JOURNAL OF PROPULSION AND POWER
Vol. 15, No. 6, November–December 1999

Burning Rate of Solid Propellant Ingredients, Part 2: Determination of Burning Rate Temperature Sensitivity

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Once the burning rate as a function of initial temperature has been measured for a particular material, it is often desirable to report its burning rate temperature sensitivity as a single value that can then be used in other applications. A few of the obstacles encountered when making the determination of burning rate temperature sensitivity, σ_p, are examined. Burning rate temperature sensitivity was evaluated for the neat ingredients AP, HMX, RDX, ADN, CL-20, and HNF.

Introduction

PROPELLANT burning rate temperature sensitivity σ_p is described as the percent change in burning rate r_b per degree change in propellant temperature T_0 (Ref. 1),

$$\sigma_p = [\delta \ln r_b / \delta T_0]_p$$

Care must be taken in how one evaluates σ_p when making comparisons of various materials. The collection of burning rate data, number of points measured at a given condition, initial test conditions, and inherent data scatter will have an effect on the value obtained for the burning rate temperature sensitivity.[‡‡,§§]

The largest variations in burning rate measurements generally occur at low pressures, where one approaches the deflagration limit of the material, and at regions where a break in the burning rate pressure exponent occurs. Coincidentally, these are often the areas of greatest interest when determining the burning rate temperature sensitivity. The changes in σ_p that occur due to data smoothing vs averaging, and with the selection of the initial pressure and temperature conditions, can be significant. The effect of initial temperature selection on σ_p will be demonstrated using the HMX data, and fitting techniques will be illustrated with the ADN data, where considerable data scatter is present.

Samples

The deflagration data for the six monopropellants listed in Table 1 of Ref. 2 will be used to demonstrate the evaluation of burning rate temperature sensitivity. The tabular burning rate data may be found in Refs. 3 and 4. The sample type and preparation was described in Ref. 4. All of the burning rate measurements used in this paper for the calculations were made using the cinephotomicroscopy technique also described in Refs. 3, 4, and elsewhere.

Received 7 February 1998; revision received 8 April 1999; accepted for publication 12 April 1999.

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‡‡Beckstead, M. W., "Determining Temperature Sensitivity; Test Conditions and Data Analysis," letter communication, 1 April 1997.

§§Davidson, J., "Calculating the Temperature Sensitivity of HMX," letter communication, 20 November 1996.

Approach

The simplest means of determining a value of σ_p is to measure the burning rate of a particular material as a function of initial temperature; take the natural log of the burning rate values and determine the burning rate temperature sensitivity as the slope of the line through a plot of the natural log of the burning rate vs the initial temperature. The first requirement is to obtain a set of burning rate data at various initial temperatures and pressures. For this paper, burning rates were measured over pressures from 0.69 to 10.34 MPa at initial temperatures from 173 to 423 K. Some researchers prefer to investigate the burning rate temperature sensitivity over a wide range of temperatures at a few selected pressures whereas others tend to evaluate a broad range of pressures at a few evenly spaced temperatures. This paper falls into the latter category. Ideally, the temperature sensitivity should be evaluated over many temperatures and pressures, but this is usually not economically feasible.

Ideally, more than a single datum point should be measured at any given temperature/pressure condition. Data scatter occurs in even the purest compounds and most ideal conditions. Repetitive experiments provide valuable mechanistic insight, particularly in the slope break regions of the burning rate curve. It is obvious that the greater the number of data points available for evaluation, the greater the confidence level of σ_p. Notice that for a large number of ingredients, a temperature step of 75 deg above and below ambient (223 and 373 K) was selected. This range in temperatures was not an arbitrary selection. Burning rate data as a function of initial temperature and pressure are used as input data in the evaluation of the global kinetics and energetics describing the combustion of the particular material.[5,6] These data are particularly useful in the description of the condensed-phase reactions.

