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Characterization of Deterred Propellants by Closed Vessel Tests: Importance of the Ignition Method

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Abstract: Different gaseous ignition systems have been used for the characterization of spherical deterred propellants in closed vessel tests. It has been observed that, with an appropriate ignition system, a good correlation is obtained between closed vessel tests, deterrent concentration profiles and ballistic firing.

Keywords: deterred propellant, closed vessel tests, gaseous ignition, IR microscopy, ballistic firing

Introduction

The ballistic performance of guns can be improved by using of less degressive propellants. For this purpose, deterred propellants are used especially in small arms. In deterred propellants, the concentration of deterrent in the outer layer is

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larger than in the core of the propellant particles. The deterrent gradient results in a larger pressure peak during the combustion process, compensating for the decreasing burning surface by an increasing burning rate.

The characteristics of the deterrent concentration gradient have an effect on the propellant combustion behavior. These concentration profiles can be obtained by infrared microscopy analysis but this procedure is highly time consuming. Standard closed vessel tests with black powder as ignition mixture do not permit to observe significant differences between the combustion of the two chemical compositions of the propellant.

In this work, different gaseous ignition systems have been investigated. These ignition systems have been tested on propellants with different deterrent concentrations. The combustion rates have been calculated and the combustion features have been correlated with the deterrent concentration profiles obtained by infrared microscopy. Furthermore, ballistic firings have been performed, and their results have been compared with both the IR analysis and the results of closed vessel test.

Experimental

Propellant used

Several formulations of deterred spherical propellants have been used in this work. Their characteristics are reported in Table 1. The used deterrent is the dibutylphthalate (DBP). Some of the propellants have all the deterrent in the outer layer of the particles, some have also dibuthylphthalate in the core of the particle.

The used propellants can be sorted in two types as a function of their size distribution, one with an average diameter of about 0.7 mm and one with an average diameter of about 1 mm.

Table 1. Characteristics of the investigated propellants

	Diameter (mm)	Average % DBP** in the ball powder*	Local % DBP** in the core
Propellant A	0.7	7.4	-
Propellant B	0.7	1.3	-
Propellant C	0.7	7.4	-
Propellant D	0.7	12.0	-
Propellant E	0.7	16.9	-
Propellant F	0.7	18.5	-
Propellant G	1.0	7.0	-
Propellant H	1.0	7.4	-
Propellant I	1.0	8.5	2.0
Propellant J	1.0	7.9	1.8

* determined experimentally by HPLC, ** dibutylphthalate

Closed vessel experiments

Closed vessel experiments were carried out in a vessel of 140 cm^3 using a piezoelectric pressure transducer (Kistler 6201B4) for recording the pressure. The output voltage of the pressure gauge was transferred to a data acquisition system (Nicolet Multipro, resolution 12 bit, sampling frequency 250 KHz). The ignition system consists of two electrodes, which are connected with a nickeline hot wire. The vessel is equipped with a valve to introduce the gaseous ignition mixture. The partial pressures of these mixtures are measured with a piezoelectric transducer (Kistler 4070). When black powder is used as ignition method, 1 g of powder is used. The combustion rate is calculated according to Stanag 4115 [1].

The compositions of the various ignition mixtures are given in Table 2. The gaseous ignition systems are characterized by their partial pressures (for the actual composition, the initial atmospheric pressure must be added). In this table, the maximum pressure of the ignition mixtures alone in the closed vessel, the oxygen balance and the energy of the ignition mixtures are mentioned. They are calculated using Eq. 1.

$$E = C_v \cdot \Delta T \cdot m_{igniter} \ , \qquad (1)$$

where C_v, ΔT, $m_{igniter}$ are the specific heat at constant volume, the difference between the adiabatic explosion temperature and the ambient temperature and the mass of ignition mixture respectively.

The others thermodynamical characteristics of these ignition systems are reported by Jeunieau *et al.* [2].

