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## Effect of Surface Microstructure on the Temperature Sensitivity of Burning Rate of Ammonium Perchlorate

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### ABSTRACT

Considering Vieille's law and the new thermodynamic model which the authors have developed recently, the true dependence of temperature sensitivity of burning rate ( $\sigma_p$ ) of ammonium perchlorate (AP) on pressure is resolved and experimentally verified for pellet burning. The value of  $\sigma_p$  decreases with pressure steeply in regime I' (below 20 atm), but gently in regime I (above 20 atm). The  $\sigma_p$  value of powder AP has been determined and it is observed that  $\sigma_{p(\text{powder})} > \sigma_{p(\text{pellet})}$ , which clearly suggests that  $\sigma_p$  is influenced by the surface temperature sensitive parameter  $(\partial T_s/\partial T_o)_p$  and hence by the surface/subsurface microstructure. In powder burning, the buoyant lifting of the particles into the gas phase occurs, which constitutes the so-called 'free board region' (FBR) extending just above the true surface. Consequent to the decomposition of AP particles in FBR, the condensed phase heat release gets curtailed and  $\sigma_{p(\text{powder})}$  becomes larger. A general relationship for  $\sigma_p$  in terms of density and surface temperature is suggested, which is applicable to both pellet and powder AP.

### 1. INTRODUCTION

Ammonium perchlorate (AP) is one of the most extensively used oxidizer in high energy formulations. Due to its unique characteristic of self-supporting deflagration, AP combustion has been studied primarily to understand the more complex combustion phenomena in AP-based composite propellant systems. Despite the profusion of studies conducted, AP deflagration mechanism still remains elusive in its various facets. AP is only one of its kind that exhibits a critical low pressure deflagration limit, (LPL: 20 atm) below which it does not burn; by suitable augmentation of the initial temperature ( $T_o$ ), it can be made to burn below LPL. The temperature dependence of burning rate is expressed in terms of temperature sensitivity of burning rate ( $\sigma_p$ ), which has been observed to increase, decrease, or both as

a function of pressure ( $P$ ). In a majority of cases, however, a decrease is observed<sup>1-3</sup>.

We have determined the values of  $\sigma_p$  and have attempted here to resolve the perplexing dependence of  $\sigma_p$  on  $P$ . The present analysis is based on Vieille's law and our novel thermodynamic model of AP deflagration<sup>4</sup>, which clearly identifies a hitherto unknown subcritical pressure regime (christened as regime I'), mechanistically distinctive from regime I (20-70 atm), which succeeds regime I'.

Most of the studies on AP deflagration have been surprisingly done on pellets and single crystals but not on the powder, despite its use as a particulate in the actual propellant systems. We have studied the deflagration of powder AP and compared it with its deflagration in pellet form in

order to understand as to how the microstructure of the burning surface of AP influences  $\sigma_p$ .

## 2. EXPERIMENTAL PROCEDURE

The methods employed for preparation of the samples, measurement of burning rate ( $\dot{r}$ ) as a function of  $T_o$  and pressure ( $P$ ), the temperature profile imprinting and analyses, etc. have been discussed elsewhere<sup>4</sup>. Surface temperature ( $T_s$ , °K), at a given pressure ( $P$ ) was obtained from the following empirical equation<sup>4</sup>

$$\ln T_s = 0.0484 \ln P + 6.6957 \quad (1)$$

The value of  $T_s$  thus obtained was verified experimentally by recording the temperature profile<sup>4</sup> of AP deflagration at different pressures and  $T_o$ 's. The temperature profile plot of  $\ln T$  vs time is linear up to the temperature corresponding to the burning surface, and thereafter it deviates from linearity. The temperature corresponding to the point of deviation was taken as  $T_s$ . The surface temperature was thus obtained at different  $T_o$ 's in regimes I' and I and from this data ( $\partial T_s / \partial T_o$ ) <sub>$p$</sub>  was computed.