Once the experimental burning rate data are collected, they must be smoothed or fitted in some way. How this fitting is accomplished should be with a minimum of disturbance to the natural shape of the burning rate curve. Over small ranges of pressure, where the data remain linear, a power law fit ($r_b = cp^n$) may be adequate; however, where there are natural changes in burning rate slope, as illustrated in the burning rate data of Fig. 1 for a typical high-energy solid rocket propellant, a single fit of this type will not suffice, and a more sophisticated fitting technique is needed.

Results

AP

The burning rate data used to evaluate the temperature sensitivity of AP were generated at temperatures greater than 298 K at pressures between 2 and 10.34 MPa. At ambient temperature, AP will not self-deflagrate below about 2 MPa. Figure 7 in Ref. 2 presents a plot of

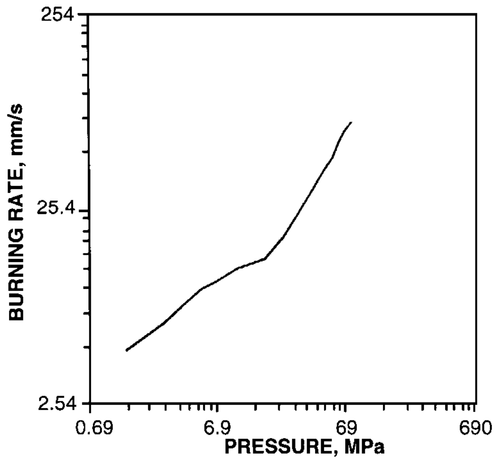

Fig. 1 Typical plot of burning rate vs pressure for a solid rocket propellant.

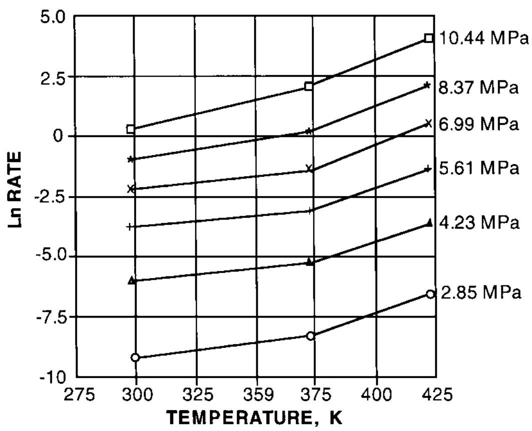

Fig. 2 Natural log of AP burning rate vs temperature.

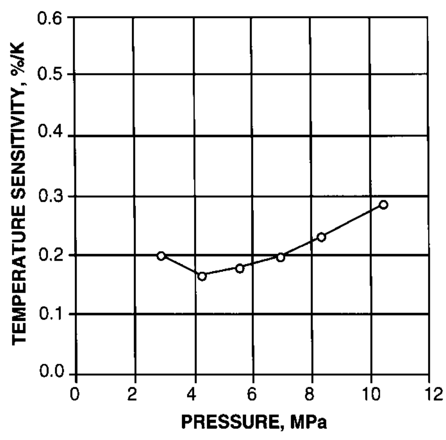

Fig. 3 AP burning rate temperature sensitivity.

the burning rate data at 298, 373, and 423 K. The natural log of the rates (fitted with a parametric spline) vs temperature is presented here in Fig. 2. The burning rate changes between temperature are not constant as seen by the uneven spacing between the burning rate curves of Fig. 7 in Ref. 2 and in the nonlinearity of Fig. 2 here. The burning rate temperature sensitivity is increasing as the initial temperature increases. The greater the nonlinearity of the natural log rate vs temperature, the greater is the error in σ_p. Figure 3 presents a plot of the burning rate temperature sensitivity of AP at six pressures based on a linear fit of the data from Fig. 2.

ADN

Only experimental data at two initial temperatures were available for evaluation of ADN σ_p. This material has a rather low melting

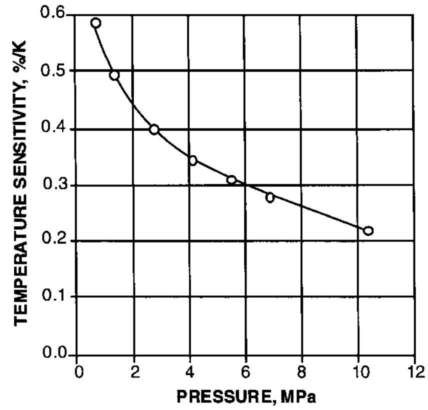

Fig. 4 ADN burning rate temperature sensitivity data.

