Ballistic Properties of Scavenged Solid Rocket Propellants

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ABSTRACT

Ignition and steady burning of scavenged composite solid rocket propellants were experimentally investigated at the Solid Propulsion Laboratory of Politecnico di Milano, using a variety of strand burners. The unusual ignition behavior of some of these compositions, tailored for burning at low burning rates and relatively low chamber pressures (11 to 35 atm), was found to be associated with a peculiar multiphase flame structure. Video recording of ignition and steady burning tests of the scavenged compositions revealed the presence of a scattered liquid film and the formation of large spherical particles at the reacting surface layer, which hindered a smooth flame development. A break in the slope of burning rate vs. pressure plots was observed for the scavenger compositions. The break, occurring at pressures above 50 atm for one composition and above 25 atm for another composition, appears to be due to different combustion regimes. In the low pressure region, the burning rate is determined by the NOx oxidation reactions; in the high pressure region, ClOx oxidation reactions prevail.

NOMENCLATURE

Latin Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>I&lt;sub&gt;sp&lt;/sub&gt;</td>
<td>specific impulse, s</td>
</tr>
<tr>
<td>I&lt;sub&gt;vol&lt;/sub&gt;</td>
<td>volumetric specific impulse, s g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>n</td>
<td>Vieille law pressure exponent</td>
</tr>
<tr>
<td>p</td>
<td>pressure, atm</td>
</tr>
<tr>
<td>q</td>
<td>radiant heat flux, W/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>R</td>
<td>correlation coefficient</td>
</tr>
<tr>
<td>r&lt;sub&gt;b&lt;/sub&gt;</td>
<td>burning rate, cm/s</td>
</tr>
<tr>
<td>t</td>
<td>time, s</td>
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Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AP</td>
<td>Ammonium Perchlorate, NH&lt;sub&gt;4&lt;/sub&gt;ClO&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>E00</td>
<td>propellant, reference composition</td>
</tr>
<tr>
<td>E101</td>
<td>propellant, scavenged composition No. 1</td>
</tr>
<tr>
<td>E125</td>
<td>propellant, scavenged composition No. 2</td>
</tr>
<tr>
<td>HTPB</td>
<td>Hydroxyl Terminated PolyButadiene</td>
</tr>
<tr>
<td>N</td>
<td>number of experimental runs</td>
</tr>
<tr>
<td>SN</td>
<td>Sodium nitrate, NaNO&lt;sub&gt;3&lt;/sub&gt;</td>
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1.0 BACKGROUND

Although the environmental impact of chemical rocket propulsion is overall negligible[1], during the last few years attention has focused on ammonium perchlorate (AP)-based propellants with the intent of improving the performance whilst reducing the hydrogen chloride HCl fraction in the exhaust products. New strategies in the development of “energetic” and “clean” solid compositions include a variety of options spanning from

propellants containing chlorine scavengers to chlorine neutralizers to energetic oxidizers. Chlorine scavenging formulations, whereby AP is partially replaced by sodium nitrate \( \text{NaNO}_3 \) (SN), are the closest to the relatively well-known class of conventional AP/HTPB composite propellants commonly used by the propulsion industries. This technique, leading to a large fraction of \( \text{HCl} \) scavenged directly in the combustion chamber, to form the common \( \text{NaCl} \) salt, allows a good compromise between performance, cost, safety, reliability, and enhanced environmental protection.

For many years FiatAvio has been investigating several innovative classes of propellants\textsuperscript{[2,3]}. Novel formulations were developed and fully characterized to address different applications of solid rocket motors. In particular, compositions containing different amounts of aluminum, binder, and AP/\( \text{NaNO}_3 \) were qualified at the laboratory and motor firing levels. Excellent results were achieved for propellant compositions burning at relatively high pressures (say, above 40 atm), leading to small-scale and full-scale motors with a scavenging effect in the range of 50 to 75\% (see Table 1)\textsuperscript{[4]}. Several motor configurations were tested. Most runs were performed in a standard 2 inches small-scale test motor; MTM is a special small-scale motor used to test propellants, thermal protections, and nozzles; E00 data are for a full-scale motor. Combustion chamber pressures cover a range from 45 to 200 atm (from E-2”-2012 to E00) and related burning rates could be tailored for the proper motor requirements. Burning rates higher than 0.6 cm/s were obtained with high gas flows in side-burning motor configurations; only one end-burning propellant grain, E-MTM-2, was fired. All of the tested motors ignited regularly and burned uniformly, featuring a pressure/time plot in agreement with the corresponding motors, using the conventional propellants.