The  $\dot{r}$  and  $T_s$  values of tamped powder at different values of  $T_o$  and  $P$  were obtained from the  $\dot{r}$  measurements of AP powder in a glass tube (diameter : 1.0 cm). About 1.5 g of AP of particle size 200 - 250  $\mu\text{m}$  was packed in the tube as a lightly tamped powder accommodating nichrome ignition wire, fuse wires (5 amp) and chromel-alumel thermocouple (beed size 0.005 in.). The packing density was determined from the weight of AP packed to a certain volume in the glass tube and was found to be 1 g/cm<sup>3</sup>. Care was taken to maintain the packing density same in all the experimental measurements.

## 3. RESULTS & DISCUSSION

### 3.1 Temperature Sensitivity and its Variation with Pressure

The LPL of AP can be brought down and it can be made to burn at atmospheric pressure by

increasing  $T_o$ . Let us first consider the following relationship between  $\dot{r}$  and  $P$  based on Veille's law<sup>5</sup>

$$\dot{r} = \left[ \frac{a_o}{T_o - T_{ig}} \right] P^n \quad (2)$$

where

$a_o$  is a constant,  $n$  is the pressure exponent and  $T_{ig}$  is the ignition temperature. From the basic definition of  $\sigma_p$ , we can write Eqn (2) as

$$\sigma_p = \left[ \frac{\partial \ln \dot{r}}{\partial T_o} \right]_p = \frac{1}{T_{ig} - T_o} \quad (3)$$

If  $T_o = T_{ig}$ , then the value of  $\dot{r}$  will be infinity. However, in the range  $T_o < T_{ig}$ , which is normally prevalent in propellants,  $\sigma_p$  will vary with  $T_o$ . Besides, it is well known that the value of  $T_{ig}$  depends upon sample size and shape. Hence, the value of  $\sigma_p$  obtained from Eqn (2) will be erroneous. We have modified Eqn (2) by replacing  $T_{ig}$  with  $T_s$

$$\sigma_p = 1/(T_s - T_o) \quad (4)$$

Since  $T_s$  is independent of sample size and shape and rests only on chemical characteristics and pressure, it is a preferable parameter to  $T_{ig}$ . The value of  $T_s$  is also affected by  $T_o$ .

The variation of  $\sigma_p$  with  $P$  is examined by differentiating Eqn (3) with respect to  $P$ :

$$\frac{\partial \sigma_p}{\partial P} = -\sigma_p^2 \left[ \frac{\partial T_s}{\partial P} \right]_{T_o} \quad (5)$$

Since  $\sigma_p$  and  $(\partial T_s / \partial P)_{T_o}$  are both positive quantities in both regimes I' and I, it is explicit from Eqn (5) that the value of  $\sigma_p$  should decrease with pressure.

In regime I, for instance, at 1 atm, the critical  $T_o$  below which AP does not burn is 245 °C; this critical  $T_o$  will have a unique value at a given pressure in the subcritical regime<sup>4</sup>. Similarly,  $T_s$