Table 2. Characteristics of the different investigated ignition mixtures

	Composition	Pmax (MPa)	Energy (J)	Oxygen balance (%)
Mixture I	0.1 MPa CH_4 - 0.2 MPa O_2	5.4	3252	+5.2
Mixture II	0.1 MPa CH_4 - 0.14 MPa O_2	4.7	2841	-13.7
Mixture III	0.05 MPa CH_4 - 0.075 MPa O_2	2.5	1632	-1.9
Mixture IV	0.1 MPa CH_4 - 0.1 MPa O_2	3.6	2308	-32.6
Mixture V	0.05 MPa CH_4 - 0.05 MPa O_2	1.9	1400	-1.9
Mixture VI	Black powder (loading density 0.007 g cm^{-3})	2.6	2186	-9.7

Infrared microscopy

The deterrent concentration profile is measured by Infrared (IR) microscopy: the propellant grain is placed into an adhesive, cut with a microtome into small slices (7 μm) and analyzed by IR microscopy. A Bruker Hyperion infrared microscope mounted on a Vector 33 Fourier-transform spectrometer is used in this study.

A medium-band MCT (HgCdTe) detector in the microscope gives high sensitivity in the 4000-600 cm^{-1} range. A 15X Cassegrain mirror objective is used to obtain the infrared spectra. The IR spectrometer is operated at a resolution of 4 cm^{-1} and 32 scans are acquired for each measurement position. The measuring window has an aperture of 10 x 50 μm, the larger side of the aperture is placed perpendicularly to the measured diameter. The step for each data point is 3 μm. The quantitative DBP concentration is obtained using the ratio of two IR bands, one typical of the DBP (1720 cm^{-1}) and one typical of the nitrocellulose (1160 cm^{-1}).

Ballistic firing

The experimental work is carried out in a .50 inch weapon instrumented with a piezoelectric transducers (Kistler 6215) coupled to a charge amplifiers (Kistler 5011A) in order to record the pressure. The pressure measurement is located in the cartridge case. The output charges of the pressure gauge is amplified and filtered to get an output voltage, which is transferred to a data acquisition system (resolution 12 bit, sampling rate 1 MHz). 13 g of the propellant are poured in a standard 12.7 x 99 mm cartridge. The corresponding loading density is 0.75 g cm^{-3}.

Results

Ignition mixtures

To investigate the role played by the ignition mixture, propellant A (see Table 1) has been used at a loading density of 0.20 g cm^{-3}. Figure 1 shows for some propellants the pressure as function of time and their corresponding derivatives. It can be noticed that important combustion instabilities are present for the ignition mixture I. As these instabilities are present in the calculated combustion rate, this ignition mixture has to be disregarded. The pressure derivative permits to distinguish clearly two phases in the combustion process when mixture II or III are used as ignition system. In fact, two different positive slopes can be observed in the pressure derivative *vs*. time.

For the sake of clarity, these slopes have been emphasized by the two drawn lines. In other cases, the variation of the derivative *vs*. time is more regular, the pressure increase is smoother and the combustion process can no more be divided into two parts. One hypothesis to explain the lack of discontinuity is the inhomogeneous ignition of the propellants by the black powder. When ignition is inhomogeneous, the deterred layers of all the particles do not burn simultaneously. When one particle has its deterred layer burnt and therefore its combustion rate increased the other particles may have their deterred layer not completely burnt.

Thus the observed combustion rate is more or less a smooth average of the overall combustion rate.

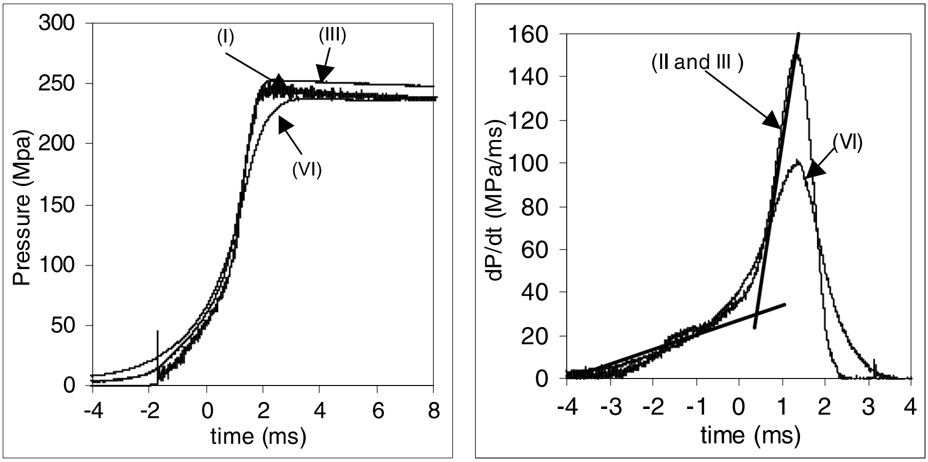

Figure 1. (1) Pressure time histories and (2) derivative of pressure *vs*. time of propellant A for different ignition systems and for a loading density of 0.20 g cm^{-3}. Numbers are refering to the formulations as reported in Table 2.

