Sensitivity of Solid Rocket Motors to Electrostatic Discharge: History and Future

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The characterization of the sensitivity to electrostatic discharge of solid propellants and the adaptation of the corresponding procedures in the production, handling, and operation of motors and systems using them have always been an essential part of the safety analysis of rocket systems. However, incidents or accidents have occurred during the past decades, which showed that the appreciation of the risks and the knowledge of the mechanisms of ignition were not sufficient. These incidents always involved hydroxyl-terminated polybutadiene based aluminized composite propellants. After an analysis of the incidents, a new test was designed in France at the beginning of the 1980s in order to characterize propellants as sensitive or not sensitive, and a criteria based on a percolation model was developed to classify propellant formulations. This test has never been contradicted by further experimental evidence. But other incidents or accidents happened later which showed that the model is not sufficient for some practical situations and that the evaluation of the level of sensitivity of a sensitive propellant remains today a difficult problem. After a history of the main events in the field and of the efforts conducted for characterization, testing, and modeling of the sensitivity to electrostatic discharge during the last 25 years, recent findings on the effect of some factors are presented, and some directions for the future are described.

Introduction

The present knowledge on the sensitivity of energetic materials to static electricity is the result of a long history of accidents and of the work conducted to understand their origin and develop safer processes. The phenomena involved are complex and related to several areas of physics and chemistry. The research programs conducted to date have not led to simple laws or models.

The main objectives of this paper are 1) to summarize 25 years of research on the sensitivity of solid propellants to electrostatic discharge; 2) to present some new results and to give some indications on the sensitivity of other types of propellants and parent materials that had not yet been published; and 3) to describe the necessity to conduct some further research with the hope to stimulate possible cooperations.

1976–1978: Incidents and Accidents at SNPE

Until 1976 accidents clearly attributed to a reaction of energetic materials to an electrostatic discharge (ESD) were only related to the reaction of finely divided powders of pyrotechnic compositions. The sensitivity to ESD of these compositions was evaluated with an electric spark test (Fig. 1), which involved a maximum energy of 726 mJ. The principle of testing consisted in the determination of the minimum energy required to observe a reaction of a specimen of a few hundred milligrams of the substance. When solid propellants were developed, this test was naturally adapted to these new compact compositions, which were tested in the shape of a chip or a disk. No pyrotechnic reaction was then observed.

From the end of 1976 to March 1978, six incidents or accidents happened during the production and handling of composite propellant grains at SNPE’s Saint-Médard plant while four others happened at SNPE’s Centre de Recherches du Bouchet. They all involved aluminized propellant formulations, which had passed the spark test with no reaction. Some incidents very clearly involved electrostatic manifestations without ignition of the propellant. In these cases the operator had opened a bag made of polyethylene in which the propellant was kept and was trying to seize a free-standing grain of propellant inhibited by a PVC restrictor. When his finger was close to the grain, an “explosion” with a noise like a loud crack occurred, and fragments of the inhibitor were ejected. A crack in the grain at the precise place where the inhibitor had been ejected was observed. The PVC restrictor and the polyethylene bag were highly resistive, and no equipotentiality between the grain and the operator was realized. All of the formulations involved used hydroxyl-terminated polybutadiene (HTPB) as prepolymer of the binder.

Systematic measurements of the electric charges generated during production and handling of propellant were implemented after these incidents. Significant electric charges were observed on the inhibitors and packing materials. It was possible to record the electric potential accumulated on a mandrel during its extraction: the potential may go up to several thousands Volts at the end of the pullout operation. Thus, a large set of preventive operations and procedures were implemented. These were in fact efficient, such as 1) the use of graphite to improve the conductivity of inhibitors; 2) electrical interconnection; 3) specific procedures for mandrel extraction.

In the field safety preventive procedures cannot provide an absolute warranty. Therefore, in the event of important electric charge generation, a research program was started to understand the behavior of propellants, (particularly of composite propellants) with regard to electric discharges, in order to distinguish sensitive and nonsensitive propellants with the idea, if possible, to use only non-sensitive propellants in applications.

