 mL/g. The AOP-7 standard requires a maximum gas release volume of 2 mL/g. The gas volume released in this test is a valid measure of the material stability (MIL-STD-1751A).

Usually, energetic materials remain in warehouses for a long period of time, and the environment conditions, such as temperature and humidity, depend exclusively on the storage location. The energetic material should maintain its performance, physical-chemical properties and safety during the entire storage time (Agrawal 2010).

The exposure of the MTV composition to the humidity transforms the magnesium in the composition into $Mg(OH)_2$ and MgO, as shown in Eqs. 2 and 3. These two products reduce the composition performance and increase the risk of accident due to the formation of gaseous hydrogen (Koc *et al.* 2009).

$$Mg(s) + 2H_2O \rightarrow Mg(OH)_2(s) + H_2(g) \quad (2)$$

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s) \quad (3)$$

Besides helping in the conception of the final product, the Viton has the function of coating the magnesium grains, which protects the magnesium from oxidation by the humidity (Yong and Smit 1991).

COMPATIBILITY

When an energetic material has direct contact with a polymer or other type of material, the following conditions can occur: (a) one or more properties of the energetic material can be affected; (b) one or more properties of the contact material can be affected; and (c) none of the properties of the energetic material or the contact material can be affected.

This test provides evidence that certain materials can be used in a pyrotechnic device without any loss in safety or reliability (STANAG 4147). The alkyl lacquer DOPE was tested in a mixture with the MTV composition to verify if these two products are compatible, since they are used in the assembly of pyrotechnic devices.

Figure 9 presents the DSC curve for the MTV composition for the alkyl lacquer DOPE and a mixture of 1:1 proportion of the two materials. Table 4 presents the temperature peaks of the samples.

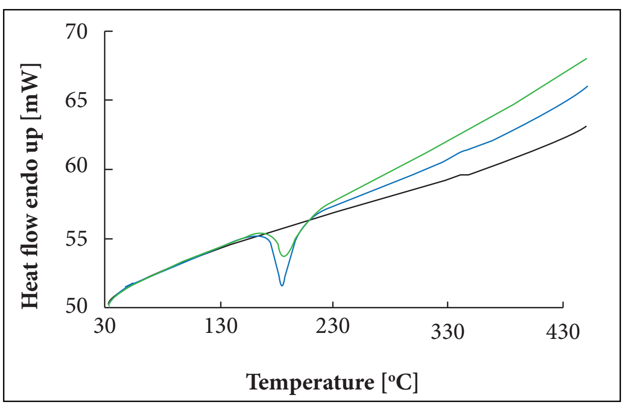

Figure 9. DSC curve of MTV, DOPE and MTV/DOPE 1:1 – heating rate of 2 °C/min at nitrogen atmosphere from 30 to 500 °C.

An exothermic peak with temperature of approximately 188 °C is identified in the DOPE curve, correspondent to the exothermic decomposition of the nitrocellulose contained in the lacquer (Andrade *et al.* 2007). It was verified before that the MTV composition has a small endothermic peak at 340 °C, relative to Teflon fusion point. Table 4 shows a small advance of 3 °C in the decomposition temperature of DOPE and the mixture MTV/DOPE. To evaluate the mixture behavior after this exothermic peak, a run was performed until 240 °C, and the mixture was analyzed visually, which resulted in a small alteration of the polymeric material in the composition. It is assumed that the energy released by the nitrocellulose decomposition caused a thermal degradation of the polymeric material at the contact area, but it was not sufficient to initiate or ignite the MTV composition, because there are no exothermic reactions depicted in the curve before 500 °C. Therefore, at the analyzed temperature range by differential scanning calorimetry, we can say that the MTV composition and the DOPE alkyl lacquer are compatible (Pinheiro 2010).

Table 4. Peak temperature of MTV, DOPE and MTV/DOPE.

Product	Peak temperature (°C)	Peak temperature (°C)
MTV	-	340.6 ± 0.3
DOPE	187.6 ± 0.7	-
MTV/DOPE	184.5 ± 0.4	340.0 ± 1.0

CONCLUSION

The MTV pyrotechnic composition was subjected to a series of tests such as sensitivity to impact, friction and ESD, contemporaneously with RDX, and the results were compared. Stability, thermal analysis and compatibility were also performed, and the MTV composition obtained satisfactory results in all of them. The composition is less sensitive than RDX in sensitivity tests, it has good stability proprieties and is compatible with the DOPE lacquer used to assemble and seal pyrotechnic devices used in the ignition system of rocket motors.

Therefore, it is concluded that the MTV pyrotechnic composition developed by IAE is now qualified, being safe for fabrication, handling and application in the ignition systems of solid propellant rocket motors as well as storage and transportation.

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