Radiative Ignition of Double-Base Propellants: I. Some Formulation Effects

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In this first paper of a two part study, the ignition response to arc image radiative heating (5 to 100 cal/cm^2 sec) of several double-base propellants is examined; comparisons with certain AP and HMX propellants are made also. Ignition delay is affected by chemical factors in propellant formulation (stability of the condensed phase, reaction rate in the gas phase) and by optical factors in propellant formulation (opacifiers affecting reflectivity and in-depth absorption). The results show that comparisons of the chemical factors in the formulation can only be made properly when the optical factors are minimized (as by carbon addition). When optical factors are minimized by opacifying the propellant, one finds, in order of increasing ease of ignitability, the formulations tested fall as follows: HMX composite, AP composite, double base (noncatalyzed), double base (catalyzed).

I. Introduction

HIGH-intensity thermal radiation constitutes an easily controlled energy input with which to probe the ignition behavior of solid propellants. The arc image furnace and the continuous wave CO_2 laser are the two most convenient laboratory sources of such radiation. The former device, particularly, is widely used and has been the subject of extensive assessment as a propellant quality control and research tool.[1]

Neither device provides the ideal energy input—a flux that is spatially uniform and totally absorbed at the propellant surface, eliciting the identical ignition response in the research device that is obtained for the same flux in an application, e.g., a rocket motor. The nonideal effects include spatial nonuniformities over the sample surface, wavelength dependent volumetric and surface reflection, in-depth radiation absorption and scattering, and suppression of gas phase reactions by cool ambient gas. All of these factors have been recognized and discussed previously to varying degrees.[2-5]

The arc image furnace and the CO_2 laser possess these various nonidealities, each to a different extent. Insofar as these factors influence the observed ignition behavior of propellants, one can expect the results from the two devices to differ. Assessment and rationalization of these differences are two of the main objectives of this study. This has been done for several propellant formulations [double-base and certain ammonium perchlorate (AP), and HMX composites] to fulfill the third goal, i.e., a comparison of compositional effects on ignition behavior when experimental nonidealities are minimized.

This work is presented in two parts. In the present paper, emphasis is on the influence of propellant formulation on ignition behavior. The data here are essentially all from the arc image furnace, but the general conclusions are independent of radiation sources. In the companion paper, emphasis is on pre-ignition events and on effects of the nature of the radiation source. It will be shown that some observed aspects (e.g., extinguishment following deradiation and strong ignition-time dependence on particulate additives) of propellant ignition behavior do, indeed, depend on the radiation source.

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II. Experimental Apparatus and Procedures

The two radiation sources used in the study were a CO_2 laser and an arc image furnace; each had separate associated apparatus for sample holding, atmosphere control, etc. The same shutters were used with both, for control of sample exposure duration.

The laser apparatus is described in detail in Ref. 6 and will be outlined only briefly here. The laser itself is a 100-W continuous wave, multimode device emitting at 10.6 μ [far infrared (IR)]. Output power is controlled continuously by varying the excitation current. The beam passes through two shutters (see below) and then through a mixing device to improve its spatial uniformity. The sample (2.5 mm diam $\times$ 1 cm long, oriented with heated side down) is irradiated by a 2.5-mm-square spot which just covers its end surface. This sample diameter is much greater than the thermal wave thickness in the solid phase and also in the gas phase (except at low pressure, e.g., 1 atm). One dimensionality in this sense is, therefore, quite good. The visible flame zone of double-base propellants stands off the surface several millimeters, even at the highest pressure used (21 atm), but the visible flame zone has only a slight effect on heat feedback to the surface.

The flux over the laser-irradiated spot varies approximately $\pm 15\%$ from the average value, but not in a simple monotonic fashion; the nonuniformities are the result of interference fringes and tend to appear as very narrow rectangular strips parallel to the sides of the square spot. Lateral conduction tends to smear these out but a 10-15% variation over the spot area in the time of onset of gasification can be seen at 36 cal/cm^2-sec.

The radiation source in the arc image furnace is a 2500 W high-pressure xenon arc lamp. The spectral characteristics are similar to the sun (peak near 5500 Å), except for some nonequlibrium, high-intensity bands in the near infrared. A conventional double elliptical mirror system (shutters at intermediate focus) images the arc onto the sample surface. Flux level is controlled discontinuously by screens in the optical path (well out of any focal plane). The sample itself (oriented horizontally) is the same size as in the laser apparatus; the holder is such that irradiation of the sides is

prevented. The sample again sees a nonuniform flux, but here it does decay monotonically along any radial line from the center; the flux at the periphery is about 15% less than the peak value at the center.

Hy-Cal asymptotic calorimeters are used to measure flux in both setups. These devices tend to average the nonuniformities more effectively than does the sample surface.

The shutters (common to both setups) are of the iris leaf type. The first opens rapidly, and the second closes rapidly; action time for both is about one millisecond but it will tend to be longer for the arc furnace (about a factor of two) because a larger portion of the aperture is used.