French Test

As we have already explained, at the beginning of the study we had only at our disposal an electric spark test, which had been used for a long time by most of the organizations that had to characterize primary explosive or initiating compositions with regard to static electricity. This test does not result in the ignition of solid propellant specimens regardless of their configurations. However, in this test propellant samples are sometimes perforated in their center after a discharge.

The analysis of these results led us to assume that the ignition of some propellants would be possible should the values of the
following parameters be increased: 1) size of samples (mass effect); 2) duration of discharge in the RC circuit (R is used as the propellants resistance, and C as the capacity applied to the propellant extremities), and 3) energy delivered. In view of the preceding parameters, an experimental apparatus was designed; it is depicted in Fig. 2. The propellant sample to be tested is a cylindrical 90-mm-diam grain, 100 mm long. The grain is located between two electrodes. The positive electrode contact is a point-plane type.

To get an adequate contact and distribution of the electric current, the surface of the propellant grain facing the negative circular electrode is coated with a silver lacquer. To be able to investigate the influence of ambient humidity level, the propellant grain was placed inside a 4 x 10^{-3} \Omega \cdot m volume resistivity Plexiglas chamber. A detailed description of the work conducted was presented by Kent and Rat in 1982.

From this setup and the work then conducted, a standardized test (SNPE No. 37) was derived, which is sometimes called in the U.S. the "French Test."\(^2\)

The conclusions from the work were the following: some propellants react, and the reaction can take two forms, ignition or cracking. In the case of ignition, movie films taken at 200 frames per second show that, during ignition, cracks appear in the propellant. Through the cracks thick bursts of flames are generated. Then the combustion spreads out. In other cases, although no ignition is obtained, large cracks are observed; X rays show that they are consist of a large quantity of small ducts (with a diameter of approximately 0.5 mm).

Nonaluminized propellants never reacted. Propellants with a volume resistivity less than 10^6 \Omega \cdot m did not react to a maximum energy of 15.6 J. Aluminized composite propellants with a volumetric resistivity ranging from 10^6 to 10^8 \Omega \cdot m are likely to react.

Table 1 illustrates the resistivities at 20°C of various binders of composite propellants. It shows that the historical development of these binders resulted in an increase in their insulating nature. It is therefore logical that during the manufacturing processes, which includes handling, friction, and movement of insulating and conductive materials, one would see an increasing number of manifestations of electrostatic phenomena.

The historical development of these propellants was also combined with the development of new insulations and cases materials. Metallic cases, for example, were replaced by highly insulating composite cases that could only aggravate the problems. The Faraday cage effect of the case disappeared, and the propellant became sensitive to outer electric fields.

**Standard Model: The Percolation Coefficient**

For propellants identified as sensitive to capacitive discharges, phenomena such as the occurrence of the cracking before the ignition suggest that the reaction mechanism can be broken down into two essential phases: 1) emergence of a cracking phenomenon, related to a critical potential and 2) emergence of an ignition phenomenon, related to a specific critical energy. All observations tend to demonstrate that the reaction begins inside the propellant. The existence of a critical potential shows that cracking is caused by one or several electric phenomena.

Among those electric phenomena that have been identified, discharges between aluminum particles may be considered as the most likely one:

1) Aluminized compositions alone were found to be insensitive;
2) The volumetric resistivity of pure aluminum powder shows that for a given critical potential the value of resistivity changes from 10^7 to 10^8 \Omega \cdot m. This corresponds to a puncture, for a certain number of particles of the aluminum oxide layer that covers the pure aluminum. An analysis of the active ingredients of propellants essentially revealed the influence of: 1) the percentage, and the particle size and shape of aluminum particles; 2) the particle size of ammonium perchlorate; and 3) the resistivity of the binder. When the aluminum percentage is constant, the decrease in diameter of the aluminum particles leads to an increase in total number and leads to compositions that are more sensitive to capacitive discharges.