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Al (%)</th>
<th>Binder (%)</th>
<th>Scavenging Effect* (%)</th>
<th>Chamber Pressure (atm)</th>
<th>Burning rate** (cm/s)</th>
<th>Propellant mass (kg)</th>
</tr>
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<tbody>
<tr>
<td>E-2”-2012</td>
<td>20</td>
<td>12</td>
<td>70</td>
<td>45</td>
<td>0.743</td>
<td>0.4</td>
</tr>
<tr>
<td>E-2”-2013</td>
<td>20</td>
<td>13</td>
<td>70</td>
<td>50</td>
<td>0.875</td>
<td>0.4</td>
</tr>
<tr>
<td>E93</td>
<td>1</td>
<td>14</td>
<td>75</td>
<td>100</td>
<td>2.13</td>
<td>0.4</td>
</tr>
<tr>
<td>E93</td>
<td>1</td>
<td>14</td>
<td>75</td>
<td>200</td>
<td>3.138</td>
<td>0.4</td>
</tr>
<tr>
<td>E91</td>
<td>1</td>
<td>14</td>
<td>55</td>
<td>100</td>
<td>2.180</td>
<td>0.4</td>
</tr>
<tr>
<td>E91</td>
<td>1</td>
<td>14</td>
<td>55</td>
<td>200</td>
<td>3.172</td>
<td>0.4</td>
</tr>
<tr>
<td>E-MTM-1</td>
<td>20</td>
<td>12</td>
<td>50</td>
<td>45</td>
<td>0.780</td>
<td>6.5</td>
</tr>
<tr>
<td>E-MTM-2</td>
<td>20</td>
<td>12</td>
<td>50</td>
<td>45</td>
<td>0.810</td>
<td>7.0***</td>
</tr>
<tr>
<td>E-81</td>
<td>1</td>
<td>14</td>
<td>75</td>
<td>100</td>
<td>2.20</td>
<td>≈ 8.0</td>
</tr>
<tr>
<td>E00</td>
<td>5</td>
<td>14</td>
<td>-</td>
<td>100</td>
<td>2.00</td>
<td>≈ 60</td>
</tr>
<tr>
<td>E101</td>
<td>4</td>
<td>14</td>
<td>75</td>
<td>15</td>
<td>0.530</td>
<td>0.4</td>
</tr>
<tr>
<td>E125</td>
<td>4</td>
<td>14</td>
<td>75</td>
<td>15</td>
<td>0.460</td>
<td>0.4</td>
</tr>
</tbody>
</table>

* Computed reduction of \( \text{HCl} \), at nozzle exit with \( p = 1 \text{ atm} \), wrt the corresponding conventional propellant.

** Burning rate suitably tuned within the required range at the operating pressure.

*** Motor configuration is end-burning, while all other configurations are side-burning.
Due to the higher density of SN as compared to AP and depending upon formulation, a small increase (1-2%) in the volumetric specific impulse can be achieved by using scavenged propellant, even if the delivered specific impulse decreases a little bit (see Table 2)\textsuperscript{[3,4,5]}. Moreover the costs (raw material and manufacture) of scavenged compositions is essentially the same of conventional composite propellants\textsuperscript{[5]}. Thus, the scavenging technique produces a good compromise between performance, cost, safety, reliability, and enhanced environmental protection.

