In missile propulsion technology, it is conventional to employ solid rocket boosters. These boosters are loaded with solid propellants, which are energetic compositions where raw materials are comprised of solid particulates, such as fuel, and oxidizer particles, in which are dispersed and immobilized throughout a binder (polymeric) matrix. The processability of these compositions is not simple because it is difficult to incorporate a high percentage of solids in polymeric matrix. It has been problematic to formulate a safe composition so as to prevent an accidental ignition of solid propellant or other device that uses energetic materials.

Accidents and incidents with solid rocket motor, during production, handling and storage, without apparent causes, led to studies by independent groups [1,2,3,4]. These studies generated important conclusions on the realm of solid rocket motor safety; furthermore, subsequent investigations suggest that spontaneous motor ignition can be attributed to electrostatic discharge.

The solid composite propellant grain can be considered in a microscale heterogeneous system in which conductive and nonconductive particles and different types of binders had direct influence in the grain electrical characteristics. Nonconductive particles have a geometrical effect to influence the spacing of the conductive particles [5].

The aim of this paper is to present the methodologies and the respective results of electrical and electrostatic discharge tests. These results allow us to choose a less ESD sensitive formulation of solid propellant increasing the reliability in manufacturing, handling and storage of solid rocket motor.

I. Introduction

Propellants, explosives and pyrotechnics are sensitive materials that have high risk of fatalities when accidents happen during their fabrication and handling/storage.

The safety tests for impacts, friction, shock and sparks provide relative scales to evaluate those risks. The safety is measured by the experience with the material. Unfortunately the experience normally involves accidents, many times including fatal victims.

When a determinate propellant rarely causes accidents or incidents, it can transmit a false impression of safety and insensitivity, creating a wrong idea of low risk. Each formulation of solid propellant needs to be investigating through different tests of safety for qualification and fabrication, because they are high risk of incidents jobs due to the sensitivity of the energetic components used.

One of accident's causes during the fabrication and application of the rocket motors using solid propellants (SRM) is the accidental ignition by electrostatic discharge. This paper intends to amplify the knowledge of some factors that contribute for the phenomenon's occurrence.

The accidental ignition of energetic materials by electrostatic discharge is an effect that's still little known and researched. The year of 1985 can be dated as the beginning of a systematic research, impelled by accidents with fatal victims occurred with Solid Rocket Motors in various places, where the accidental ignition happened by effects of electrostatic discharge [1-6].

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A. Electric and electrostatic properties of composite solid propellant

The majority of electric properties of solid propellants of composite type are influenced by the binder, the concentration and size of the aluminum particles that is applied like fuel metallic additive. The oxidant's particles, usually the ammonium perchlorate (not conductive), geometrically contribute to influence the space between the aluminum's particles.

Obtained data from recent studies [6-8] shows that, for propellants with polimeric binder based in a reaction of Hydroxyl Terminated Polybutadiene - HTPB with Diisocyanate of Isoforona – IPDI, resulting in Polyurethane – PU, the aluminum strongly influence the electric properties of the whole composite.

An important observation made by Covino and Hudson [7] is that the solid propellant's dielectric constant is proportional to the amount of aluminum in the system.

The reduction of the average diameter of the aluminum particle increases the potential of the dielectric's rupture. These results [6,7] lead to a conclusion that in HTPB based propellants is possible to make them safer, on Electrostatic Discharge, if the aluminum concentration id reduced (below 20% in volume), or if the average diameter of the aluminum particle is, likewise, reduced.

The aluminum particles are surrounded by an alumina layer (Al₂O₃) that has a volumetric resistivity in the order of 2x10¹⁸ Ω.cm. This insulation layer of alumina makes the resistivity of the propellant increase its number. This increase of the resistivity means that there is a bigger accumulation of electric charges on the propellant, if there are no mitigating measures to release these charges safely.

In actual researches, the ignition of energetic materials with relative low levels of energy, in the order of 10 mJ, has been associated with the induction of an exothermic reaction sustained in these materials [9]. Those energies are in a level that can be stored in the cases made of composite material and subsequently transferred to the energetic material [8].

With the industrial development of formulations based on aluminized HTPB, accidental ignitions have been observed in propellant's grains, without any significant shock or stimulus by friction.