Figure 2 shows the calculated combustion rate of propellant A when different ignition mixtures are used. The largest combustion rates of the second part of the combustion, *i.e.* the combustion rate of the inner part of the propellant grain, are obtained when mixtures II and III are used. For these mixtures two parts in the combustion rate *vs*. pressure can also be observed. When ignition mixture II is used, instabilities are present in the curve; this can be related to the high energy of this ignition mixture (see Table 2). For the others gaseous ignition systems, a similar combustion rate to the one obtained with black powder are obtained.

For the observation of a discontinuity, two factors seem important: the total ignition energy and the oxygen balance (Table 2). For mixture IV, there is a great lack of oxygen and no discontinuity is observable despite the large energy value. For mixture V, the oxygen balance is close to zero but the energy is low. For mixture II, the oxygen balance is negative, but as the energy is high, a discontinuity is observable in the combustion rate. For mixture VI, the type of ignition mixture is different and the pressure history has to be taken into account. In fact, the pressure increase of the ignition mixture is much slower than for the gaseous ignition mixture (see ref. [2]). This could explain an inhomogeneous ignition and therefore the absence of a discontinuity in the combustion rate curve.

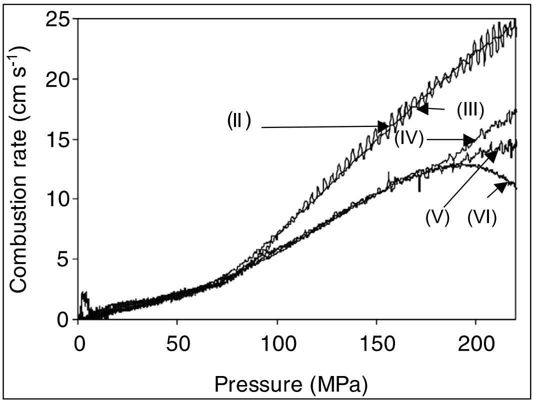

Figure 2. Combustion rate of propellant A obtained with different ignition mixtures I to VI as defined in Table 2. The loading density is 0.20 g cm^{-3}.

From these results, the ignition mixture III and II have been selected and will be tested on different propellants. The mixture VI will also be used, as it is used traditionally in closed vessel tests.

At this stage of the discussion, the fact that the observed discontinuity in the derivative curve corresponds to the burning of the deterred layer has to be confirmed. This will be done by using different propellants with different deterrent concentrations and different concentration profiles. If the discontinuity corresponds to the burning of the deterred layer, its location will vary with the deterrent concentration profile.

Correlation between closed vessel tests and infrared microscopy

The propellants have been divided in two series, one with an average diameter of 0.7 mm and one with an average diameter of 1.0 mm.

Propellant with an average diameter of 0.7 mm

Figure 3 shows the deterrent concentration profiles of the four propellant formulations with an average diameter close to 0.7 mm.

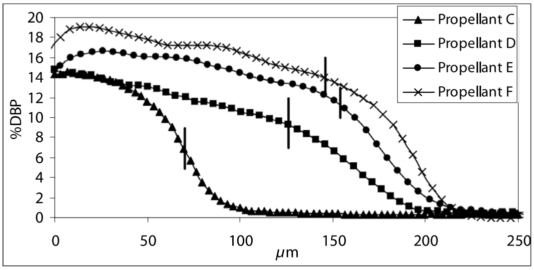

Figure 3. Deterrent concentration profiles of the propellant with an average diameter of 0.7 mm. The vertical lines corresponds to the values of the deterrent penetration depth calculated from the closed vessel tests (see further in the text).

Figure 4 shows the combustion rate of propellants C, D, E and F obtained with the ignition mixtures II, III and VI. Figure 5 shows the corresponding derivative curves. It can be observed that if mixture VI is used, no discontinuity is observed in the derivative curve and the variation of the combustion rate with pressure evolves regularly.

When mixture III is used, an important sharp discontinuity is observed for propellant C in the combustion rate curve and in the derivative curve. A less important discontinuity is observable for propellant D which is consistent with its deterrent concentration profile.

If mixture II is used, the discontinuity is observable for propellant D, E and F. As propellant E and F have a higher deterrent concentration and a smaller percentage of propellant volume without deterrent, a more energetic mixture (see Table 2) is needed for the observation of the two propellant chemical compositions.