### Table 2: Impulse of Scavenger Propellants (Taken from Ref. 3)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Al/Binder (HTPB)</th>
<th>AP/NaNO\textsubscript{3}</th>
<th>\textit{I}_\text{sp} (s)</th>
<th>\textit{I}_\text{vol} (sgcm\textsuperscript{-3})</th>
<th>HCl (%)</th>
</tr>
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<tbody>
<tr>
<td>Ariane V</td>
<td>18/14</td>
<td>68/-</td>
<td>265.3</td>
<td>464.7</td>
<td>21</td>
</tr>
<tr>
<td>1814scav1</td>
<td>18/14</td>
<td>32/29</td>
<td>244.4</td>
<td>443.7</td>
<td>1.4</td>
</tr>
<tr>
<td>1814scav07</td>
<td>18/14</td>
<td>50/18</td>
<td>252.3</td>
<td>451.8</td>
<td>8.4</td>
</tr>
<tr>
<td>1814scav05</td>
<td>18/14</td>
<td>54/14</td>
<td>255.0</td>
<td>454.3</td>
<td>10.5</td>
</tr>
<tr>
<td>2013scav1</td>
<td>20/13</td>
<td>36/31</td>
<td>244.8</td>
<td>457.1</td>
<td>1.9</td>
</tr>
<tr>
<td>2013scav07</td>
<td>20/13</td>
<td>49/18</td>
<td>249.8</td>
<td>462.2</td>
<td>5.4</td>
</tr>
<tr>
<td>2013scav05</td>
<td>20/13</td>
<td>53/14</td>
<td>253.7</td>
<td>465.9</td>
<td>9.2</td>
</tr>
<tr>
<td>2012scav1</td>
<td>20/12</td>
<td>32/29</td>
<td>244.2</td>
<td>461.0</td>
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<td>2012scav07</td>
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<td>50/18</td>
<td>249.7</td>
<td>467.1</td>
<td>5.4</td>
</tr>
<tr>
<td>2012scav05</td>
<td>20/12</td>
<td>54/14</td>
<td>254.3</td>
<td>471.6</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Reduced aluminum content compositions tailored for burning at low burning rates and chamber pressures, say in the range of 11 – 35 atm, showed however some anomalies in terms of ignition and burning behavior under small-scale motor testing. All propellant formulations are multimodal in AP and monomodal in the scavenging agent. Two of these specific compositions, respectively called E101 and E125, are reported as the last two entries in Table 1. Tests at the motor level conducted by FiatAvio showed unexpected pressure/time combustion profiles. A detailed testing of transient and steady burning of E101 and E125 was subsequently conducted at the Solid Propulsion Laboratory of Politecnico di Milano, over the same range of operating conditions. In order to obtain a better understanding, experimental results were compared with those obtained from a reference or base-line composition called E00 (a conventional AP/HTPB composite propellant containing about the same Al fraction), even if the combustion requirements of E00 (high burning rate and high pressure) are drastically different from those of E101 and E125. The measured densities of the three composite propellants under examination were found to be:

- 1.679 ± 0.009 g/cm\textsuperscript{3} for E00;
- 1.743 ± 0.024 g/cm\textsuperscript{3} for E101;
- 1.740 ± 0.009 g/cm\textsuperscript{3} for E125.

The objective of this paper is to report the findings of the experimental investigations on transient and steady state burning measurements for the above compositions.
2.0 LABORATORY EXPERIMENTAL INVESTIGATIONS

Radiative ignition was tested by means of a continuous wave, closed circuit water-cooled, CO₂ laser with 200 W maximum power output and 11 mm beam diameter (1/e² Gaussian beam). Full opening of the mechanical shutter required about 3 ms. The resultant thermal flux impinging on the surface samples was in the range of 100 to 500 W/cm². Testing was performed in the combustion chamber depicted in Fig. 1, over the range of 11 to 35 atm of nitrogen, with an internal chamber volume of 2.8 lt. A small brass dish was set under the propellant sample to collect the combustion residues. The residues were analyzed by scanning electronic microscopy (SEM).