A model based on percolation theories was proposed. A "percolation" or breakdown percolation coefficient \( P \) was identified, such that

\[
P = N_r / N_i / C V_0
\]

**Table 1 Typical volumetric resistivities at 20°C of the major binders of composite propellants and of some insulating materials**

<table>
<thead>
<tr>
<th>Nature</th>
<th>Resistivity, ( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether polyurethane binder</td>
<td>( 6 \times 10^6 )</td>
</tr>
<tr>
<td>Carboxy Terminated Polybutadiene binder</td>
<td>( 7 \times 10^6 )</td>
</tr>
<tr>
<td>HTPB binder</td>
<td>( 2 \times 10^{12} )</td>
</tr>
<tr>
<td>PVC inhibitor</td>
<td>( 10^{12} )</td>
</tr>
<tr>
<td>Thermal insulation rubber</td>
<td>( 10^{12} )</td>
</tr>
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</table>

Fig. 1 Schematic arrangement of a test by electrostatic spark.

Fig. 2 Schematic arrangement for the capacitance discharge test.
where $C_b$ is the conductivity of the binder, $V_b$ the unit volume of the binder, $N_c$ the number of conductive particles (aluminum), and $N_i$ the number of insulating particles (ammonium perchlorate, HMXX).

The risk of being sensitive is higher when the value of $P$ is higher. For a nonaluminized composition $P = 0$. With ammonium perchlorate (insulating particles) the influence of the particle size is inverse to what it is for aluminum. In addition, the volumetric resistivity measurements of binders have demonstrated that the polyurethane binder with a polyether prepolymer base is the least resistive. Polytetrafluoroethylene binders, on the contrary, are much more resistive. $P$ has the dimensions of a resistivity and is expressed in $\Omega \cdot m$. Compositions with values of $P$ higher than $10^{10} \Omega \cdot m$ were always sensitive. Some examples of calculations of the coefficient $P$ are given in Agardograph 316, edited by Boggs and Derr.

The validation of the model, which became in France for some time a "standard model," was conducted over about 50 different formulations. Over some range the criterion was uncertain, but above a certain value of $P$ the formulations are always sensitive and under another value they are always insensitive: compositions with values of $P$ higher than $10^5 \Omega \cdot m$ were always sensitive. Compositions with values of $P$ under $10^3 \Omega \cdot m$ were always insensitive. This model gave directions for new insensitive formulations.

Test No. 37 was systematically performed at SNPE for new compositions—at least at $20^\circ C$. Sensitive compositions were as much as possible eliminated. It was quickly discovered that the total elimination of all sensitive compositions was impossible. In that case adequate dispositions were taken. No other incident was observed for some years.

**Pershing II Accident (1985)**

In January 1985, during a period of severe cold weather in Europe an accident happened on a U.S. Army Base in Germany near Heilbronn during the extraction of a Pershing II Rocket Motor (first stage) from its container during assembly of the missile. This motor had a Kevlar-epoxy (very resistive) composite case. The propellant (mass approximately 4 tons) was an Al-AP-HTPB propellant.

After separation from the container, a movement of the motor led to a contact with some type of metallic container part. According to witnesses, the motor then caught fire and burned. The ignition occurred inside the propellant grain with a totally abnormal combustion, which resulted in a rupture of the case and ejection of the rear part of the motor. The igniter was recovered in an unconfined condition.

Because it happened in Germany and because the Pershing II deployment was at that time a very important strategic issue (it was just after the so-called crisis of the "Euromissiles"), it became a major political issue. The accident was announced, but without any details in newspapers all over the world. At the end of January, SNPE began to receive at Le Bouchet Research Center (Ralph Kent) and at the Saint-Medard plant (Roger Rat) some phone calls from the Martin Marietta and other organizations that were asking for some details on SNPE's experience and on the work described in the Kent and Rat paper of 1982. The authors soon discovered that a very impressive investigation team had been assembled in the U.S., which after a systematic analysis had eliminated nearly every possible cause except for static electricity. At the middle of February 1985, Ron Derr and Bert Sobers of the U.S. Navy, who were involved in a Data Exchange Agreement between France and the U.S. that Ron had initiated, called and asked if we could come to the U.S. to present in detail the accidents that had occurred at SNPE in the past, as well as the investigations we had conducted and the scenarios we had developed.