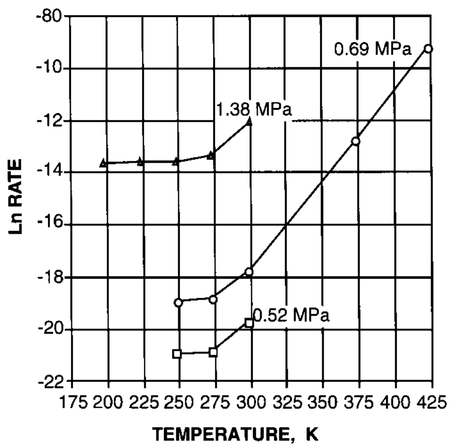

Fig. 5 Natural log of HMX burning rate vs temperature at 0.52, 0.69, and 1.38 MPa.

point (365–367 K), which prevents the evaluation of this material over the usual ranges of initial temperature. Because only data for two initial temperatures were available, a simple differencing technique $(\Delta \ln r_b/\Delta T_0)$ was used. Caution must be employed in the use of the ADN σ_p value not only because of the reduced data set but also due to the large amount of scatter in the experimental ADN burning rate data as shown in Fig. 9 of Ref. 2. A linear fit of the burning rate data was used to obtain the burning rate temperature sensitivity data of Fig. 4 here.

The effect of fitting technique on σ_p is easily illustrated with the scattered ADN burning rate data. If one uses the average of the burning rates at 0.69 MPa to calculate σ_p, a value of 0.44 is obtained as opposed to the value of 0.58 obtained by using the data of the linear fit. Although this does represent an extreme example, the effect of fitting on the final value of temperature sensitivity cannot be ignored.

HMX

HMX burning rate temperature sensitivity was evaluated using data at pressures from 0.52 and 10.34 MPa at initial temperatures from 173 to 423 K. Looking at the HMX burning rate data plotted in Fig. 11 of Ref. 2 for four initial temperatures (223, 298, 373, and 423 K), it can be seen that σ_p decreases with increasing pressure. The increase in burning rate temperature sensitivity with increasing initial temperature is also apparent.

The experimental burning rate data were fit with a parametric spline, and the natural log of the fitted rates vs temperature are presented for pressures of 0.52, 0.69, and 1.38 MPa in Fig. 5; 2.07, 2.76, and 3.45 MPa in Fig. 6; 4.14, 4.83, and 5.52 MPa in Fig. 7; and at 6.21, 6.9, and 10.34 MPa in Fig. 8. The nonlinearity of these data is due to the change in σ_p with initial temperature and pressure. It appears that, at pressures below about 3 MPa, there are two distinct levels of burning rate temperature sensitivity. The very

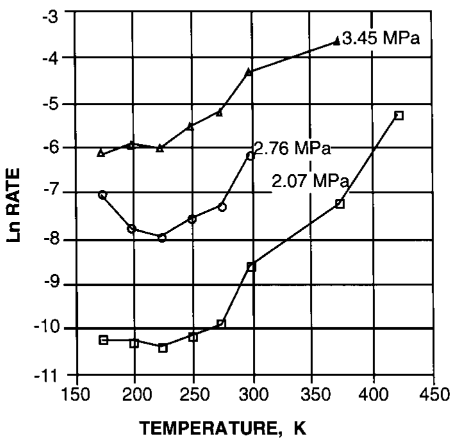

Fig. 6 Natural log of HMX burning rate vs temperature at 2.07, 2.76, and 3.45 MPa.