The open/close sequence of the shutters provides a go/no-go type of test. For a fixed ambient pressure, the intensity of irradiation and its duration are varied in sequential tests until boundaries between regions of differing propellant behavior are found. As is customary, these boundaries are plotted on a log-log graph of irradiation time vs incident irradiation flux. The value of such a plot is that certain types of boundaries have simple, well-recognized interpretations, e.g., a straight line with a slope of -2.0 is the locus of times to reach a fixed surface temperature in an inert, opaque material.

Statistical treatments were not applied to the data, since it was not feasible to perform the very large number of tests required for the large number of propellants surveyed. Several figures in the text incorporate the data points (generally from 20 to 30) used to locate the boundaries they straddle. From these figures it is clear that the locations and slopes are justified but must be considered somewhat uncertain. Small differences (several percent) in boundary location and slope for different propellants cannot be termed significant.

The compositions of the various propellants tested are summarized in Table 1. Most of these were tested with the arc and laser apparatus at 5, 11, and 21 atm pressure; flux levels from 5 to 100 cal/cm^2-sec were used. The response of the propellant was in all cases noted as ignition/no ignition (go/no-go). For certain cases, this information was supplemented by high-speed shadowgraph and color movies (16 mm, 1000 frames/sec) to ascertain the underlying sequence of events.

Table 1 Propellants used in ignition experiments[a]

Ammonium perchlorate (AP)/hydrocarbon binder composite propellants:
Nonmetallized
1. 75% AP (45 μ) without C (batch 1086)
2. Same as 1 but with 1% C (batch 1087)
3. 80% AP (30% 15μ and 70% 180μ) (batch 1020)
Metallized
4. 24% AP and 51% boron
Nitrocellulose (NC) double base (DB) propellants:
5. Standard U.S. Army M-9 (39.6% NC, 49.4% NG, 11.0% plasticizer and stabilizer)
6. Nitrocellulose (NC) Plastisol [53.7% NC, 39.2% trimethylolethane trinitrate (MTN), 7.1% triethylene glycol dinitrate (TEGDN)] (batches 1069 and 1070)
7. Opacified NC plastisol, No. 6 with 0.2% C (batch 1059)
8. Opacified NC plastisol, No. 6 with 1.0% C (batch 1088)
9. Standard U.S. Navy N-5 (50.0% NC, 34.9% NG, 12.5% plasticizer and stabilizer, 2.6% Pb salts) (a JANNAF reference propellant)
10. Catalyzed NC plastisol, No. 6 with 2.0% lead salicylate (PbSa) and copper salicylate (CuSa) and 0.2% C (batch 1050)
Nitramine (HMX)/polyurethane (PU) propellants:
11. High energy propellant (85% HMX, 15% PU)
12. Cool propellant (75% HMX, 15% PU, 10% oxamide)

[a] Propellants 1, 2, and 3 were processed at Princeton using standard techniques.[18] Propellant 4 was supplied by the Huntsville Division of the Thiokol Corporation. Propellants 6, 7, 8, and 10 were processed at Princeton using the technique described in Ref. 17. Propellants 11 and 12 were supplied by the Wasatch Division of the Thiokol Corporation. Propellants 9 and 10 were catalyzed to produce increased burning rates and plateaus between 10 and 80 atm. Carbon was added to propellants 2, 7, 8, and 10 in the form of a powder (Neo Spectra TA, manufactured by Columbian Carbon Co.) with a mean diameter on the order of 0.01μ.

The monochromatic, far infrared (10.6 μ) nature of the CO_2 laser radiation essentially eliminates it as an interference if one wishes to observe emitted radiation from the irradiated propellant and its developing flame. In contrast, the arc radiation largely masks such observations. A gold-doped germanium infrared detector was used in the laser apparatus to monitor emitted radiation from the surface region of the sample. Its viewing angle was 90° from the sample axis and its field of view such that the radiation it sensed came predominantly from the region up to a few millimeters out from the surface; the surface itself was viewed only at grazing incidence. The radiation seen thus consisted, presumably, of that from gaseous and solid emitters in the developing flame above the surface, plus some contribution from the surface itself.

The IR detector output during a test consisted, generally, of a monotonically rising signal, whose gross slope depended on propellant type and ambient conditions. The first appearance of an IR signal generally followed closely upon first gasification of the surface and is interpreted here as the beginning of exothermic reaction in the gas phase near the surface; this time was noted. Also noted was the time at which an arbitrary but fixed, large IR signal was reached ($\sim 50\times$ the miniminum detectable signal); this is interpreted as an indication of substantial flame development in the gas phase. Such IR signals are subject to some ambiguities, but it is believed that their utilization here is reasonable and useful.