This kind of apparatus[6,7] is becoming rather common nowadays thanks to its easy control of the ignition stimulus (both in terms of the energy flux and the exposure time). Data concerning the appearance of the first flame and its development were systematically collected using a standard infrared (IR) photodiode. The latter has a view angle of 30° and a spectral sensitivity in the range of 0.35 to 1.1 µm with maximum response at 0.8 µm. The photodiode’s, 5 mm² active surface, was placed in front of the combustion chamber at a distance of about 70 mm from the propellant sample. In addition, a high-speed color video camera (up to 2000 frames/s) was systematically used to supplement or corroborate the IR photodiode information. The pressure was monitored/controlled with a piezoresistive transducer, 20 kHz natural frequency and 68 atm full scale, calibrated before testing and mounted flush with the chamber wall. Propellant samples consisted in parallelepipeds, 3.5 x 3.5 mm² in cross-section and 5 mm in thickness. The burning surface was freshly cut and no lateral surface inhibitor was used. All runs were performed in a nitrogen atmosphere at ambient temperature. The measured ignition delay, defined as the time of first appearance of the flame from the shutter opening, was reported in a standard time (t) vs. radiant flux intensity (q) bilogarithmic plot. The total error in measuring the ignition delay has been estimated[8] to be smaller than 1 ms.

Ignition testing, with at least five runs at each investigated point, was performed under both continuous and go/no-go radiation. As expected[9,10], no difference could be detected as far as the first flame appearance is concerned. However, experimental results point out a relatively large scattering of the data probably due to the heterogeneity of the propellant samples and multiphase effects at the burning surface layer. The complete set of results obtained for the investigated compositions were reported[8] in a previous work. Figure 2 shows the ignition delays measured at 35 atm. Best linear fitting laws were used to find the associated log t vs. log q plots by a least squares method. The latter are reported below, along with the correlation factor R and the total number of experimental points N. For all the tested compositions, the slope of the straight lines of the
The log $t$ vs. log $q$ plot is much larger than the theoretical -2 value, as commonly found for AP-based composite propellants irradiated with a CO$_2$ laser, essentially due to radiation penetration. In summary, the following results were obtained for the time of first flame appearance ($t$ being in s and $q$ in W/cm$^2$):

at 11 atm

- E00: $t_{ign} = (39.79 \pm 9.870) \cdot q^{-1.262 \pm 0.046}$, $R^2=0.969$ N=50
- E101: $t_{ign} = (65.29 \pm 18.42) \cdot q^{-1.336 \pm 0.050}$, $R^2=0.980$ N=15
- E125: $t_{ign} = (46.04 \pm 16.27) \cdot q^{-1.271 \pm 0.065}$, $R^2=0.953$ N=20

at 25 atm

- E00: $t_{ign} = (43.21 \pm 10.80) \cdot q^{-1.282 \pm 0.047}$, $R^2=0.969$ N=25
- E101: $t_{ign} = (58.72 \pm 12.17) \cdot q^{-1.314 \pm 0.037}$, $R^2=0.989$ N=15
- E125: $t_{ign} = (45.19 \pm 16.10) \cdot q^{-1.281 \pm 0.065}$, $R^2=0.953$ N=40

at 35 atm

- E00: $t_{ign} = (71.83 \pm 17.58) \cdot q^{-1.381 \pm 0.045}$, $R^2=0.980$ N=20
- E101: $t_{ign} = (42.96 \pm 10.48) \cdot q^{-1.252 \pm 0.044}$, $R^2=0.983$ N=15
- E125: $t_{ign} = (51.31 \pm 17.16) \cdot q^{-1.308 \pm 0.063}$, $R^2=0.948$ N=25

Figure 2: Ignition Results for the Tested Propellants under 35 atm of N$_2$. 
The ignition delay times (in terms of the first flame appearance) can be considered similar for all tested compositions; only slightly shorter for the reference composition E00.

For all three tested compositions the influence of the pressure appeared negligible, as shown in Fig. 3 for propellant E101. Likewise, ignitability is similar for all tested compositions and only slightly easier for the reference composition E00; see Fig. 4 for propellants E125. In summary, the ignition delay (in terms of time of first flame appearance) and ignitability, features common trends for all tested compositions and therefore cannot explain the poor performances under the small-scale motor testing manifested by E101 and E125 with respect to E00.