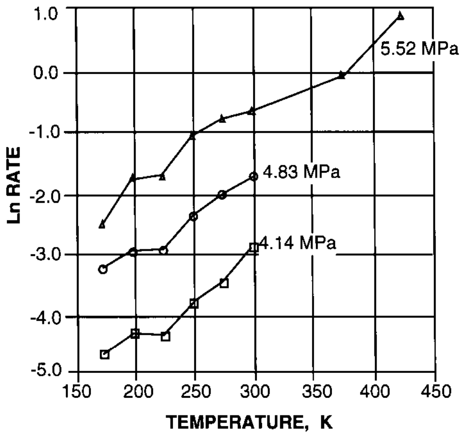

Fig. 7 Natural log of HMX burning rate vs temperature at 4.14, 4.83, and 5.52 MPa.

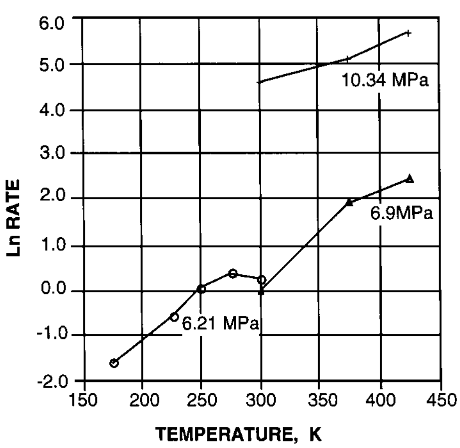

Fig. 8 Natural log of HMX burning rate vs temperature at 6.21, 6.9, and 10.34 MPa.

low-temperature sensitivity (as indicated by low slope in Figs. 5 and 6) region occurs at initial temperatures below ambient, with a break to higher temperature sensitivity at temperatures above ambient. This phenomenon may be due to the shift in the dominant decomposition reaction path at roughly 300 K. These data also demonstrate how the selection of initial temperatures for σ_p evaluation can influence the final results. Figure 9 presents a plot of the HMX temperature sensitivity. The effect of using either all of the points, three points, or the low-temperature points at 0.69 MPa changes the value of σ_p from about 0.23 to nearly 0.59.

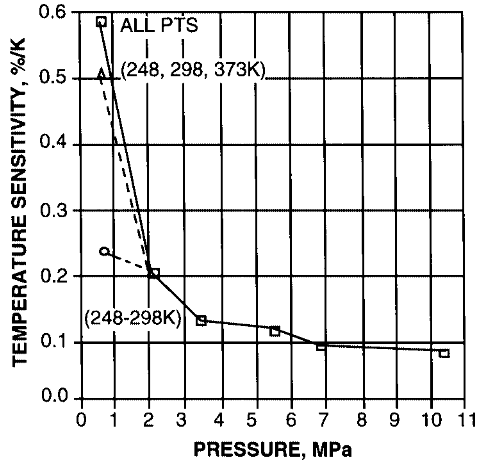

Fig. 9 HMX burning rate temperature sensitivity and the use of part or all of the data.

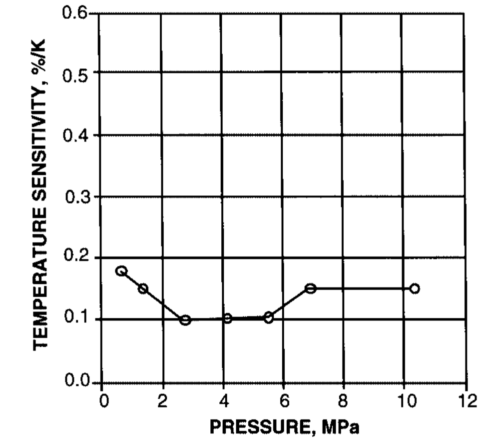

Fig. 10 RDX burning rate temperature sensitivity.

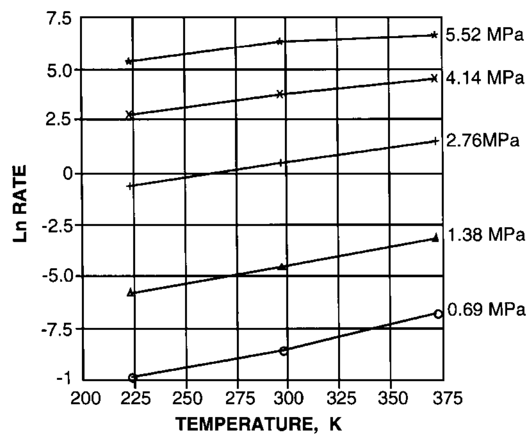

Fig. 11 Natural log of the CL-20 burning rate vs temperature at five pressures.