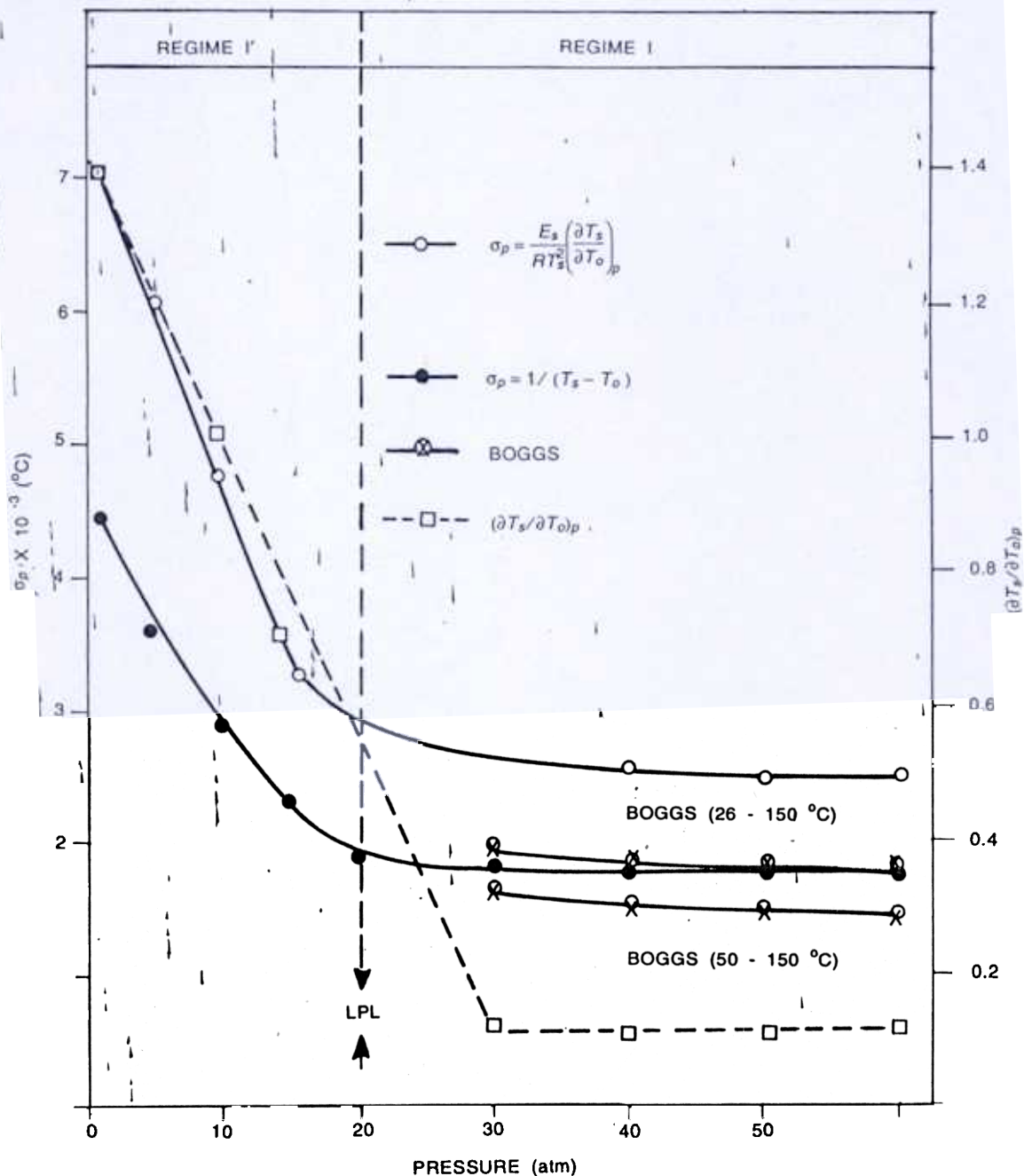


Figure 1. Dependence of  $\sigma_p$  and  $(\partial T_s / \partial T_o)_p$  on pressure

will also have a unique value at a given pressure in the subcritical regime. Accordingly, for a given pressure, the critical  $T_o$  and the corresponding  $T_s$  ( $T_o$  and  $T_s$  taken from Ref. 4) were substituted in Eqn (3) and  $\sigma_p$  values obtained at various pressures in the regimes I' and I, and plotted against  $P$  in

Fig. 1; the figure also includes the experimental data of Boggs and Zurn<sup>1</sup> for regime I. The variation of  $\sigma_p$  with  $P$  shows a steep decrease in regime I' and a marginal decrease in regime I, which is comparable with that observed by Boggs and Zurn<sup>1</sup>.