Figure 1 is intended to assist the reader in distinguishing the spectral regions involved with the various radiation emitters and the IR detector; note that the different ordinates on the figure are not drawn to the same scale. Note first that the laser and the xenon arc are at opposite ends of the wavelength scale; the laser is monochromatic and the arc panchromatic. Also shown are two blackbody curves for temperatures encountered near the propellant surfaces at about the time of ignition; the IR detector is quite sensitive to these emissions, and to those of higher temperature emitters. On the other hand, its sensitivity is greatly reduced at the laser wavelength.

III. General Ignition Behavior Boundaries for an Arbitrary Propellant

In order to facilitate subsequent discussion of the behavior of various propellants, it is useful to summarize in one general figure the various types of boundaries seen on the ignition maps (log of ignition time vs log of heat flux) to follow. Figure 2 is such a general map. It derives from the present study and that of many previous investigators; here, however, more attention is given to the sequence of processes within the ignition event.

Figure 2 is most easily understood if one considers the timewise sequence of events occurring when a propellant is subjected to a fixed incident radiant flux (recall also that pressure is fixed). Such a sequence occurs along a vertical line in Fig. 2; irradiation time increases as one goes up the line.

There are at least two ways of locating the position of the propellant on the line of constant flux as irradiation time increases. (Alternatively stated, there are at least two ways to locate the points where the propellant crosses a behavior boundary.) First, as the go/no-go test implies, the flux can be terminated and the subsequent behavior of the propellant can be determined. This locates the crossing of one of three boundaries, the crossing of a "first-effect" boundary (first discernible change in the propellant), the crossing of a self-sustaining ignition boundary, or the crossing of a dynamic extinction boundary. Second, the IR emissions can be monitored, as described in Sec. II; these emissions locate the crossing of "weak flame" boundary or the crossing of a

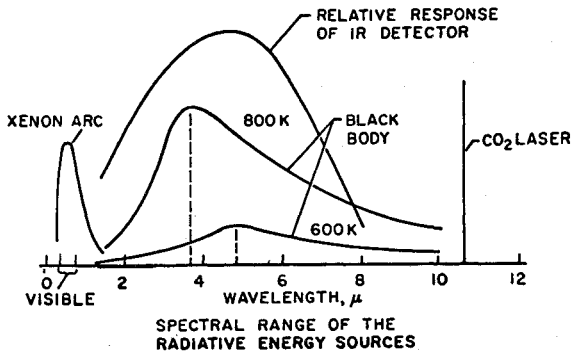

Fig. 1 Spectral range of energy sources (not to scale) and IR detector response.

"substantial flame" boundary. These terms are explained in the following paragraphs. This information is supplemented by the use of high-speed motion pictures.

Consider a propellant subjected to a fixed flux corresponding to the vertical line in Fig. 2. At short times, the rise in surface temperature will be insufficient to induce any significant reaction; if the flux is ended at such times, the propellant will appear to be macroscopically unchanged. If instead the flux is continued, the surface temperature will reach a level at which reactions leading to propellant gasification begin abruptly. This sudden change in behavior defines the "first effect" or gas evolution boundary; this is denoted in Fig. 2 as the L_{1a} boundary. It is usually the result of chemical processes in the condensed phase and is, therefore, pressure independent. Its dependence on flux suggests that it corresponds roughly to attainment of a fixed surface temperature (slope of -2 would yield exact correspondence for an opaque body). The location and behavior of this boundary is better described by thermal ignition theories,[7,8] which incorporate a description of the condensed phase reactions.

If the flux is continued past the crossing of L_{1a}, gas evolution continues and the various species entering the initially cold gas phase begin to undergo further reaction, evolving heat. The IR detector senses this; the first departure of the IR detector signal from zero thus denotes the location of this behavior boundary, defined as L_{1b} in Fig. 2. Since it depends on the sensitivity of the IR detection system, this boundary is less precise than the gasification boundary that precedes it; nevertheless it is indicative of the onset of flame development in the gas phase. The same remark applies to the next boundary encountered as irradiation continues. This is the substantially developed flame boundary L_{1c}. This corresponds to an arbitrary, fixed large value of the IR detector signal. For uncatalyzed double-base propellants it is near the final (fully developed) level; for catalyzed double-base propellants, it is about midway to the final value; for AP composites it is a fairly small fraction of the final signal. The evolution of the gas phase flame is, of course, a continuous process that, in general, does not pass through sharply defined phases. The L_{1b} and L_{1c} boundaries serve mainly to elucidate the rate of flame development and its dependence on ignition parameters.

