Particle Radiative Feedback in Ammonium Perchlorate Deflagration

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The deflagration behavior of ammonium perchlorate (AP) with carbon black and copper chromite catalyst additives was studied over a pressure range of 4.3-171 MPa (50-2500 psig) using light transmission and emission measurements in a window bomb and burn rate measurements in a conventional strand burner. It was found that a maximum value of the lower pressure limit P_{DL} exists at intermediate values of carbon black concentration similar to that already reported for copper chromite catalyst. It was also found that sufficiently high concentrations of carbon black augment the steady deflagration rate of AP. Since carbon black is not a catalyst of AP decomposition, it is postulated that particle radiative feedback is more likely to be the cause of the observed behavior than previously suggested catalyst effects. To quantify the amount of radiative heat feedback, flame temperature and emissivity values were calculated from light emission/transmission measurements. These calculations yielded flame temperatures between 1406 and 1449 K and a value for the effective particle absorption efficiency over diameter Q_a/d of 4.1 μm^{-1} in good agreement with expected values. A simple analysis shows that the observed trends (increasing P_{DL} at low particle concentrations and decreasing P_{DL} at higher concentrations) can be predicted from simple radiative transfer considerations together with particle and matrix continuity equations.

Nomenclature

a = absorption coefficient, μm^{-1}
C_a = absorption cross-section, cm^2
C_s = AP specific heat, 0.33 cal/g·K
d = particle diameter
D = diameter of pellet and flame, 1.27 cm
f_m = mass fraction of particles
f_v = volume fraction of particles
H = thickness of isothermal radiative surface zone, μm
I = intensity, $W/cm^2 \cdot nm \cdot sr$
I_0 = incident intensity
k = proportionality constant, including efficiency of optics and detector sensitivity, $V/(W/cm^2 \cdot nm \cdot sr)$ or imaginary component of refractive index, $n-ik$
L = height of flame zone, cm
M_g = mean molecular weight of combustion product gases, 28.4 g/mole
n = real part of refractive index, $n-ik$
N = number density of particles, cm^{-3}
P = pressure, psi or Pa
q = net radiative heat loss from surface, $cal/cm^2 \cdot s$
Q_a = particle absorption efficiency
r = linear burn rate, cm/s, or particle radius, μm
$\bar{R}$ = universal gas constant, 1206.2 psia·cm^3/mole·K
S_{1-4} = signal voltages
SI = spectral irradiance = $I\Delta\Omega$, $W/cm^2 \cdot nm$
T = temperature, K
T_2 = overall transmittance for two combustion bomb windows
T_f = flame temperature, K
T_s = surface temperature, K
TCP = tricalcium phosphate
U = gas velocity above propellant
ϵ = monochromatic flame emissivity
κ = monochromatic flame optical depth
λ_s = AP thermal conductivity, 9×10^{-4} cal/cm·s·K
ρ = directional-hemispherical monochromatic reflectivity
$\rho_{g,s,p}$ = density of gas (from ideal-gas law), solid 1.95 g/cm^3, or particles
σ = Stefan-Boltzmann constant, 1.37×10^{-12} $cal/cm^2 \cdot s$
τ = monochromatic flame transmissivity
τ_w = window transmissivity

Subscripts

b = blackbody
DL = deflagration limit
g = gas phase
s = solid (or condensed) phase
w = window

Introduction

AMMONIUM perchlorate (AP) has been the subject of many combustion studies due to its importance as a composite propellant ingredient. Among the various factors known to influence the deflagration behavior of AP are particle additives,[1-5] dopants,[6] external radiation,[2,7] and sample preparation effects,[8,9] including AP purity, pellet density, AP size, AP type, and initial temperature. Among these, the influence of particle additives has received particular attention.

Of the various particle additives tested, copper chromite has achieved a considerable reputation as an effective catalyst of AP decomposition. Friedman et al.[1] and Levy and Friedman[2] noted that, while small amounts of copper chromite tend to inhibit AP deflagration as evidenced by lower burn rates and higher low-pressure deflagration limits (P_{DL}), large amounts of the catalyst actually enhance burning as evidenced by higher burn rates and much lower values of P_{DL}. Cohen Nir[4] reported similar behavior upon addition of the catalyst cuprous oxide.