The early standard test used low quantity of propellants and gave results that didn't indicated Electrostatic Discharge as the major cause of the ignition [10]. The principal reason that the phenomenon wasn't observed before, was the fact that there was a systematic increase of the resistivity of the propellants when the formulations of the binders went from Polybutadiene Acrylic Nitrile (PBAN) to Carboxyl Terminated Polybutadiene (CTPB) and, then, to Hydroxyl Terminated Polybutadiene (HTPB) [8, 11, 12]. The most used binder's resistivity increased from 6 x 10⁸ Ω (PBAN) to 2 x 10¹² Ω (PBLH).

B. Theories of ignition of solid propellants

Solid propellants are complex systems from the point of view of combustion process. The ignition of solid propellants is a transient process that occurs between an application of a energetic stimulus in a propellant block (grain) and the total combustion of it [13, 14]. Intrinsically, the ignition is an energetic stimulus that can be physic-chemical, thermal, or eventually photochemical. To understand the physic-chemical process of the ignition in solid propellant, three principal theories were proposed:

- **Theory of thermal ignition:** This theory, proposed by Hicks [13], suggests that the chemical exothermic reaction that occurs in the solid increase the temperature of the surface until the ignition point. Due to this, the ignition is governed by the increase of temperature in the solid under the surface exposed to the heat flux [13].

- **Theory of gas-phase:** Accord to this theory, the conditions of heat are due to the result of the chemical exothermic reaction in the gas phase between the constituents of the propellant in a small, but finite, distance of the surface [13].

- **Theory Heterogeneous:** This theory establishes that the primary reaction occurs on the surface or below it between the gas products from the decomposition of the oxidant and the solid matrix of the organic binder. This heterogeneous reaction controls the ignition process [13].

Those theories started researches under the influence of pressure, catalysts and other propellant's components, about the necessary energy to initiate the propellant's burn. This burn can be sustainable or not [8].

C. Solid propellant ignition by electrostatic discharge

Solid propellants of composite type have a very complex microstructure consisting in a dense package of particles surrounded by a polymer matrix. The particles are typically fuels, oxidants, and ballistics additives, among others. These particles have a large variety of size, form and electric properties. Electrostatic charges normally arise on the interfaces binder/charge(solids), on the surface of the propellant grain, like on other interfaces between other propellant's components, this is, on the interface between the conductive particles like the aluminum particles and a not conductive binder or less conductive.

Charges of static electricity are normally presents on the interfaces of the various phases of the solid propellant rocket motor: in the composite, thermal isolation, liner and in other parts of the SRM. The charging
of the surfaces of the various constituents of the solid propellant grain can occur by contact between them (Triboelectric contact) and by cracks or separation of the solid phase like in fractal-electrification.

Unexpected discharges of electrostatic energy can result in ignition, deflagration and, even, explosion of the rocket motor in case that there is no planner countermeasures in the process of production and loading of the grain in the rocket-motor tube. Among the chemical species that have the formulation of the composite, the ammonium perchlorate represents a potential risk to this electrostatic phenomenon, given that, in function of its high hygroscopic, needs to have its moisture content reduced before it incorporate to the net mass that will be transformed to a grain after the healing process of the solid propellant [16].

Occurs that its process of drying normally is done in counter flow with dry air that drags its humidity. Then it can result in your electrostatic charging by friction and by reducing of its intrinsic humidity.

Ground points correctly placed in the industry production's plant can reduce and, even, eliminate this phenomenon.

The mechanisms of ignition of the solid propellants proposed in the literature try to study the phenomenon through the approach of the “heat points” that can develop to a sustained reaction or evolution to a crack. The heat points can results also from glass transition of the AP.

In the ignition analysis caused by events of electrostatic discharges in solid propellants, needs to be included the study of:

- Electric energy available to initiate the ignition in a typical geometry on the system level.
- Deposition of electric energy in typical arcs, like a function of the samples size and technical features, like resistivity.
- Electric energy, power, and the time for the electric arc cause ignition.
- Mechanisms of resistivity lost in arcs.
- Physics properties of the solid propellant that are directly related to the ignition. Ex. Heat capacity

Figure 1 below shows the various ways for the ignition of a solid propellant.

![Figure 1 – Ways of energy absorption of the electrostatic discharge in solid propellant.](image-url)
II. Experimental Procedures

To obtain the concerning data of electric and physic characteristics of the propellant samples, has been utilized the following equipments: High resistance meter, inductor meter, LCD meter, Electrostatic Discharge Simulator, Scanning Electronic Microscope and Optic Microscope.