Continued irradiation leads next to a sharp boundary defined by the go/no-go nature of the test; this is the self-sustained ignition line, denoted L_{1d}. As the name implies, when this boundary is crossed, removal of the radiation is followed by sustained burning of the propellant. (Passage of the L_{1a} to L_{1c} boundaries does not assure continued burning after irradiation.) In general, the position of this boundary is pressure-dependent (as is L_{1c}), since it reflects the time of attainment of a gas phase flame that has steady-state flame characteristics (the exact requirement fulfilled at this boundary is unclear; it is discussed in Part II of the paper). Prediction of the location and behavior of this line is difficult, but reasonably successful models do exist.[9,10]

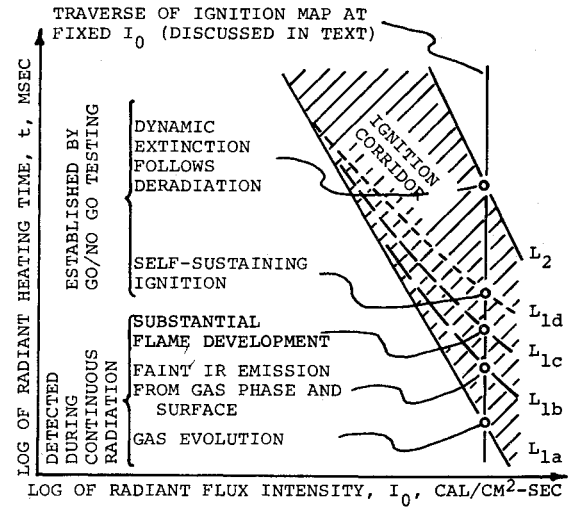

Fig. 2 Generalized ignition map showing event limits or signals that occur during radiant heating of solid propellants.

In nearly all studies, this L_{1d} limit has been the last one encountered with increasing irradiation time; all longer exposures led to continued burning. A series of experiments at Princeton University has shown that this may not always be so.[11]. Continued irradiation forces the flame into a steady burning condition that is artificially forced to a higher (as compared in the steady-state value without radiation) rate by the external radiation. The sustained combustion of certain propellants (notably uncatalyzed double base) cannot survive the disturbance induced by abrupt termination of the radiation; when the radiation stops, the propellant is extinguished in much the same way as if it had been rapidly depressurized. Prediction of the location and behavior of this L_2 line requires all of the same theoretical inputs as predictions of L_{1d}. A successful quantitative model has been presented previously;[11] an additional theoretical study of the dynamics of deradiation will be published.[12] It should be noted that this boundary is a property of the propellant and the speed of deradiation. Certain nonidealities, e.g., 3-D heat losses in the gas phase due to finite sample size, will affect it only minimally. Other nonidealities (especially propellant transparency) can affect it drastically, as will be seen in Part II.

As will be seen in the following sections and in the companion paper,[13] for many propellants, the map of ignition behavior is far simpler than that in Fig. 2. For certain conditions, the L_{1a} to L_{1d} boundaries collapse to a single line (L_1); in addition, the L_2 boundary does not always exist.

IV. Effects of Propellant Formulation on Ignition Behavior

High ambient pressure greatly simplifies the ignition behavior in go/no-go testing. This point will be discussed further later; at this point it should be noted that, particularly with the arc image, the "map" for a fixed propellant at a fixed high pressure reduces to a single line above which self-sustained ignition ensues. In effect, this says that the L_{1d} limit (self-sustained ignition) becomes indistinguishably coincident with the L_{1a} limit (first gas evolution). For the propellants tested and the range of heat flux considered, 21 atm was sufficient to achieve this.

When the ignition "map" is thus simplified by high ambient pressure, only three major factors contribute to the location and local slope of this L_1 boundary. These are surface reflection, in-depth extinction coefficient, and propellant reactivity. All three factors are sensitive to the propellant formulation; the first two are essentially physical effects, and the third reflects the thermal stability of the ingredients.

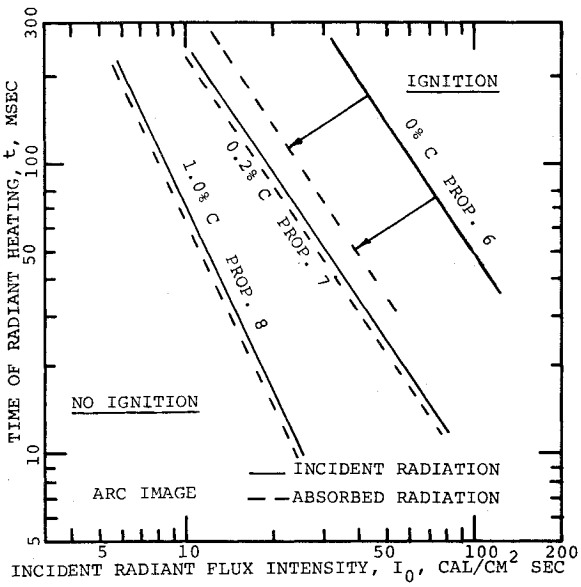

Fig. 3 Ignition times as a function of incident and absorbed radiation showing that reflectivity corrections alone do not fully account for the effects of particulate carbon additives.