A second series of tests was carried out in the same ignition apparatus, see Fig. 1, to try to elucidate the transient flame development from the appearance of the first flamelet to full flame development, rather than just detecting the first flame appearance. Although it has been known for a long time that flame development during ignition transients can follow a wide range of patterns leading to all sorts of combustion pathologies\[6-12,13\], this is usually not a problem for motor applications due to the implementation of well-behaved propellants under well-controlled operating conditions. However, in this instance, detailed visual analyses immediately confirmed a scattered occurrence of the first flame with the formation of hot spots on the burning surface, likely due to the combined effect of non-uniform laser heating and heterogeneous mixture composition, as clearly manifested from the experimental results reported in Fig 2. Surprisingly, both the high-speed color video camera and the IR photodiode also revealed a flame development which is sluggish in time and erratic in space for E101 and E125 as compared to the reference composition E00, see Fig. 7-5. Results obtained under continuous irradiation at 11 atm are reported in Fig. 5; flame development is obviously even slower under go/no-go testing (see E125 at 11 atm in Fig. 5). The overall flame structure appears typical of compositions with low aluminum content for E00, but strongly irregular and heterogeneous for E101 and E125.

![Figure 3: Ignition of Propellant E101 under 11, 25, and 35 atm of N₂.](image-url)
A third series of experiments was conducted, under steady-state operating conditions, in a windowed Crawford burner to verify if and how the sluggish flame development observed for compositions E101 and E125 under ignition would affect the steady-state burning. Testing was performed in a different combustion
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chamber, 0.8 l of internal volume, under a low nitrogen flow and at ambient temperature. Propellant samples were placed over a small brass dish allowing the collection of some solid combustion residues. The residues were subsequently analyzed by infrared spectroscopy to obtain some qualitative data about their chemical composition. Pressure was controlled by a pneumatic feedback system. At least three runs were performed at each investigated point and five readings were obtained at each run. Propellant samples consisted in parallelepipeds about $3.5 \times 3.5$ mm$^2$ in cross-section and 30 mm in thickness, with a freshly-cut burning surface and a lateral surface inhibitor. Ignition was initiated with a hot Nichrome wire. Burning rate measurements were carried out by analyzing the digital video records. The total error in burning rate measurements was estimated to be about 0.5%. While it was possible to burn the reference composition E00 at a steady rate from 70 atm down to 1 atm, E101 and E125 could not be burnt steadily below respectively about 9 and 7 atm. In addition, as shown in Fig. 6, steady burning rates of compositions E101 and E125 were systematically lower compared to the reference composition E00, while exhibiting a relatively larger pressure exponent. Compositions E101 and E125 show a break in the pressure exponent located respectively at 50 and 25 atm, in both cases the pressure exponent values decreased from about 0.8 to 0.5 and 0.65 respectively, approaching values of 0.48 measured for the reference composition E00. In summary, the following results were obtained for steady burning rates ($r_b$ being in cm/s and $p$ in atm):

\[
\begin{align*}
E00 & \quad r_b = (0.149 \pm 0.003) \cdot p^{0.480 \pm 0.007} & R^2=0.991 & N=21 & p= 1-70 \text{ atm} \\
E101 & \quad r_b = (0.035 \pm 0.002) \cdot p^{0.791 \pm 0.016} & R^2=0.994 & N=15 & p= 11-50 \text{ atm} \\
E101 & \quad r_b = (0.106 \pm 0.010) \cdot p^{0.504 \pm 0.024} & R^2=0.985 & N= 9 & p= 50-70 \text{ atm} \\
E125 & \quad r_b = (0.029 \pm 0.001) \cdot p^{0.821 \pm 0.018} & R^2=0.996 & N= 12 & p= 11-25 \text{ atm} \\
E125 & \quad r_b = (0.049 \pm 0.001) \cdot p^{0.652 \pm 0.007} & R^2=0.998 & N= 18 & p= 25-70 \text{ atm}
\end{align*}
\]