The probable explanation for the inhibiting effect of the particles at relatively low concentrations is that the effective

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emissivity of the surface is increased by their presence. Spalding[10] demonstrated that radiative heat loss from the propellant surface can lead to the existence of both lower and upper limits to the pressure under which stable burning is possible. Thus, increasing the propellant emissivity by the addition of black particles causes steady deflagration to be increasingly more difficult.

At high particle concentrations, however, the opposite trend is observed. Beyond a certain amount, further addition of catalyst causes the burn rate to increase above that for pure AP and the lower pressure limit to decrease. One explanation offered for this behavior is that, at higher additive concentrations, catalysis of the gas-phase reactions offsets the heat loss effect, thus enhancing deflagration.[2]

The purpose of this study was to investigate another possible explanation for the enhancement of AP deflagration at relatively high particle concentrations—that of particle radiative feedback. It is likely that the observed augmentation of deflagration at higher particle loadings could be due to increased thermal radiative feedback coming from the hot particles in the gas above the propellant surface rather than more effective catalysis of gaseous reactions. To test this hypothesis, two types of experiments were performed. First, standard burn rate measurements of pressed AP pellets containing carbon black were made to determine if the same deflagration enhancement existed for a noncatalytic additive at high particle loadings, as was observed for known catalytic materials. Second, in-situ measurements of flame temperature and emissivity were made for AP pellets containing carbon black to determine whether sufficient radiative feedback may be present to offset the surface radiative loss.

Sample Preparation

Cylindrical pellets for use in both the strand burner tests and the window bomb studies were formed by pressing AP in a cylindrical die. The pellets were 1.27 cm (0.5 in.) in diameter and 1.17 cm (0.46 in.) in length. They were pressed hydraulically to 54.4 MPa (8000 psi) and held for approximately 60 s. Effects of variation in pressure and duration of compression have been discussed elsewhere.[9] The percent theoretical maximum density of the pellets was not determined. All of the pellets were prepared in the same manner, however.

The AP used to make the pellets was reclaimed AP that had been recoated with tricalcium phosphate (TCP) for anticaking behavior. Because the AP had been recoated with TCP, the burn rate was substantially suppressed below that of pure AP. Boggs et al.[9] discuss the influence of TCP as well as other factors on the deflagration of pure AP. Two sizes of AP were used in the present studies, 24 and 50 μm.

Two types of particles were investigated, Thermax carbon black and Harshaw "copper chromite," coded Cu0202. As discussed by Boggs et al.,[5] Harshaw Cu0202 is actually not copper chromite, $Cu_2Cr_2O_4$ or $CuO \cdot CuCr_2O_3$, but a compound containing 65.1% Cu and 11.8% Cr, with an average particle diameter of 0.54 μm which is more nearly described by the chemical formula $9CuO \cdot Cr_2O_3$ or $8CuO \cdot CuCr_2O_4$.

Both the window bomb and strand burner samples used in this study were coated with a thin layer of ignitor paste to facilitate ignition. Inhibition of the sides of the pellets was not found to be necessary.

Strand Burner Measurements

Burn rate measurements were made in a conventional strand burner, pressurized with nitrogen, with the burn rate determined from acoustic emission. Four particle concentrations were used, approximately 0.1, 1, 10, and 20% by mass, with two particle types, carbon black and Cu0202. For the carbon black, two AP sizes were used, 50 and 24 μm. For the Cu0202 only 24 μm AP was used. For each mixture burn rate was measured at five pressure, 3.4, 6.8, 10.2, 13.6, and 17.0 MPa (500, 1000, 1500, 2000, and 2500 psi). The results for burn rate are presented in Table 1 and Figs. 1-3. In Table 1, the mass fraction f_m is listed only approximately as either 0, 0.1, 1, 10, or 20% so that burn rates for different particle types with similar mass fractions can be compared. The exact values of f_m are listed in Figs. 1-3. For some of the tests involving carbon, the samples did not burn or burned only partially. These cases are noted in Table 1.