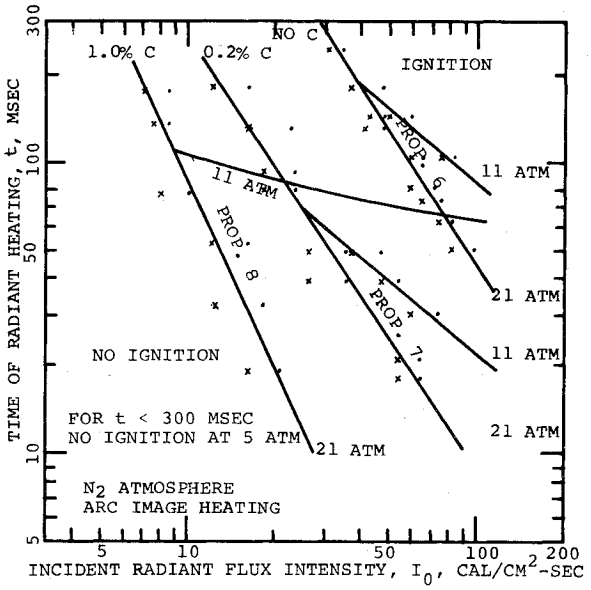

Fig. 4 Arc image ignition data showing decrease of ignition delay with increase of carbon content and pressure dependent delay at low pressure, which varies substantially with carbon content.

A. Carbon Addition

The influence of these first two physical factors on the ignition behavior of a nitrocellulose/TMETN double-base propellant is shown in Fig. 3, obtained with the arc image. The optical properties of the basic composition (#6 in Table 1) can be altered substantially by the addition of carbon black (0.2%-#7; 1% – #8). (Some chemical effects of the carbon black cannot be ruled out, but the results are qualitatively consistent with optical changes). The basic propellant has a quite high diffuse reflectivity (60% average from 0.4 to 2μ) because of in-depth back-scattering; 0.2% carbon decreases this to about 5%, while increasing the average in-depth extinction coefficient by a factor of 20; 1% carbon leaves the reflectivity at 5%, but increases the extinction coefficient by a factor of five.[14]

Figure 3 shows that the combined effects of carbon on optical properties (reflection and in-depth absorptivity) yield a dramatic shift of the L_I boundary to shorter times with a simultaneous increase in slope. A reflectivity decrease alone will shift the line to the left but leave the slope unaltered; an extinction coefficient increase will shift the line to the left and raise its slope toward -2.[15,16] Both effects are operative in Fig. 3. (Note: Some caution is indicated here. The shift of the dashed lines in Fig. 3 should show the effect of carbon on extinction coefficient alone. Comparison of propellants 6 and 8 shows a shift that is plausible in light of the measured increase in extinction coefficient. The shift seen in comparing propellants 6 and 7 is in the right direction, but it is not as large as the increase in extinction coefficient would predict. The reason for this discrepancy is not known at the present time.) Further evidence of such optical effects on the L_I boundary will be pointed out elsewhere, in the context of other comparisons.

When these same propellants are ignited under lesser ambient pressure, conditions are less conducive to very rapid flame development, so that processes occurring after first gasification limit the attainment of self-sustaining ignition. (The L_{Ia} to L_{Id} boundaries spread apart, as indicated in Fig. 2). The simplest possible additional factor that this could add to the ignition behavior would be a fixed "flame development time," whose value depends only on pressure. Certain arc image data have been shown to be qualitatively consistent with this simple idea.[16] Reference to Fig. 4 shows that this is not always so. The lower lines for each propellant are the same boundaries as those shown in Fig. 3. When the pressure is lowered to 11 atm, these boundaries (above a certain flux level) become merely the L_{Ia} (first gasification) lines; the branch lines, labeled 11 atm, indicate the locations of the L_{Id} (self-sustained ignition) boundaries. Inspection of the figure shows that as carbon addition shifts L_{Ia} to shorter times, the L_{Id} boundaries do not behave simply as though the same fixed "flame development time" was additive to the time given (at each flux) by L_{Ia}. Comparing the gap (at a given flux) between L_{Ia} and L_{Id} for propellants 7 and 8, one finds that 8 has a substantially longer "flame development time." There may be many factors contributing to the differences. Among them are experimental nonidealities, such as variations in radiation penetration through the gases coming from the propellant surface. This is discussed in further detail in Part II of this paper. (Note: an alternative to carbon addition as a propellant opacifier is a black, inert surface coating.[5] This is useful in locating the L_{Ia} line for any condition, or the L_I line for high pressure. It is undesirable when there is a substantial gap between L_{Ia} and L_{Id}, because the coating is blown off the the surface absorptoin properties change).

B. Propellant Class

Returning again to the high ambient pressure situation (to simplify the ignition "map"), one can attempt to bring out the chemical influence on ignition behavior by looking at different classes of propellants. Unfortunately, these propellants also have differing optical properties, and this may obscure the chemical effects somewhat.