**Figure 6: Steady Burning Rates of Tested Propellants.**
The solid residues collected both during ignition and steady burning tests primarily consisted of big spherical particles, about 100 \( \mu \text{m} \) in diameter. The simple collection technique implemented most probably did not allow the collection of smaller particles. Particles from the ignition tests were analyzed by SEM microscopy, see Fig. 8. The particles had a relatively smooth external surface, with the interior of some of the broken particles showing a porous and coral like structure. The SEM observations also allow analysis of the surface composition in terms of the elemental chemical species, see Fig. 9, indicating that for the scavenged propellant the residue surface is mainly composed of Na, Cl, with some traces of Al. Analyses conducted by infrared spectroscopy show the presence of the NO3 and NO2 functional groups, likely derived from the thermal decomposition of SN. No differences could be observed between the combustion residues of propellants E101 and E125. Video recordings show that the residues originate from the liquid layer, which partially covers the burning surface, and seems to originate at the burning surface, or just below it, from the melting/decomposing SN. Droplets appear in the liquid layer and grow in dimensions, as combustion proceeds, until ejected from the burning surface. The growth is due to agglomeration with other droplets and to collection of material from the liquid layer. Sometimes a “small explosion” with both a luminous flash and the ejection of small luminous particles (likely burning Al) from the surface layer, accompanies the droplets ejection. Bigger particles appear to be liquid just prior to impact on the collection dish; as a matter of fact, the impact side of the big residues is flat. Also, from the ignition video records, it was observed that the diameter of the residues decreases as either the pressure or the radiant heat flux increases.
Figure 8: Combustion Residues of Propellant E101 observed by SEM. A Qualitative Chemical Composition of Region 1 and 2 is Shown Fig 9.

Figure 9: Qualitative Chemical Composition of Residues Surface, Region 1 (left) and Region 2 (right) of Fig. 8, obtained by SEM Microscopy.
3.0 DISCUSSION OF RESULTS

The effect of pressure and composition was found to be negligible, under the investigated set of operating conditions. Overall, ignition delays of the tested compositions fall in the general class of AP-based composite propellants\(^6,7,14,15,16\). However, this may be misleading for practical applications. Detailed visual observations and testing under a variety of operating conditions revealed a slow time development and non-uniform spatial propagation of E101 and E125 flames compared to the baseline E00. Likewise steady burning rates of E101 and E125, with and without laser radiation assistance, are decreased compared to the baseline E00. The difference decreases with either increasing pressure or increase in the radiant flux. A much larger value of the pressure deflagration limit (PDL)\(^17\) of compositions E101 and E125 with respect to the reference E00 was observed.

A slope break occurs in the burning rate vs. pressure plots for propellants E101 and E125, while the baseline composition E00 in the range 1-70 atm did not show any, see Fig. 6. A possible explanation of the scavenger composition ballistic behavior has been given by Kondrikov et al.\(^18\). The unusual form of the \(\frac{R_b}{P}\) plot for propellants E101 and E125 is connected with two different forms of burning wave propagation which are related in turn to the presence of two different subsystems in the propellant: subsystem 1 consisting of big particles of SN and AP, and subsystem 2 (called the matrix) which includes HTPB, Al, and small and medium sized particles of AP. At low pressures, the rate of gaseous reactions over the burning surface is low and the reaction layer is relatively thick. The reaction determining the burning rate of the propellant proceeds as an interaction of the overall mass of the reactants in the upper layers of the condensed phase, including the liquid layer, on the one hand, and the first flame zone, on the other. Since the pressure exponent of E101 and E125 is quite high in this pressure region, \(n = 0.8\), it is argued that the reaction proceeds primarily in the kinetic regime, in a well-stirred layer due to molecular diffusion and gas bubble formation.