A team from SNPE composed of Roger Rat, Jean Goliger, Bernard Keller, and Alain Davenas was constituted. The U.S. investigation team and the SNPE team met for two days via a meeting organized by Bill Stephens at Military Command in Huntsville, Alabama. It is our opinion that at the beginning of the meeting only 50% of the U.S. team members were really convinced of the ESD origin of the accident. At the end probably more than 95% of the attendees were convinced. Among some of the conclusions of the meeting was the decision to test the sensitivity to ESD of the Pershing II propellant using a test similar to the French test. In fact, in order to save time it was asked if the test could be performed on SNPE's Research Center of Le Bouchet test setup, under the guidance of SNPE but by U.S. personnel (in fact two engineers of Martin Marietta).

The tests were conducted in March. During the first two days of experimentation, at ambient temperature no reaction of the samples was observed. Then the samples were preconditioned at the temperature estimated for the propellant when the accident happened ($-12^\circ C$). An immediate ignition was observed.

After many other tests in the U.S., including a "scale one" test, the final scenario advanced by the investigation team was that during the separation of the rocket motor from the rubber pads, static charges were created on the surface of the very resistive case at a specific location through rupture of contact and/or triboelectricity. The charges in the cold and dry environment conditions and because of the high resistivity of the material could not dissipate. This gave rise to considerable electric fields in the propellant and to a discharge in the propellant between the rear "charge patch" and the conductive parts of the metallic assembly in contact, which created a grounding.

Modifications of the motors were later implemented to restore a good margin of safety. Among these was the application of a conductive paint on the metallic parts to reduce some Faraday cage effect, a measure that had been already implemented by SNPE since 1980 on the French M4 SLBM.

**Peacekeeper Accident (1988)**

The increase in the sensitivity to ESD caused by the lowering of the temperature of the propellant could have been in fact predicted—at least qualitatively—through the percolation coefficient because the resistivity of the propellant increases when the temperature is decreased. The occurrence of another accident in 1988, again involving an HTPB propellant, showed among many other lessons the serious limitations in the modeling of propellant ignition through ESD with the percolation coefficient. The analysis done by Thiokol showed a very significant effect of pressure and/or confinement on the level of sensitivity of the propellant.

The following description of the work conducted at Thiokol is a direct citation of a publication by Magann et al.: The propellant ignition and resulting catastrophic fire of the Peacekeeper (PK) (PK-322) first stage motor resulted in extensive hazards testing being performed. Isolated stimuli such as friction or electrostatic discharge (ESD) failed to explain the cause of the ignition in that the stimulus levels required to initiate TP-H1270C propellant combustion are much more severe than those that would conceivably be experienced in extracting a PK first stage core. Largely as a result of these findings, hazards testing was initiated combining ESD, sliding friction, and pressure/confined in order to explore any synergistic effects which might exist. The testing was designed to simulate real world scenarios, specifically a worst-case scenario of the PK core/fin former dovetail interfaces, which is where the PK-322 ignition is thought to have originated. At this location thin ribbons of propellant penetrated the dovetail gaps, became sandwiched between the hard surfaces and experienced simultaneous pressure, sliding friction, and triboelectrically induced charge build-up on the ungrounded fin former when the core was extracted. The objectives of the combined stimuli propellant hazards testing were to determine the sensitivity of the TP-H1270C propellant to combined friction and confined electrostatic stimuli, and to establish minimum propellant ignition ESD/voltage levels as functions of pressure, propellant thickness, friction and confined surface materials. In addition, the sensitivity of PK bulk cast propellant was to be compared to propellant residue removed from the cores of PK motors.