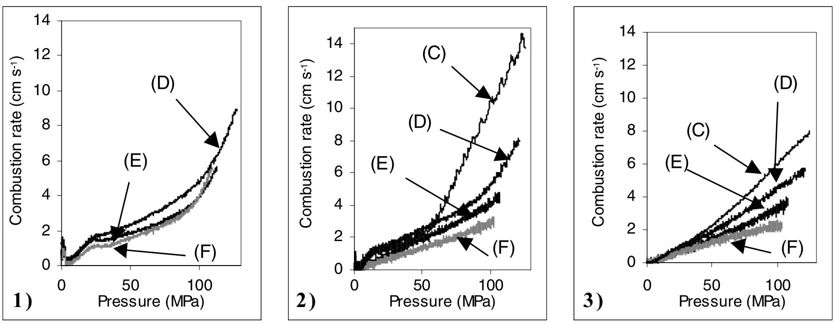

Figure 4. Combustion rate of propellant C, D, E and F (gray line). The labels in brackets refer to the type of propellant. The ignition mixture is (1) igniter II, (2) igniter III and (3) igniter VI. The loading density is 0.15 g cm^{-3}.

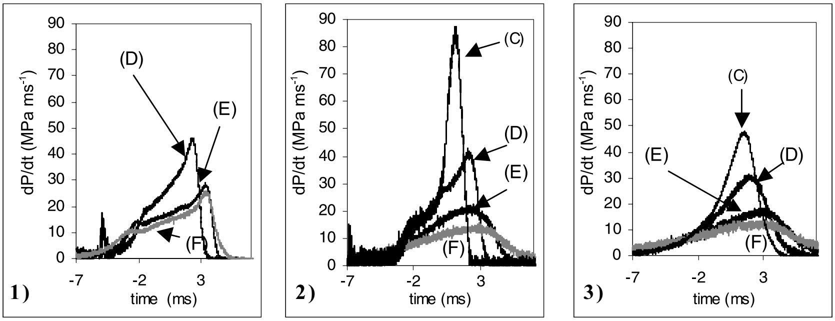

Figure 5. Derivative of the pressure *vs*. time of propellant C, D, E and F (gray line). The labels in brackets refer to the type of propellant. The ignition mixture is (1) igniter II, (2) igniter III and (3) igniter VI. The loading density is 0.15 g cm^{-3}.

The burnt mass fraction corresponding to the discontinuity in the derivative time curve can be calculated using Eq. (2) [3].

$$z_{break} = \frac{\frac{1}{\Delta}-\frac{1}{\rho}}{\frac{\alpha P_{max}-P_{min}}{\Delta}\frac{1}{P_{break}}-\frac{1}{\rho}+\eta-\eta\frac{\alpha P_{max}}{P_{break}}+\frac{1}{\rho}\frac{P_{min}}{P_{break}}} - \frac{\frac{1}{\Delta}-\frac{1}{\rho}}{\frac{\alpha P_{max}-P_{min}}{\Delta}-\frac{1}{\rho}P_{break}+\eta P_{break}-\eta\alpha P_{max}+\frac{1}{\rho}P_{min}}P_{min} \tag{2}$$

where: Δ, ρ, P_{max}, P_{min}, P_{break}, η are the loading density, the propellant density, the experimental maximal pressure, the pressure due to the ignition system, the pressure corresponding to the discontinuity in the derivative curve and the covolume respectively. In this equation α is the ratio between the theoretical maximal pressure of the propellant, which has the chemical composition of the deterred propellant, and the theoretical maximal pressure, which has the actual composition of the propellant. More information about this equation can be found in [3].

As the burnt mass fraction is defined by Eq. (3) where V is the propellant volume and V_0 is its initial value, the burnt thickness can be easily calculated.

$$z = 1-\frac{V}{V_0} \tag{3}$$

The obtained results are given in Table 3. These values are in good agreement with the deterrent penetration depths measured by infrared microscopy, excepting for propellant E and F (values for propellant F should be greater than the one of propellant E). But the difference between these two values is lower than the experimental uncertainty (at least 10 μm). These values have been added to the chart of the deterrent concentration profile (Figure 3). It is observed that the calculated deterrent penetration depth are generally not situated at the end of the deterred layer (Figure 3) but before the large drop of the deterrent concentration. In fact, the discontinuity in the derivative curve occurs between the combustion of a more or less constant deterred layer and the combustion of a less deterred layer with an abrupt variation of the deterrent concentration.