The chemical reactions, taking place both in the liquid layer and in the hot gas, may be described only in an approximate and generalized form. The elementary steps of this complex sequence of chemical reactions are not fully known, but the main overall processes appear to be the following:

1. \(\text{NH}_4\text{ClO}_4 + \text{NaNO}_3 \rightarrow \text{NaClO}_4 + \text{NH}_4\text{NO}_3 \rightarrow \text{NaClO}_4 + 2\text{H}_2\text{O} + 3/4\text{N}_2 + 1/2\text{NO}_2\)
2. \(\text{NH}_4\text{ClO}_4 \rightarrow \text{ClO}_x, \text{H}_2\text{O}, \text{HCl}, \text{Cl}_2, \text{O}_2\)
3. \((\text{ClO}_x, \text{Cl}_2, \text{HCl}) + \text{NaNO}_3 \rightarrow \text{NaCl} + (\text{NO}_x, \text{H}_2\text{O}, \text{O}_2)\)
4. \(\text{HTPB} \rightarrow \text{Gaseous fuel (hydrocarbons)} + \text{solid carbonaceous residue}\)
5. Fuel + NO\(_x\) \(\rightarrow\) NO + (CO,CO\(_2\), H\(_2\)O, N\(_2\))
6. Fuel + Cl\(_2\) \(\rightarrow\) HCl, Cl\(_2\), CO,CO\(_2\), H\(_2\)O
7. NO + 1/2O\(_2\) \(\leftrightarrow\) NO\(_2\)
8. NaClO\(_4\) \(\rightarrow\) NaCl + 2O\(_2\)

Reaction (1) between solid AP and liquid SN may proceed, in particular, in the reaction zone that defines the burning rate of the scavenged propellant in the low pressure regime. The sodium perchlorate formed in the course of this reaction is a relatively stable solid, and, at low pressures, reaction (1) is just one of the different ways to eliminate the active chlorine oxides from the reaction zone thereby preventing interaction of the chlorine oxides with the fuel. Ammonium nitrate, on the contrary, decomposes quickly at 300-400 °C,
Ballistic Properties of Scavenged Solid Rocket Propellants

giving rise to nitrogen dioxide, the common oxidizer produced from the burning of nitrocompounds and double-base propellants.

Reaction (2) outlines the process of AP degradation. The latter primarily produces the chlorine oxides, ClO\textsubscript{x}, the main oxidizing agents from the burning of AP composite propellants. It also produces HCl, Cl\textsubscript{2}, H\textsubscript{2}O and some O\textsubscript{2}. The chlorine oxides react with the liquid SN (reaction (3)) forming the most important final product, NaCl, and a mixture of nitrogen oxides and Cl\textsubscript{2}. In the case of HCl, acting as a reagent, a small quantity of water is also formed. The reactions of Cl\textsubscript{2} and HCl with sodium nitrate proceed more slowly than the ClO\textsubscript{x} + NaNO\textsubscript{3} reactions, but they also take part in forming the corresponding quantities of NaCl, and, what is especially important, the production of the NO\textsubscript{x} species, in the low pressures burning processes.

The main heat generating reactions are reactions (5) and (6). In the sequence of oxidizing agents that take part in the reactions (5) and (6), the first one, NO\textsubscript{x}, is much less active as oxidizer than the second, ClO\textsubscript{x}. But owing to the reactions (1) and (3), the NO\textsubscript{x} concentration in the liquid and in the first flame under low pressure burning grows, whereas that of the chlorine oxides, as well as chlorine itself, reduces. Moreover, the product of the nitrogen dioxide reaction, nitrogen oxide, may produce NO\textsubscript{2} in the course of reaction (7). Correspondingly, at low pressures, the NO\textsubscript{x} is the oxidizer, which is suggested to be primarily responsible for the rate of heat evolution.

Under higher pressures, the combustion mechanism is drastically changed as compared to the low pressure regime. The flame reactions responsible for the overall burning wave propagation are located in narrow regions, quite close to the surface of the small matrix inclusion sites. In these small flames the reaction of the chlorine oxides with the fuel is completed within the classic framework of composite propellants: the diffusion regime results in the formation of the combustion products, CO, CO\textsubscript{2}, H\textsubscript{2}O, etc. and the chlorine in the form of Cl\textsubscript{2} and HCl, before noticeable quantities of NO\textsubscript{x} evolve in the course of the decomposition of the large SN particles. In the first approximation, only very small concentrations of nitrogen oxides are present in these small flames, and, accordingly, only traces of the reaction (5) are assumed. The burning reactions satisfy the well-known laws of AP/HTPB composite propellants combustion, with the only exception that burning rate is smaller due to cooling effects for the large SN particles.