According to our newly proposed thermodynamic model<sup>4</sup>, the surface activation energy ( $E_s$ ) is represented as

$$E_s = E_{s,c} + E_{s,g} \\ = \frac{\sigma_p RT_s^2}{(\partial T_s / \partial T_o)_p} + \frac{(n/P) RT_s^2}{(\partial T_s / \partial P)_{T_o}} \quad (6)$$

where

$E_{s,c}$  and  $E_{s,g}$  are the condensed and gas phase activation energies just below and above the apparent surface respectively;  $R$  is the gas constant and  $(\partial T_s / \partial T_o)_p$  and  $(\partial T_s / \partial P)_{T_o}$  are the surface temperature sensitive parameters related to condensed and the gas phase, respectively.  $\sigma_p$  was examined by rearranging Eqn (6) as follows<sup>4</sup>

$$\sigma_p = \frac{E_{s,c}}{RT_s^2} \left[ \frac{\partial T_s}{\partial T_o} \right]_p \quad (7)$$

Substituting the appropriate values of  $E_{s,c}$ ,  $T_s$  and  $(\partial T_s / \partial T_o)_p$  in Eqn (7),  $\sigma_p$  was calculated at various pressures in regimes I' and I. The plots obtained are shown in Fig. 1. It may be seen that the extent of decrease in regime I' is large, and it is marginal in regime I. This may be attributed to a steep decrease in the value of  $(\partial T_s / \partial T_o)_p$  in regime I' compared to regime I (Fig. 1). Hence, it is said that  $\sigma_p$  strongly depends upon  $(\partial T_s / \partial T_o)_p$ . In the present investigation, at LPL,  $(\partial T_s / \partial T_o)_p$  is 0.5 (Fig. 1) and hence Eqn (6) becomes<sup>4</sup>

$$\sigma_p = E_{s,c} / RT_s^2 \quad (8)$$

Equation (8) is similar to that obtained from Belayaev-Zel'dovich model<sup>6</sup>. By applying the condition that at higher pressures,  $T_s \approx T_m'$  we get the following equation

$$\sigma_p = \left[ \frac{E}{2RT_s^2} + \frac{L}{RT_s^2} \frac{T_m' - T_s}{T_s - T_o} \right] \left[ 1 + \frac{L}{RT_s^2} (T_m' - T_s) \right] \quad (9)$$

Strunnin and Manelis used the following simplified equation for  $\sigma_p$

$$\sigma_p = E_s / 2RT_s^2 \quad (10)$$

which is similar to the equation obtained on the basis of Belayaev-Zel'dovich model<sup>6</sup>. Eqns (10) and (8) are similar and hence it may be concluded that they can be used for calculating values of  $\sigma_p$  for AP, but only at LPL.

Above LPL (beyond 20 atm), as seen from Fig. 1,  $(\partial T_s / \partial T_o)_p$  is almost constant having a value of 0.1 in regime I,  $\sigma_p$  can, therefore, be written as<sup>4</sup>:

$$\sigma_p = E_{s,c} / 10RT_s^2 \quad (11)$$

Dependence of  $\sigma_p$  on pressure can also be examined by differentiating Eqn (10) with respect to  $P$

$$\frac{\partial \sigma_p}{\partial P} = - \frac{E_{s,c}}{5RT_s^3} \left[ \frac{\partial T_s}{\partial P} \right]_{T_o} \quad (12)$$

The quantities  $E_{s,c}$ ,  $T_s$  and  $(\partial T_s / \partial P)_{T_o}$  are all positive and hence the value of  $\sigma_p$  should decrease with  $P$ . This is yet another evidence to show that  $\sigma_p$  should decrease with  $P$ .

### 3.2 Calculations of $T_s$ from $\sigma_p$

In regime I, for constant  $T_o$ , Eqn (4) suggests that the value of  $\sigma_p$  varies with  $1/T_s$ , whereas it is proportional to  $1/T_s^2$  according to Eqn (11). To verify which of the dependences is better, experimental data of Boggs and Zurn<sup>1</sup> and Cohen Nir<sup>8,9</sup> were used and a plot of  $\sigma_p$  as a function of both  $1/T_s$  and  $1/T_s^2$  was drawn. The correlation coefficient for both,  $\sigma_p$  vs  $1/T_s$  and  $\sigma_p$  vs  $1/T_s^2$  plots was found to be 0.98 for the Bogg-Zurn's data, and 0.99 for Cohen Nir's data. Although, both the curves fit well, Cohen Nir's data shows a slightly better fit than that of Bogg-Zurn for the dependence of  $\sigma_p$  with both  $1/T_s$  and  $1/T_s^2$ . Apparently, the  $\sigma_p$  data are not sufficiently precise to decipher the superiority of the dependence of  $\sigma_p$  either on  $1/T_s$  or  $1/T_s^2$ . However, Eqn (11) can be used to calculate  $T_s$  at different pressures in