There have been used samples of solid propellant composite from various industrialized formulations. The oxidant used on the fabrication of the samples is the Ammonium Perchlorate (NH$_4$ClO$_4$), a crystalline substance in the standard environmental conditions and with good chemical stabilities further the high oxygen content.

The metallic additive used is the aluminum that has particles with average diameter defined by the formulation that will be used. The particle has to have preferably the spherical shape. The combustion of the aluminum is a very complex process. The aluminum is a fuel very exothermic producing alumina that is found in the liquid state in the flame's temperature (~3500K)[17].

The binder is based on the HTPB described previously. The HTPB is a synthetic resin rich in carbon and hydrogen on its molecular structure.

The best performance is obtained with a percentage of Ammonium Perchlorate (AP) ranging from a minimum of 60 % to a maximum of 89% of the total mass of the propellant, but the mechanical properties require a minimum valor (in mass) of binder. The normal concentration of Ammonium Perchlorate is about 70% of mass, of the aluminum is about 16% and of the binder is about 14 % [18].

A. Sample Evidence

The evidence bodies consist of five groups of samples from four distinct formulations, according to the table 1 presented below:

<table>
<thead>
<tr>
<th>Group</th>
<th>Qty</th>
<th>Formulation</th>
<th>(% AP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prop A001</td>
<td>06</td>
<td>AP/HTPB/Al- Bimodal</td>
<td>w ~70%</td>
</tr>
<tr>
<td>Prop B001</td>
<td>06</td>
<td>AP/HTPB/Al - Bimodal</td>
<td>w ~75%</td>
</tr>
<tr>
<td>Prop C001</td>
<td>06</td>
<td>AP/HTPB/Al - Bimodal</td>
<td>w ~69%</td>
</tr>
<tr>
<td>Prop D001</td>
<td>06</td>
<td>AP/HTPB/Al - Bimodal</td>
<td>w ~69%</td>
</tr>
<tr>
<td>Prop E001</td>
<td>06</td>
<td>AP/HTPB/Al - Trimodal</td>
<td>w ~69%</td>
</tr>
</tbody>
</table>

The particle grain distribution of the ammonium perchlorate may contain two or three principal average diameters of particles on the formulation. When there are two distinct diameters of ammonium perchlorate, the distribution is called bimodal and when there are three distinct diameters of AP is called trimodal.

The samples were prepared with the application in one of the surfaces of a resin with colloidal silver to standardize the electric contact between the sample and the negative electrode according to Figure 2.

![Figure 2 – Preparation of the propellant sample](image-url)
B. Electrical Characterization Tests

For the electrical characterization measurements, the samples were inserted on a device (Figure 4) and a value of 100 Volts DC for 4 minutes, was applied on each sample for the volumetric resistivity measurement test. For the capacity measurement test were used a maximum value of 2 Volts and a frequency of 1kHz, 100kHz and 1MHz.

![Figure 4 - Device for electrical tests](image)

- Electrostatic Discharge

The electrostatic discharge test was made on the groups of solid propellants samples. It was developed a device (Figure 5) to shelter the sample and make an electric contact between the Electrostatic Discharge Simulator and the sample. The device was constructed to allow the visualization of eventual ignition or crack during the energy injection. The tests were done with two levels of energy: 12kV and 26kV. The accumulated energy in a capacitor depends on two values: the capacity of the same and the square of the charge’s tension where: \[E=0.5 \times C \times V^2\] (4)

The capacitor used in the tests is of the value of 500 pF, generating energies of 0.36 J and 1.69 J to each level of voltage applied (12kV and 26kV).

This test uses a discharge Resistive-capacitive (RC) through the samples of propellants on the tubular shape and of different dimensions (10 mm of diameter x 6 mm of length and 40 mm of diameter x 70 mm of length).

The results are the occurrence or not, of the ignition or crack on the propellants samples, in function of the temperature and humidity [19].
• Percolation Factor

The theory of percolation to solid propellants was developed connected to the study of new tests, and applied to study the sensibility of the composite propellant. The theory of percolation is the study of the geometry of aleatory materials [20]. In the context of solid propellants, is the influence of the geometry of the metallic agglomerates in an insulating medium and how the particles affect the level of the rupture voltage of the propellant’s dielectric [7].