In the high pressure combustion regime, the layer of liquid mixture of sodium nitrate and sodium chloride has a thickness much greater than the thickness of the flame generated from burning of mixture composed by HTPB and small AP particles. The diameter of the particles is approximately on the order of 0.01 mm and the thickness of the gas-zone where mixing of the gaseous oxidizing agents and fuel completes, is approximately of the same order of magnitude. Presumably, the average thickness of the liquid layer is at least one order of magnitude greater. This offers an additional explanation to the fact that at pressures higher than the transition point, burning of the matrix inclusions may proceed independently and nitrogen oxides would only slightly affect it.

At the same time the thickness of the gaseous layer at low and moderate pressures, where mixing of the oxidizing agents produced by decomposition of the large AP particles is complete, should be about the same order of magnitude as the thickness of the liquid layer on the surface. Consequently, the layer takes part in all of the processes taking place in the burning zone, first of all, generating nitrogen oxides instead of oxides of chlorine as the main oxidizing agents and consequently suppressing the velocity of flame propagation.

Attention has to be placed on the potentially corrosive action of the NaCl product from the scavenging reactions, on the internal walls of the combustion chamber. For this purpose various solutions are being developed. The sodium chloride is potentially corrosive due to the existence of the chlorine in the highly
reactive Cl- ionic state. The chlorine must thus be reduced to a less reactive state. This can take place through reaction with the gaseous combustion products from the propellant burning, to incorporate the chlorine into a less reactive functional group or chemical species. Furthermore, the pressures and temperatures together with efflux of the exhaust fumes can be optimized to increase the expulsion of the sodium chloride and reduce its potential accumulation or deposition on the walls of the combustion chamber.

4.0 CONCLUSIONS

Ignition and steady burning of scavenged composite solid rocket propellants were experimentally investigated at the Solid Propulsion Laboratory of Politecnico di Milano. A digital high speed camera allowed a visual analysis of both the ignition and steady burning tests, revealing a liquid layer flowing over the burning surface originating droplets, and large spherical particles. The liquid layer and particles appear to disrupt the regular gas flow from the burning surface, hindering flame propagation of E101 and E125 compared to E00. A slope change in the burning rate vs. pressure plot was evidenced for the scavenged compositions only. In the high pressure region the pressure exponent decreases to about 0.5-0.65 from about 0.8 observed under low pressure. The suggested explanation for this phenomenon is that two competing processes participate in defining the propellant burning rate at low and moderate pressures, reactions (3) and (5), on one side, and reactions (2) and (6), on the other. The first pair of reactions is responsible for the propellant burning at lower pressures whereas the second pair, reactions (2) and (6), are more effective at higher pressure where ClO$_x$ is evolved immediately near the burning surface. Under high pressures, where the high temperature zone is close to the surface, reaction (6) taking place in the diffusion regime becomes a dominant factor of the process as a whole. In addition, effects of regression rate and extent of reaction for the participating large sodium nitrate particles at different pressures need to be considered.

One of the results which is apparent from this model and which seems useful for practical applications, consists in the fact that one may move the transition point toward lower pressures by just increasing the volume fraction of the HTPB/AP/Al matrix in the overall mixture. This might be achieved by increasing the mass fraction of the small and/or medium particles of AP. It might be useful to vary also the sodium nitrate particle size. For this purpose, future tests will be conducted with different sodium nitrate particle sizes.

From the point of view of performance, scavenged propellant are comparable to conventional AP-based composition. Due to the higher density of SN as compared to AP a slight increase in the volumetric specific impulse can be achieved, while a small loss in the specific impulse has to be paid[3,4]. By using scavenged propellant a reduction of HCl emission can be achieved[3,4] up to 75%. Being SN a cheap raw material and being the propellant manufacture essentially the same of AP-based composite propellants, the cost of scavenged composition is equivalent to the cost of classical composite propellants[5].

Finally, attention has to be placed on the potentially corrosive action of the NaCl on the internal walls of the combustion chamber.

5.0 ACKNOWLEDGMENTS

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6.0 REFERENCES


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