RDX

RDX burning rate data generated at four initial temperatures (223, 298, 373, and 423 K) plotted in Fig. 13 of Ref. 2 were used to generate the burning rate temperature sensitivity data of Fig. 10 here. Burning rate data were generated at the initial temperature of 423 K at only two pressures, 0.69 and 1.38 MPa.

CL-20

Burning rate data generated at three initial temperatures (223, 298, and 373 K) at pressures from 0.69 to 10.34 MPa are plotted in Fig. 14, Ref. 2. As in HMX, the highest burning rate temperature

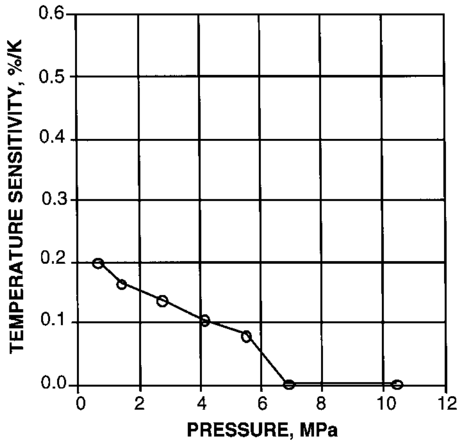

Fig. 12 CL-20 burning rate temperature sensitivity.

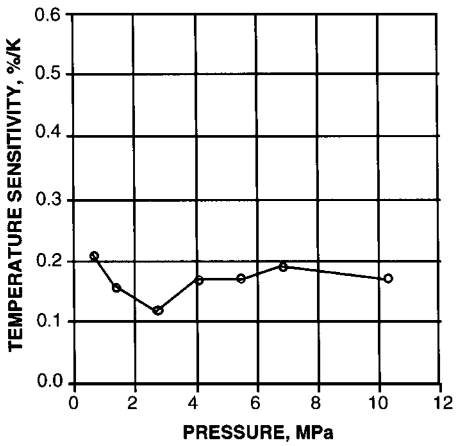

Fig. 13 HNF temperature sensitivity.

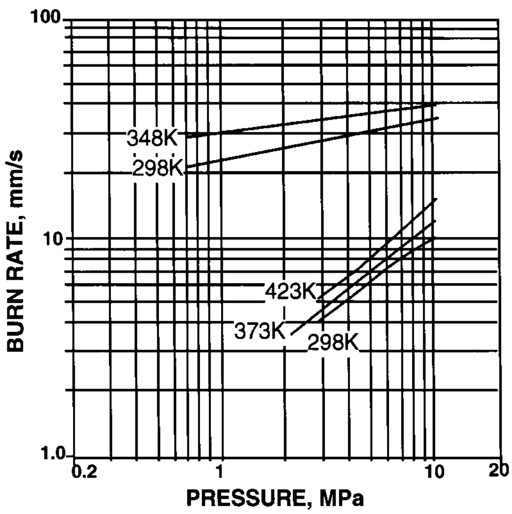

Fig. 14 Comparison of AP and ADN self-deflagration data.

sensitivity occurs at low pressure. The experimental data were again fit using a parametric spline, and the natural log of the fitted rates vs temperature is plotted in Fig. 11 here. These data are more linear than those of HMX, but there are considerably fewer data points as well. CL-20 σ_p data are plotted in Fig. 12. The burning rate temperature sensitivity goes to zero at pressures above about 7 MPa.

HNF

HNF burning rate data generated at three initial temperatures (223, 298, and 348 K) plotted in Fig. 17 of Ref. 2 were used to generate the burning rate temperature sensitivity data of Fig. 13 here. Like ADN, this material has a low melting point, which prevents an evaluation of σ_p over a broader range of temperatures.

Comparisons

As long as one understands the shortcomings of σ_p values, they provide a useful means of comparing the various materials.