Table 3. Values of the deterrent penetration depths calculated from the closed vessel experiments. Experiments with two ignition mixtures are reported

	Deterrent penetration depth (μm)	
	Igniter II	Igniter III
Propellant C	-	70
Propellant D	124	127
Propellant E	154	-
Propellant F	146	-

Propellant with an average diameter of 1.0 mm

A study similar to the one described in the previous section has been performed on the propellants with the larger average diameter. Figure 6 shows the deterrent concentration profiles of the propellant with an average diameter of 1.0 mm.

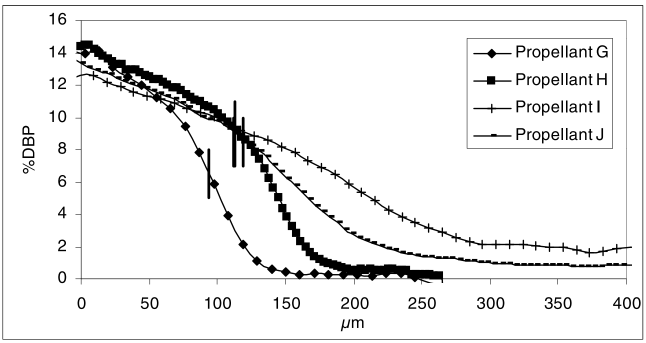

Figure 6. Deterrent concentration profiles of propellant G, propellant H, propellant I and propellant J. The vertical lines correspond to the deterrent penetration depths calculated from the closed vessel tests.

Figure 7 shows the corresponding combustion rate obtained with ignition mixtures III and VI and Figure 8 shows the corresponding derivative curves. When ignition mixture VI is used, a difference is observed only between propellant G, H and propellant I, J. If ignition mixture III is used, a difference is observed between all the propellants. For this ignition mixture, a discontinuity is observable for all the propellants in the derivative curves and the order of appearance of this one corresponds to the difference of deterrent penetration depth.

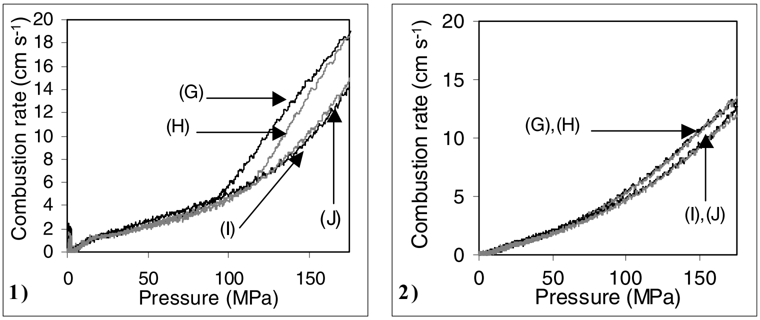

Figure 7. Combution rate of propellant G, H, I and J. The labels in bracket refer to the type of propellant. The igniton mixture for (1) is mixture III and for (2) is mixture VI. The loading density is 0.20 g cm^{-3}. The curves of propellant H and J are in gray.

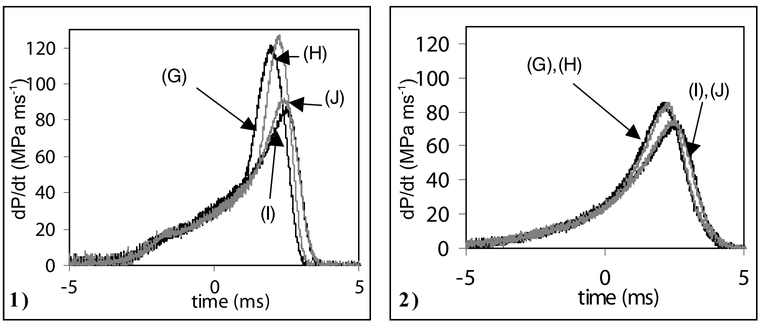

Figure 8. Derivative of the pressure *vs.* time of propellant G, H, I and J. The ignition mixture for (1) is mixture II and for (2) is mixture VI. The loading density is 0.20 g cm^{-3}. The curves of propellant H and J are in gray.

The calculated deterrent penetration depths from Eq.(1) and (2) are listed in Table 4 and these values are located on the deterrent concentration profiles in Figure 6, accounting for a good agreement with the actual deterrent profiles.