A limited look at the effects of propellant class on ignitability was undertaken here; the double-base behavior is contrasted with that of an AP and HMX composite (see Table 1 for complete formulations). Since the ignition boundaries are indicative of the temperature needed to initiate rapid decomposition of the propellant, one could reasonably expect that the ordering of ease of ignition will be the same as the ordering of burning surface temperatures for these different propellent classes; the latter are also some measure of ease of decomposition of the solids. These burning surface temperatures are approximately: double base, 260-340° C,[17] AP composite, 700-800°C,[18] HMX composite, 1050°C.[19] Thus, double-base propellants are expected to ignite much more easily than HMX composites, and AP composites should fall between these two.

Figure 5a shows the ignition behavior of seven propellants in these three classes as found in the arc image; note that the

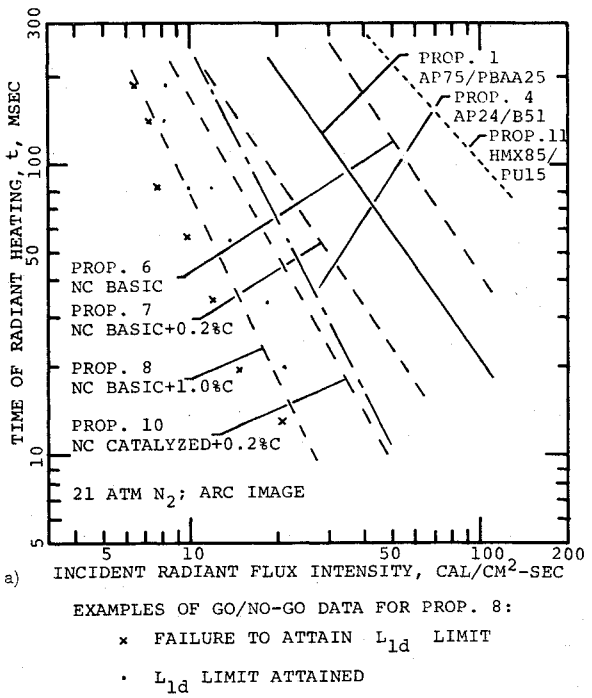

Fig. 5a Arc image ignition limits of several propellant classes (based on incident radiant flux).

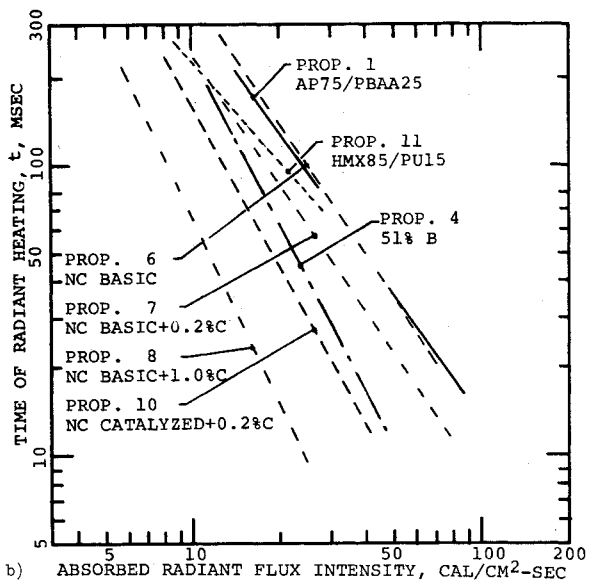

Fig. 5b Arc image ignition limits of several propellants (based on radiant flux corrected for reflection).

horizontal axis is incident flux. No pattern is immediately apparent and, indeed, one of the major problems with the arc image is that the data have such mixed dependencies on optical properties and chemistry that reliable trends are difficult to sort out.

First note that, in light of Fig. 3, the line for the nitrocellulose, NC, basic propellant, which most accurately reflects its ease of ignitability exclusive of optical properties, is that for propellant 8. The boundaries for propellants 6 and 7 should be excluded in the present comparison of chemical reactivities. Also, some of the propellants have quite substantial reflectivities for the xenon arc radiation; in view of this, comparisons are better made on the basis of absorbed radiant flux, as is shown in Fig. 5b.

Optical effects are not eliminated in Fig. 5b since the various propellants have differing extinction coefficients. These extinction coefficients are the result of in-depth scattering and absorption. They are quite difficult to measure and correct for, although some success has been reported.[14] A significant problem is that reflectivity and extinction coefficients are dependent on propellant temperature and the state of degradation. Sufficient data are not available to eliminate by computation the in-depth effects on the slope of the L_l boundary. The closer this slope is to -2, the more opaque the propellant is and the less its ignition delay has been distended. (There are chemical effects on the slope, but for the usual rather high activation energy they are appreciably less than the optical effects.[7,8]) The slopes of the L_l boundaries for all the propellants in this study are summarized in Table 2.