Ignition was obtained with very thin specimens, and a very strong influence of pressure was observed. Energies as low as 13.5 mJ were sufficient to obtain a reaction at 80 bars. The confinement of the specimen tested had eventually to be maintained for some time to sustain a combustion.

Experimental work conducted at SNPE on a 68% AP 20% Al HTPB propellant has shown that for a thickness of 1 mm the
breakdown tension under a pressure of 10 MPa is divided by 15 (30 to 2 K) compared to what is measured in test No. 37. Some analogy can however be made between the reaction of small confined samples and the reaction in the internal confinement obtained “naturally” inside the big specimen used in SNPE’s test. This work was not reported in the open literature. The same type of work was apparently also conducted in the U.S. by Hodges and MacCoy, but the results appeared only in Chemical Propulsion Information Agency publications with limited distribution.

This work induced another experimental program to study the influence of pressure on larger samples at the Philips Lab, which confirmed the influence of pressure also on massive specimens. The same type of program conducted at SNPE gave very clear results for a 68/20 propellant as shown in Table 2.

**Table 2 Sensitivity vs pressure at two ambient temperatures of a 68% AP, 20% Al, HTPB-based propellant**

<table>
<thead>
<tr>
<th>Pressure, MPa</th>
<th>0.1</th>
<th>1</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>5 J</td>
<td>760 mJ</td>
<td>—</td>
<td>340 mJ</td>
</tr>
<tr>
<td>~20°C</td>
<td>460 mJ</td>
<td>460 mJ</td>
<td>230 mJ</td>
<td>80 mJ</td>
</tr>
</tbody>
</table>

Some Recent Findings

Most of the experimental research had been done on HTPB propellants in a range of solids from 88 to 90% with moderate rates of combustion. Because propellants with high rates of combustion like those obtained with ferrocene derivatives exhibit higher sensitivity to many stimuli (temperature, shock, friction) SNPE conducted an experimental research program on his type of propellants, which showed extreme sensitivity at low temperature (−50°C) and under high pressure (15 MPa) for some propellants.

Other types of pyrotechnic materials like pressed or cast compositions with high level of magnesium used as flares also shown a sensitivity to ESD through the same type of electrical breakdown. It was observed in this case that the size of the sample used for characterization of the sensitivity has nearly no influence.

**Present Knowledge on Mechanism of Initiation of Composite Propellants by Static Electricity**

Percolation theory as applied after the incidents at SNPE to the modeling of initiation of aluminized composite propellants by an electric discharge has been fruitful. The percolation coefficient based on this model explains the variations in the behavior of various propellant formulations. It constitutes a first tool for an a priori evaluation of a new formulation and a guide for decisions to be taken to reduce or if possible suppress the sensitivity.

The critical values of this coefficient have been built empirically, taking into account in the simplest possible way identified parameters of influence known in percolation phenomena mechanisms. However this coefficient is very limited in the way it models the ignition phenomena. By construction it deals only with the electrostatic discharge in the material, which is only the first step of the initiation process. It does not take in account the thermodynamical and mechanical conditions for the propagation and maintenance of the reaction. In the first “electrical” step of the initiation process, important factors like the shape and morphology of aluminum particles, the geometry of the aluminum oxide layer, and the distribution of aluminum particles in the AP-binder matrix are neglected.

The effect of temperature is only taken in account through the variation of conductivity of the binder. The influence of this factor through the mechanical properties of the propellant is not considered (the influence of mechanical properties was in fact initially ignored).

Finally, this first model does not explain the necessity of a sample of a significant size to obtain a truly discriminating response to the test.

Later, as explained before, informations obtained through the research work conducted to understand the accidents where ESD was involved enabled a more thorough identification of the parameters of influence. They allowed the introduction of thermodynamic factors that control the propagation of a local initiation, like the influence of temperature and later the influence of confinement (which had also certainly a role in the case of the Pershing II and in the case of ignitions or cracks under the inhibitor of free-standing grains observed at SNPE). All observed facts can now be qualitatively described in a coherent way.