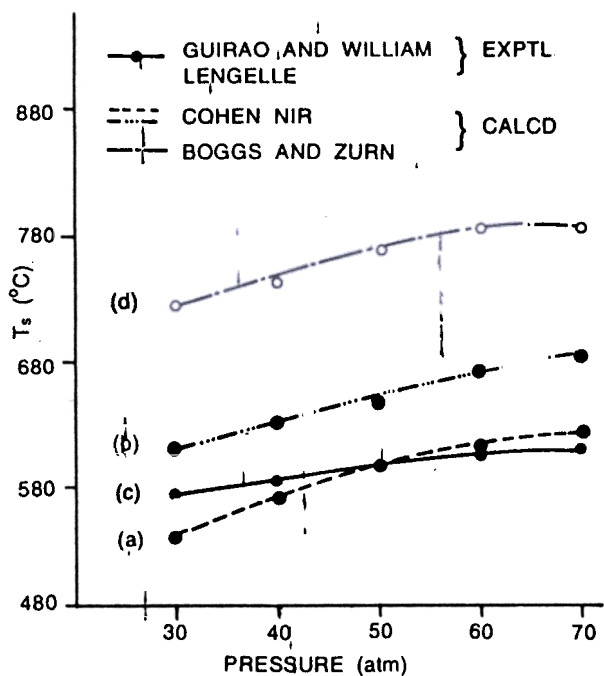


Figure 2. Dependence of  $T_s$  on  $P$ ;  $T_s$  calculated using the  $\sigma_p$  data, (a) particle size: 200-315  $\mu\text{m}$ , (b) particle size: > 1000  $\mu\text{m}$ , (c) experimental and (d) at  $T_o = 26-150^\circ\text{C}$ .

regime I where  $E_{s,c}$  is 35 kcal/mole. A plot of  $T_s$  [calculated from Eqn (11)] as a function of  $P$  is shown in Fig. 2. From a comparison with the data<sup>8-11</sup> of Guirao and Williams<sup>10</sup>, Lengelle, *et al*<sup>11</sup>, Cohen Nir<sup>8,9</sup> and Boggs & Zurn<sup>1</sup>, it may be seen that Cohen Nir's data<sup>8,9</sup> gives a better dependence of  $T_s$  on  $P$ , comparable to the experimental curves of Guirao and Williams<sup>10</sup> and Lengelle<sup>11</sup>.

### 3.3 Temperature Sensitivity of AP Deflagration as Tamped Powder

It is apparent from Eqn(7) and our analysis of pellet AP deflagration that  $\sigma_p$  depends on the condensed phase sensitive parameter  $(\partial T_s / \partial T_o)_p$ . This suggests that any variation in the surface/subsurface microstructure of deflagrating AP would alter this parameter and hence  $\sigma_p$ . We have, therefore, examined the deflagration behaviour of AP as tamped powder, where the burning surface will be more particulate and  $\sigma_p$  different from that observed for the pellet form.