In the calculation of percolation the “binder” influences a lot on the P value, which is the index of percolation used as the final parameter to perform the sensibility evaluation. This effect has been validated by measurements of electrostatic discharge executed in propellants with “binders” more conductive, where the electrostatic discharge sensibilities of these systems are dramatically reduced.

\[
P = \frac{N_c}{N_i C_b V_b}
\]

Where:
- \(N_c\) = number of conductive particles (aluminum)
- \(N_i\) = number of insulating particles (ammonium perchlorate)
- \(C_b\) = binder’s conductivity
- \(V_b\) = binder’s volume unit

The risk of being more sensitive is major when the P value is higher. To non-aluminizated compounds \(P = 0\) because \(N_c\) is equal to zero. With ammonium perchlorate (insulating particles, \(N_i\)) the influence of the particle’s size is inverse to the aluminum. The measurements of volumetric resistivity of the “binders” have shown that the “binder” of polyurethane with a pre-polymeric of polyether base is less resistive. The “binders” of polybutadiene, on the opposite, are more resistive.

The percolation factor P has the dimension of resistivity and it is expressed in \(\Omega\).m. Compositions with values bigger than 1010 \(\Omega\).m are always sensitive to electrostatic discharge. The validation of the model was performed in France with 50 different formulations [6,7].

### III. Results and Discussion

In order to obtain a classification of the propellant’s susceptibility to ignition or generation of cracks due to liberated energy during an electrostatic discharge, is necessary electric characteristics data obtained through measurements in samples of the ligand and the cured propellant.

The measurements performed of Resistivity, Dielectric Constant, Rupture Voltage of the dielectric and the discharge RC allow to classify the energetic material in relation to the sensibility to ignition by effect of electrostatic discharge.

The analysis of the active ingredients of the propellant shows that the aluminum’s particle diameter and the “binder” electric properties (binder = pre-polymeric + additives) are the principals factors in the determination of the propellant’s electric properties. With the constant concentration of aluminum, when the particle’s diameter decreases (the number of particles increases), the propellant’s sensibility to capacitive discharges increases.
Another relevant data is that the fine layer of aluminum oxide that covers the particles can be broken by an electric field and this disruption establishes a way of energy’s conduction, facilitating an electrostatic discharge of the accumulated tension in the material.

The optic images obtained from the tested samples allow observing that the distribution of solids on the material, in this case a solid propellant sample, can’t get homogeneity in the distribution and in the shape factor of the solids. These characteristics influence directly in the sample’s electric size value.

![Figure 6- Optic image 100x – Prop C001](image1)

![Figure 7- MEV image - 100 μm–Prop. C001](image2)

The propellant C001, shown in Figure 7 and 8 presents the modal distributions of the Ammonium Perchlorate. We can see the occurrence of particulate non spherical in the mass and the visualization of the particle’s shape factor of the Ammonium Perchlorate from the propellant.

The Figure 7, obtained with SEI detector, (this kind of detector uses the secondary electrons ejected from the sample with an energy minor than 50 eV), of the propellant C001 presents a shape factor where is also observed the deficient wetting indicating a possible absence of ligation additive. The images also show a fine particulate that can be originated from the maceration process. This particulate can influence the burn raising the velocity of the same modifying the projected motor’s characteristics.

The table 2 shows the values of resistivity measured on the samples. These values allow to classify the sensibility of the samples in order of susceptibility to “ignite” for accumulated electrostatic charge.
Table 2 – Values of Resistivity of the Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Formulation AP/HTPB/Al</th>
<th>$\rho$ ((\Omega).cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propellant A001</td>
<td></td>
<td>$3.9 \times 10^{11}$</td>
</tr>
<tr>
<td>Propellant B001</td>
<td></td>
<td>$4.2 \times 10^{10}$</td>
</tr>
<tr>
<td>Propellant C001</td>
<td></td>
<td>$7.4 \times 10^{11}$</td>
</tr>
<tr>
<td>Propellant D001</td>
<td></td>
<td>$9.1 \times 10^{11}$</td>
</tr>
<tr>
<td>Propellant E001</td>
<td></td>
<td>$6.7 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Figure 8 – Test of Electrostatic Discharge

The figure 8 shows a changing on the way of the voltaic arc, parting from the sample’s body and ionizing the surrounding air; indicating that there is an increasing on the sample’s volumetric resistivity on the vanishing point.

This increase in the resistivity develops an increasing of the area’s dielectric rigidity that gets bigger than the air’s. Due to failure in the maceration, there are aluminum bridges that allow the escape of electric stream to the sample’s sides making possible the rupture of the air’s dielectric rigidity appearing the voltaic arc on the side of the sample.