Table 2 Measured slopes of ignition boundaries at 21 atm N_2 showing dependence of results on radiative energy source and optical properties of propellants

Propellant #	Laser heating	Arc heating
1	−1.3	−1.4
2	−1.6	−1.5
3	−1.3	Not determined
4	−2.0	−2.0
5	−2.0	Not determined
6	−1.5	−1.5
7	−1.6	−1.5
8	−1.6	−2.0
9	−1.7	Not determined
10	−1.6	−1.8
11	Not determined	−1.8
12	Not determined	−2.0 (air)

Propellant 8, with a slope of -2.0, has negligible optical effects, so that its position on Fig. 5b is firm. Propellant 4 also is firmly placed. It behaves according to the expectation that an AP composite is harder to ignite than a double-base propellant, although it must be admitted that propellant 4, with its very high metal loading, is quite atypical. Propellant 1 is more typical; it falls well above propellant 8. Although part of this lower ignitability of propellant 1 is due to transparency effects, part is very likely due to the greater stability of the AP. The situation with respect to the relative ignitability of AP and HMX composites is not clear, since the lines are close and the slopes fall in the range of -1.5 to -1.7; optical effects are not negligible. One can conclude from these data only that the ignitability of these two types of propellants is not greatly different, at least at high pressures in an inert atmosphere.

The behavior of the AP and HMX composites does differ when the pressure is not so high as that in the preceding. Figure 6a shows arc image data for three AP composites. For propellants 1 and 2, the same L_l boundary is found at 5, 11, and 21 atm of nitrogen; for propellant 4, the same boundary holds at least down to 11 atm (no data obtained at lower pressure). Thus, despite the rate-retarding effect on flame development of a factor of four decrease in pressure (21 to 5 atm), evolution of the gas phase flame still proceeds far enough in such a short time that there is no discernible separation between the L_{la} and L_{ld} boundary. This is consistent with the usual picture of the flame zone in such propellants—AP decomposition provides substantial heat release very close to the surface, and the remaining heat release occurs in a closely coupled diffusion flame.[18] Sufficient decrease in pressure will, of course, weaken this coupling to the surface; various researchers have found a pressure-dependent L_{ld} boundary in AP composites near 1 atm.[3,10,20]

Figure 6b illustrates that the HMX/polyurethane composite propellants have the slowest flame development of the propellants tested. Indeed, in order to achieve ignition of propellants 11 and 12, it was necessary to conduct the experiments at the highest pressure or in air. Within the domain of Fig. 6b, propellant 11 would not ignite at 11 atm of N_2 and propellant 12 would not ignite even at 21 atm of N_2.

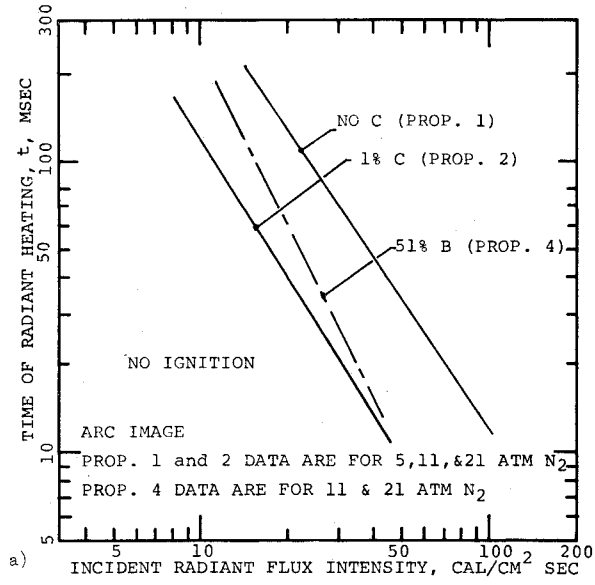

Fig. 6a Ignition of AP composite propellants 1, 2, and 4 demonstrating independence of pressure (contrast with Fig. 4).

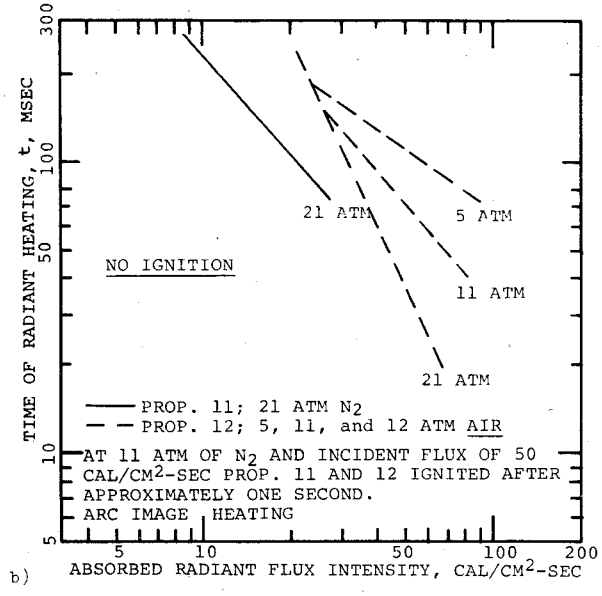

Fig. 6b Arc-image ignition data for HMX composite propellants 11 and 12 in N_2 and in air showing resistance to ignition.