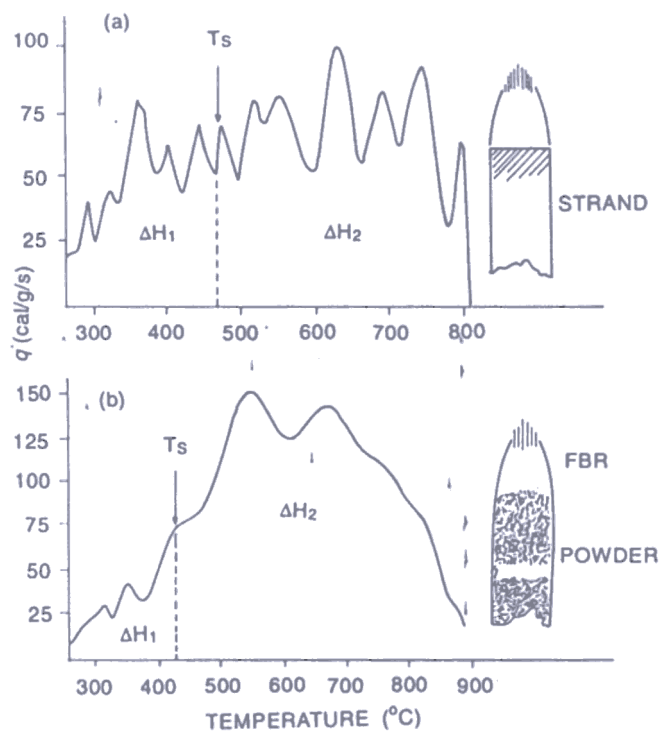


Figure 3.  $\dot{q}$  vs  $T$  profiles for AP (a) pellet strand ( $1.93 \text{ g/cm}^3$ ) (b) powder ( $1 \text{ g/cm}^3$ ) burning at  $T_o = 245^\circ\text{C}$  and  $P = 1 \text{ atm}$ .

The  $\dot{r}$  and  $T_s$  values for powder AP deflagration were obtained experimentally, as described elsewhere<sup>4</sup>. The identification of true  $T_s$  is much easier in the case of compressed pellets because of a distinct gas-solid interface. In powder form, however, such a clear surface demarcation is not possible, because AP particles at the surface are so loosely held that some of them are carried away buoyantly by the upstream gases from the surface into the gas phase. In the process, exothermic decomposition of AP particles continues all along their travel from the surface into the gas phase, thus adding to the gas phase exothermicity. As a result, the proportion of the heat of decomposition in the condensed phase will be curtailed compared to that for pellet burning. In view of such a deflagration behaviour, the surface in the case of powder burning can be best called as 'interfacial region' or 'transition region'. The zone in which the driven AP particles are present in the gas flame is called

pellet and the powder are  $1.93 \text{ g cm}^{-3}$  and  $1.0 \text{ cm}^{-3}$ , respectively compared to the AP single crystal density ( $d_o$ ) of  $1.95 \text{ g cm}^{-3}$ . Hence, the approximate numerators in Eqns (4) and (13) are 1 and 2 respectively.

Thus, the higher value of  $\sigma_p$  for the powder, obtained from (a) Eqn (13), (b)  $\ln \dot{r}$  vs  $T_o$  plot and (c) Eqn (7) may be attributed to the substantial decrease in  $\Delta H_1$  value due to the upstream lifting of the particles in the gas phase as well as to the surface erosion caused by it, resulting in an apparent enhancement in the value of  $\dot{r}$ . Further, from  $T_s$ ,  $\sigma_p$  and  $(\partial T_s / \partial T_o)_p$  data, the  $E_{s,c}$  value, calculated using Eqn (6), is found to be 10.4 kcal/mole for powder AP, which matches with the  $E_{s,g}$  for pellet AP in regime I<sup>A</sup> which suggests that the burning surface, and hence  $T_s$  is actually in FBR in the gas phase.

#### 4. CONCLUSION

The value of  $\sigma_p$  has been estimated (i) by modifying the well-known identity equation derived from Veille's law, and (ii) from our thermodynamic model. The elusive variation of  $\sigma_p$  value with pressure has been verified. It has been found to decrease with increase in pressure. Further, it is also found to depend on the surface temperature sensitive parameter, which is condensed phase-related. The larger value of  $\sigma_p$  observed for AP burning as a tamped powder compared to its burning as pellet is attributed to the curtailed surface/subsurface heat release owing to the buoyant lifting of AP particles into the gas phase. This study reveals that the  $\sigma_p$  value of AP is influenced by the surface microstructure, depending upon whether it is compact as in pellet or particulate form as in the tamped powder.

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