Burning rate and pressure exponent effects can be examined by comparing the oxidizers AP and ADN. The burning rates are plotted in Fig. 14. AP has a burning rate of 0.81 cm/s with a burning rate pressure exponent of 0.73; ADN has a burning rate of about

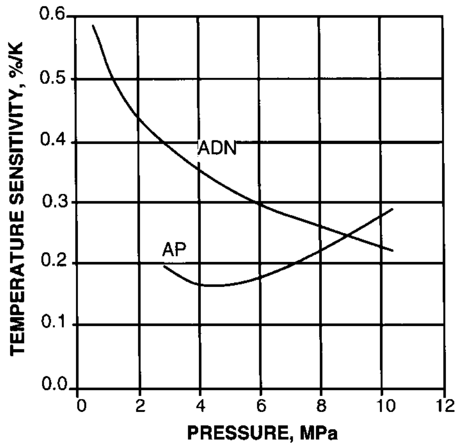

Fig. 15 AP and ADN burning rate temperature sensitivity.

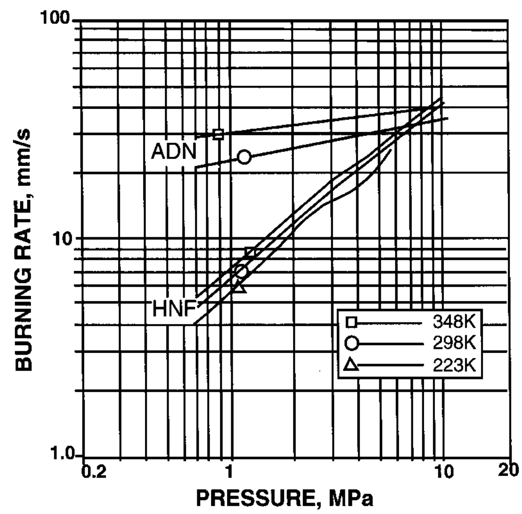

Fig. 16 Comparison of ADN and HNF self-deflagration data.

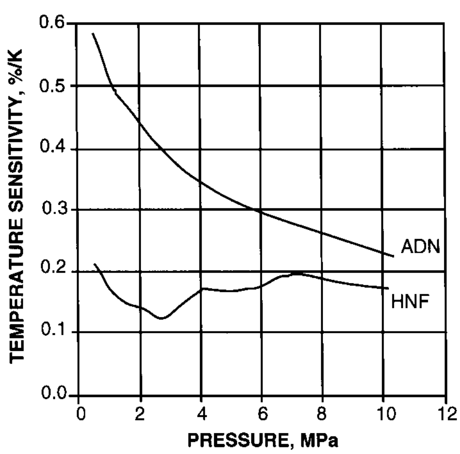

Fig. 17 Comparison of ADN and HNF burning rate temperature sensitivity.

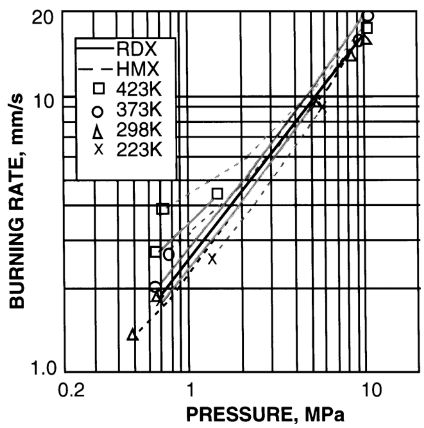

Fig. 18 Comparison of RDX and HMX self-deflagration data.

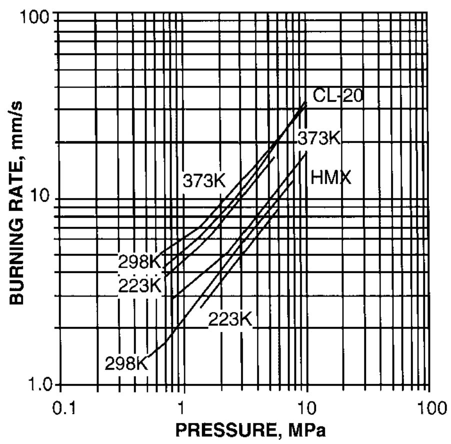

Fig. 19 Comparison of HMX and CL-20 self-deflagration data.