Table 4. Values of the deterrent penetration depth calculated from the closed vessel tests. Mixture III is used as ignition mixture

	Deterrent penetration depth (μm)
Propellant G	94
Propellant H	113
Propellant I	119
Propellant J	112

Correlation between the two series of propellant

In Figure 9, the obtained combustion rate at 30 MPa has been plotted as a function of the average DBP concentration (obtained by HPLC) and of the percentage of DBP in surface for ignition mixtures III and VI. The combustion rate at 30 MPa corresponds to the burning of the outer surface of the propellant. It can be observed that only a roughly linear variation of the combustion rate as a function of the average concentration can be observed when ignition mixture VI is used. If this combustion rate is plotted as a function of the surface deterrent concentration, a linear variation can be observed as well for mixture III as for mixture VI. In this chart, the linear trendline is calculated using only the propellant with an average diameter of 0.7 mm. The values corresponding to the propellant

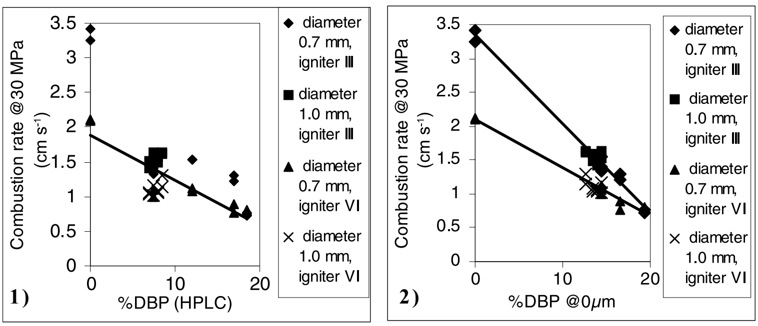

Figure 9. Variation of the combustion rate at 30 MPa as a function of the percentage of (1) average DBP concentration and (2) DBP in surface for the different propellants (from B to J) and for igniting mixture III and VI. The loading density is 0.20 g cm^{-3}.

with an average diameter of 1.0 mm put themselves nicely on these trendlines. The slope of this trendline is smaller for mixture VI than for mixture III. This could be an explanation of the better differentiation of deterred propellant by mixture III than by mixture VI. As the variation of the combustion rate with the deterrent concentration is greater for mixture III than for mixture VI, two propellants with a small variation of the DBP concentration are only distinguishable with mixture III. The presence of the discontinuity is also explainable by this regression. When the propellant deterred part is burnt, the combustion of the center part begins. As the difference between the combustion rates is high for mixture III, this is expressed by a discontinuity in the derivative curve.

Correlation between ballistic firing, closed vessel tests and infrared microscopy

First, it must be mentioned that only propellant C is manufactured for the used weapon system. For the others propellants, the combustion is incomplete, residues have been observed during the firing.

Propellants with an average diameter of 0.7 mm

Figure 10 shows the pressure records in the cartridge for the different propellants with an average diameter of 0.7 mm. This has to be correlated with Figures 3 and 4 showing their respective deterrent concentration profiles and their corresponding combustion rates. The peak pressure of propellant C shows an asymmetric shape. At the beginning of the combustion, the deterred part of the propellant burnt, the burning rate is low but the propellant surface is high, when the deterred part of the propellant is burnt the combustion rate is higher but the propellant surface is smaller and the gas production remains more or less constant. This explains the particular shape of the peak pressure. This peak corresponds to a sequence of two phenomena, the burning of the deterred part of the propellant and the combustion of the inner core of the propellant.

This asymmetric shape of the peak is no more present for the other propellants, due to incomplete combustion. It is probable that only the deterred part of the propellant is burnt.

The slopes of the pressure buildup correspond to the deterrent concentration profiles of the different propellants and their respective combustion rates. When the deterrent concentration in surface is higher, the pressure increase is slower. By consequence, the maximum pressure is lower. During the ballistic firing, a difference is observed between propellant E and F. This difference corresponds to the beginning of the combustion (burning of the propellant outer layer), as the combustion is incomplete. This discrepancy is not noticeable in the closed vessel tests if igniter VI is used, in this case a difference is only present at the end of the combustion (combustion rate at the high pressure values).