Propellant 12 is the same as propellant 11, except that it contains 10% oxamide, an ingredient which is commonly used to suppress burning rate by reducing the exothermicity near the propellant surface. In the present test situation, relatively slow decomposition of oxamide could be partially responsible for the pressure-dependent L_{Id} boundary at 5 and 11 atm of air. The endothermicity of the oxamide decomposition is also the probable reason for the lesser ignitability of propellant 12 compared to 11, as indicated by the higher L_{Id}. The retardant effect on the flame development is countered partially by the oxygen present in the ambient gas.

The data in Fig. 4, particularly for propellant 8, when compared with that in Fig. 6a and 6b, indicate that the noncatalyzed double base propellant has the slowest flame development of the three classes examined here. There is a long delay, even at 11 atm, between onset of gasification and attainment of self-sustained ignition. Again, this is consistent with the accepted picture of the double-base flame zone. There is moderate exothermicity in the decomposing surface region, followed by a closely coupled but only mildly exothermic gas phase flame (fizz zone); the bulk of the heat release is in the visible flame zone that, at pressures examined here, stands well off the surface [0(1 cm)].[17]

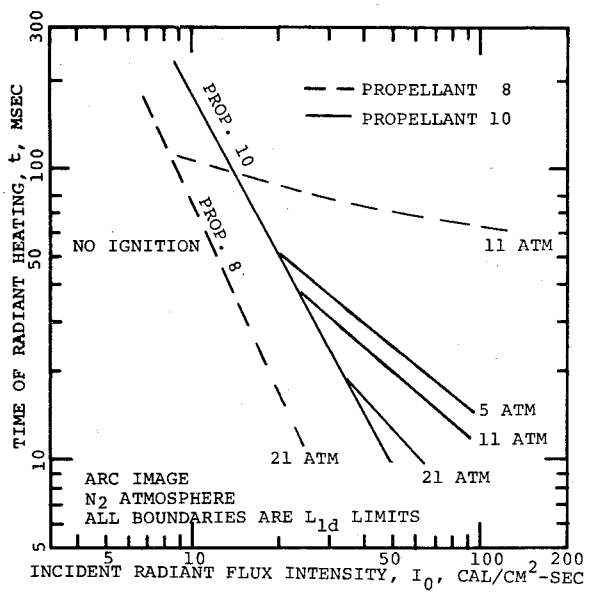

Fig. 7 Effect of catalyst on ignition of double base propellant.

C. Effect of Catalyst in Double-Base Propellants

Various lead and copper salts, when added to nitrate ester propellants, cause large pressure-dependent increases in burning rate; thus these additives frequently are called catalysts, although this may be a misnomer in the strictest sense.

The effect of 1% each of lead and copper salicylate on the arc image ignition behavior of the basic double-base propellant is shown in Fig. 7. Looking first at the L_I boundaries for the two propellants at 21 atm, one again encounters the ambiguities caused by mixed optical and chemical effects on ignitability. The two propellants have essentially the same reflectivity but may differ significantly in extinction coefficient. As noted previously, the -2.0 slope of the L_I boundary of propellant 8 indicates that it is essentially opaque, the -1.77 slope of the L_I boundary of propellant 10 indicates that it is somewhat transparent. One can conclude then only that the true L_I boundaries (minus optical effects) of the two propellants are not greatly different; there seems to be no dramatic effect of the catalysts on the initial decomposition process in the condensed phase.

At lower pressures, where gas phase flame development is slower, distinct effects of the catalyst are noticeable. From Fig. 4 it can be observed that at 11 atm the gap between L_{Ia} and L_{Id} is considerably lessened by the catalysts. This effect is consistent with the experimentally determined role of these catalysts on the steady-state flame structure.[17] They act to accelerate the rate of reaction in the fizz zone, yielding a more closely surface-coupled flame at any given pressure.

V. Conclusions

The position of the ignition behavior boundaries of a given propellant can be rationalized in terms of the reactivity of the material and the efficiency with which it utilizes incident radiant heat. The latter problem is peculiar to radiative heating and can obscure the underlying propellant reactivity effects in comparative ignitability testing. When the inefficiencies in energy use are factored out by opacifying the propellant and subtracting the reflected energy, the true underlying chemical effects can be seen. With the possible exception of the relative ignitabilities of HMX and AP composites at high pressures, the ignitability vs composition then

seen is consistent with information derived from other sources on flame structure and thermal stability.

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