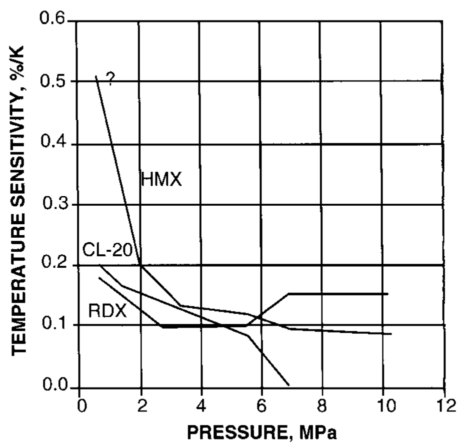

Fig. 20 Comparison of nitramine burning rate temperature sensitivity.

3.29 cm/s at the same pressure and a burning rate pressure exponent of about 0.19. The σ_p data for the two oxidizers are compared in Fig. 15.

ADN and HNF represent two materials with relatively low melting points. Their burning rates are compared in Fig. 16. HNF has a relatively high burning rate pressure exponent (~0.9) as compared to ADN. Burning rate temperature sensitivity vs pressure data are compared in Fig. 17.

The burning rate data at four equivalent initial temperatures for the nitramines RDX and HMX are compared in Fig. 18. It appears that HMX has a higher burning rate temperature sensitivity than RDX, particularly, at low pressures and elevated temperatures. The burning rates of CL-20 are compared to HMX in Fig. 19. The burning rate of CL-20 is approximately two times that of HMX. The burning rate pressure exponent of the three nitramines is approximately 0.8. The σ_p values for the three nitramines are compared in Fig. 20. The σ_p values of HMX using the 248, 298, and 373 K data were used in Fig. 20 as some questions concerning the HMX burning rates at 423 K have arisen. Further testing is currently in progress at this time.

Conclusions

The burning rate temperature sensitivity expressed as σ_p was determined for six energetic monopropellants using a set of burning rate data collected using a single experimental technique. The effect of initial temperature, data scatter, and smoothing on the final value of σ_p was demonstrated. The burning rate temperature sensitivity, or σ_p value, is not only a function of the intrinsic chemistry of the material but is also a function of the experimental conditions and even the method of data reduction. The sensitivity of burning rate to initial temperature is complex and is probably not adequately described by a single parameter, particularly when the apparent values are so heavily influenced by analytical techniques. As a comparative tool, σ_p may be useful, but the test conditions of temperature and pressure should be consistent for all of the materials being evaluated. If, for example, one material has been tested at low pressures and high temperature, it would not be wise to compare it to one tested at higher pressures and lower temperatures.

In general, as the experimental pressure is increased, the burning rate temperature sensitivity decreases. This is most apparent in the nitramines, particularly, CL-20. The only exception to this observation is AP; perhaps further testing is warranted at higher pressures just as further testing at low pressure of HMX has been initiated to verify what appears to be an unusually high σ_p result. At pressures below 4 MPa, RDX had the lowest value of σ_p.

It appears from the ADN and HNF data that a lower burning rate pressure exponent may result in a higher temperature sensitivity to burning rate. Burning rate temperature sensitivity and pressure exponent may both be influenced by the dominant levels of condensed- vs gas-phase reactions occurring in the materials.

When evaluating the burning rate temperate sensitivity of a material, the burning rates should be measured over evenly spaced temperature intervals that cover a range above and below ambient temperature to avoid extreme conditions. Burning rate measurements should be made over a large enough pressure range to ascertain the effect of pressure on burning rate temperature sensitivity. The experimental burning rate data should be examined for consistency and smoothed judiciously, and extrapolation should be avoided.

As stated earlier, a single parametric value for burning rate temperature sensitivity σ_p does not adequately describe the complexities of the combustion process and is best used for comparative purposes only.

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