**Effect of the Size of the Specimen and of Mechanical Properties on the Efficiency of SNPE Test 37**

Combustion always starts in the heart of the specimens, never on the surface. At atmospheric pressure the internal confinement necessary to develop a “hot spot” as a starting point of the combustion is increased by the size of the specimen. Also a propellant with higher mechanical properties should be easier to ignite (to our knowledge no uncured propellant has ever been found sensitive).

**Effect of the Temperature**

Through the percolation coefficient and the mechanical properties’ evolution a lowering of the temperature will increase the sensitivity of the propellant.

**Quality of the Aluminum**

Propellants with spherical aluminum particles are less sensitive than propellants with particles of irregular shape of the same average particle size. The regularity of the alumina layer over the aluminum particles is important. These two factors will influence the percolation threshold.

**Combustion Accelerators and High Rate of Combustion**

These accelerators through a lowering of the thermal sensitivity will increase the ability of the propellant to react to a hot spot formed by an electrical breakdown.

**Magnesium Compositions**

These compositions are designed for an operation at atmospheric pressure. Contrary to most rocket propellant compositions, good conditions for the propagation of combustion exist already at this pressure, and this will not change much with an increase in pressure.

**Aussois Seminar, Other Modeling Efforts, and the Future**

The percolation model has not been contradicted by new findings over 25 years. During this time, simulations and computing power have rapidly increased, which allowed some significant progress in the modeling. A synthesis of the work in progress in France at various universities, national laboratories, and laboratories of companies was presented and discussed in 1996 at a seminar held in Aussois in the French Alps.

Five areas were covered during the seminar: 1) sensitivity of solid and liquid materials, 2) sensitivity of systems and components, 3) mechanisms of initiation, 4) simulation of electric breakdown, 5) standards and specifications.

Among many interesting presentations we will mention a review by Rat et al. of the present knowledge of the sensitivity to ESD of energetic substances as a function of their nature and physical state and the works of Giraud et al. and Robin and Souillard on electrical models of composite materials including the effect of possible aggregation of aluminum particles. Four round tables and many debates showed that the community is still very far from being able to model accurately the behavior of our materials under electric and electromagnetic fields. Even at the start of the reaction (a shock or a hot point like we implicitly assumed in this paper), there were very strong discussions.

We could recently, with the help of Susan Peters of Naval Surface Warfare Center Indian Head, learn that evidence in favor of the thermal initiation model has been shown in an experimental work conducted by R. J. Lee. More generally his report on the ignition of solid energetic materials as a result of ESD discusses most of the modeling efforts conducted in the U.S. to go in the directions we underlined before.
Conclusions

Directions for future research are quite well defined. It is clear that we must still be very careful and consider that we have a limited knowledge of the subject of sensitivity of energetic materials.

One particularly important point is, of course, the validity of the test used to characterize the sensitivity of a propellant, in our case: test No. 37. This test in its nominal version gives only an answer by yes or no. The experience of 20 years of use shows that it has never been contradicted by further experimental evidence. This feeling of reliability of the test could be in fact reinforced by testing propellant formulations found nonsensitive but having a percolation coefficient in the intermediate range between sensitive and insensitive in conditions leading to easier initiation (elevated pressure, low temperature).

Since the beginning, this test has been designed to separate sensitive and nonsensitive formulations for control of safety in production and handling. The idealistic first idea to develop and use only insensitive propellants was impractical. It is also clear to the authors that sensitive propellants may have various level of sensitivity. Today’s knowledge should allow the development of a new test to characterize levels of sensitivity. It would be applied under pressure, at a level sufficient to reduce the variations in mechanical and thermodynamical properties of the propellants tested.

In conclusion we are convinced that the fact that a propellant is sensitive or not is an intrinsic characteristic, whereas the level of sensitivity is a function of many factors: great care must be applied in the utilization of sensitivity data in the analysis of risks in the production of motors.

References