Table 3: Results of the Test of Electrostatic Discharge

<table>
<thead>
<tr>
<th>Identification of the Samples (Test on 3 specimen of each propellant)</th>
<th>Formulation AP/HTPB/Al</th>
<th>Occurrency of Ignition</th>
<th>Occurrency of Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy 1 (0.36 J)</td>
<td>Energy 2 (1.69 J)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Number of Discharges</td>
<td>Number of Discharges</td>
<td></td>
</tr>
<tr>
<td>Propellant A001</td>
<td>30</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>Propellant B001</td>
<td>30</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>Propellant C001</td>
<td>30</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>Propellant D001</td>
<td>30</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>Propellant E001</td>
<td>30</td>
<td>30</td>
<td>No</td>
</tr>
</tbody>
</table>

The values of the resistivity obtained were submitted together to the formulation of each propellant to an analysis using a calculation of the percolation factor as it is presented by Covino et al [7] and the results are shown in the table 4.
Table 4 – Values of Volumetric Resistivity and Percolation Factor

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volumetric Resistivity - $\rho$ ($\Omega \cdot \text{cm}$)</th>
<th>Percolation Factor - $P$ ($\Omega \cdot \text{m}$)</th>
<th>Formulation Characteristics. (% in mass of Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propellant A001</td>
<td>$3.9 \times 10^{11}$</td>
<td>$1.09 \times 10^{14}$</td>
<td>$-15$</td>
</tr>
<tr>
<td>Propellant B001</td>
<td>$4.2 \times 10^{10}$</td>
<td>$9.99 \times 10^{13}$</td>
<td>$-15$</td>
</tr>
<tr>
<td>Propellant C001</td>
<td>$7.4 \times 10^{11}$</td>
<td>$1.08 \times 10^{14}$</td>
<td>$-18$</td>
</tr>
<tr>
<td>Propellant D001</td>
<td>$9.1 \times 10^{11}$</td>
<td>$1.08 \times 10^{14}$</td>
<td>$-18$</td>
</tr>
<tr>
<td>Propellant E001</td>
<td>$6.7 \times 10^{11}$</td>
<td>$6.08 \times 10^{14}$</td>
<td>$-16$</td>
</tr>
</tbody>
</table>

Using the experimental results of the published works in the open literature [7, 8, 21, 22] to compare with data obtained in this work, observed that the quality of the aluminum and also the solid’s particles diameter influence significantly the value of the percolation factor that defines the sensibility to the electrostatic discharge of the studied propellant.

The tests were done in room temperature and the static occurrence factor of ignition or crack by phenomenon of electrostatic discharge doesn’t allow assuring the level of sensibility of the propellant only with these results of injection of energy by electrostatic discharge. When, however, analyses the assembly results of the different tests, observed that the results obtained in the calculation of the percolation factor $P$ are above of the critic value $P_{\text{crit}} \sim 10^{10} \Omega \cdot \text{m}$, obtained by experimental studies [7, 8], minimum wanted limit.

Values superior to this minimum or critic limit, foresee the possibility to occur an accidental ignition by Electrostatic Discharge. The resistivity of the samples has a high value, what indicates a bigger capacity of storage of electrostatic discharges.

The percolation factors ($P$) of the samples are above of the missile’s propellant’s percolation factor Pershing II, which initiated an accidental ignition by effect of an Electrostatic Discharge [7].

Some formulations studied are more sensitive at low levels of energy due to an apparent absence of the ligand agent in the formulation, making possible the initiation of ignition by impact (ballistic or not) [23] or by energy of an electrostatic discharge.

Another relevant data to be observed is the modal distribution of the ammonium perchlorate. If there is prevalence of particles with bigger diameters (eg. 400 $\mu$m) the sensibility to the electrostatic discharge increases. The data of volumetric resistivity ($\rho$) and the percolation factor ($P$) analyzed simultaneously indicate that all the formulations studied are sensitive to ignition phenomenon or appearance of cracks due to an Electrostatic Discharge in the propellant.

IV. Conclusion

The contribution of this work was to demonstrate that the formulations of solid propellants using polymers of polybutadiene hydroxyl-terminated, oxidant of ammonium perchlorate and aluminum as fuel can give rise to accidents for be sensible to electrostatic discharge. The results and data obtained indicate that the applied methodology can be used to the evaluation of the formulations. To minimize the risks, the involved in the research activities, fabrication and operation of energetic materials should try to develop methods and equipments of analyzis and new materials that increase the security mitigating the present risk in the use of solids propellants.

V. References