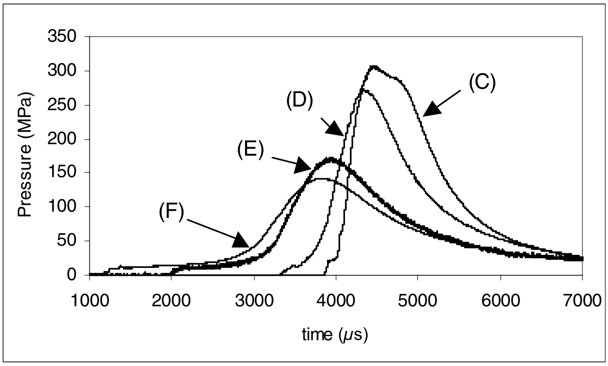

Figure 10. Pressure time curve of propellant C, D, E and F measured in the cartridge during the ballistic firing (pretrigger from muzzle flash at 10 000 μs). The labels in brackets refers to the type of propellant.

Propellants with an average diameter of 1.0 mm

Figure 11 shows the pressure time curves measured in the cartridge during ballistic firing for the propellant with an average diameter of 1.0 mm.

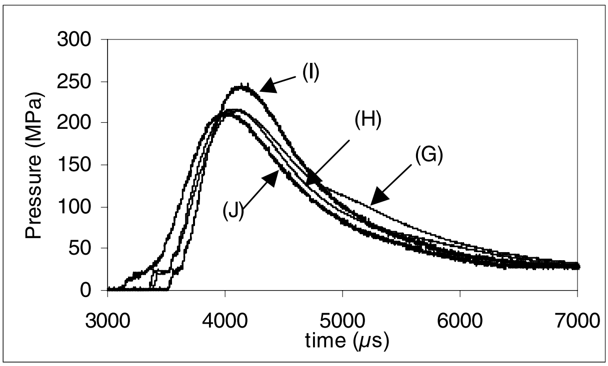

Figure 11. Pressure time curve of propellant G, H, I and J measured in the cartridge during the ballistic firing (the curves are not correlated in time). The labels in brackets refer to the type of propellant.

A difference is observable between all the propellants. This difference is not observable in the closed vessel tests when mixture VI is used. The curve of propellant G shows a discontinuity in the pressure decrease. This is due to the presence of the two chemical compositions. For the other propellants this discontinuity is no more present, due to incomplete combustion and corresponding to their greater deterrent penetration depth. In fact, as the combustion is incomplete, only the outer layer of the deterrent burnt during the ballistic firing.

Conclusions

Different gaseous ignition mixtures have been tested on a deterred propellant. It has been shown that the selected ignition mixtures permit to observe a difference between the two chemical compositions during the closed vessel tests, namely mixtures II and III.

Ignition mixtures II and III have been used on different deterred propellants with mixture VI as benchmark. It has been observed that a greater difference is observed between the deterred propellants if a gaseous ignition system is used. A discontinuity is present in the pressure derivative curve when an appropriate gaseous ignition system is used. From this discontinuity a deterrent penetration depth has been calculated. These calculated values correspond to the propellant thickness with has a high deterrent concentration. The combustion rate corresponding to the combustion of the deterred part of the propellant is linear as a function of the percentage of DBP in surface. The slope of this linear variation is greater for a gaseous ignition than if mixture VI is used as ignition system.

To explain the presence of a discontinuity in the closed vessel tests when a gaseous ignition system is used, two hypotheses have been proposed:

- The gaseous ignition is more homogeneous than the ignition by black powder.
- The variation of the combustion rate with the deterrent concentration is higher when mixture II or III is used and this permits to differentiate the two chemical compositions of the propellant.

These two hypotheses are not incompatible, if the ignition is not homogeneous with black powder, the combustion rate will be an average of the combustion rate corresponding to the different deterrent concentrations. This will decrease artificially the calculated combustion rate. To differentiate these two hypotheses, propellants with a constant DBP concentration will be manufactured. With these propellants ignition will have no influence on the combustion rate and the effect of the ignition method will be investigated.

Ballistic firing of different deterred propellants have been realized. It has been observed difference between the pressure records of different propellants which exhibit none difference in the closed vessel tests when mixture VI is used.

This work permit to observe that there is a good correlation between infrared microscopy, ballistic firing and closed vessel tests if an appropriate ignition system for the closed vessel tests is used. It shown that closed vessel tests can be used as a rapid method of characterization of deterred propellants. In fact, infrared microscopy is highly time consuming and for ballistic firing appropriate laboratory conditions are needed.

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