Table 1 Burn rate in strand burner

Carbon P=psig	(MPA)	f_m, %	Burn rate, cm/s: 24 μm AP Cu0202	24 μm AP carbon	50 μm AP carbon
2500	(17.0)	0	—	0.65	1.1
		0.1	1.8	No burn	0.94
		1	3.1	0.93	0.31
		10	4.0	1.1	0.87
		20	5.3	1.7	2.8
2000	(13.6)	0	—	0.52	1.1
		0.1	2.1	0.43	0.83
		1	2.7	0.83	0.20
		10	3.9	0.93	0.63
		20	3.6	1.3	2.1
1500	(10.3)	0	—	0.44	0.90
		0.1	1.3	0.35	0.57
		1	2.3	0.30	Partial
		10	5.3	No burn	Partial
		20	2.5	1.2	0.84
1000	(6.9)	0	—	0.29	0.86
		0.1	1.0	Partial	0.37
		1	1.5	Partial	No burn
		10	No data	No burn	No burn
		20	3.6	1.9	0.98
500	(3.5)	0	—	Partial	0.41
		0.1	1.2	No burn	Partial
		1	1.1	No burn	No burn
		10	No data	No burn	No burn
		20	1.5	0.6	No data

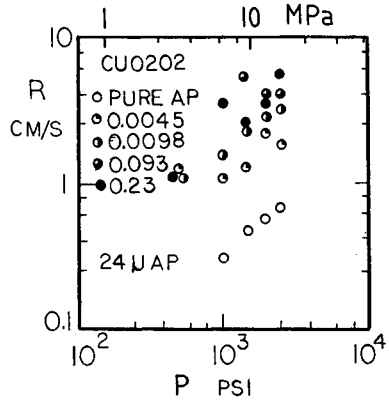

Fig. 1 Deflagration rate for 24 μm AP/Cu0202 (strand burner).

Several observations can be made about the results in Figs. 1-3.

1) The results for Cu0202 (Fig. 1) compared with those of carbon black (Figs. 2 and 3) demonstrate clearly that Cu0202 enhances burn rate better than carbon black, presumably due to a catalytic effect.

2) Although 50 μm AP clearly burns faster than 24 μm AP without an additive (due to a smaller amount of TCP inhibitor present in the 50 μm pellets), with carbon black present such a clear distinction is not evident.

3) While small amounts of carbon black tend to depress the burn rate below that of pure AP, larger amounts augment the burn rate even above that for pure AP.

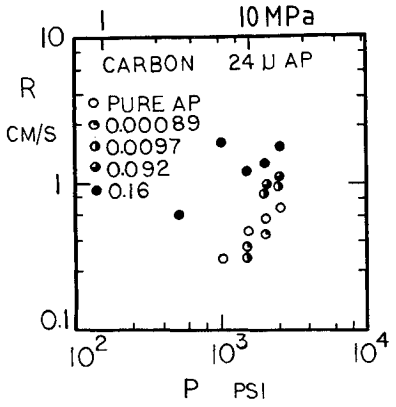

Fig. 2 Deflagration rate for 24 μm AP/carbon black (strand burner).

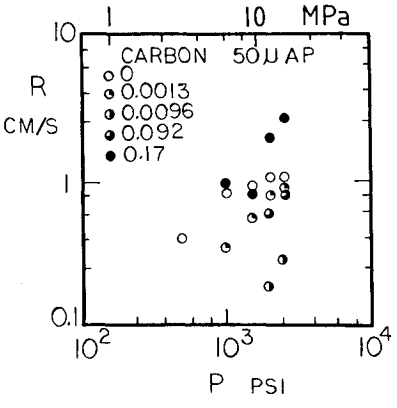

Fig. 3 Deflagration rate for 50 μm AP/carbon black (strand burner).

The latter observation is the same one that has been made with regard to the addition of catalyst particles, Cu_2O and Cu0202, indicating that either the carbon black is effectively catalyzing the combustion reactions or that another mechanism is responsible for the observed behavior. The unlikelihood of effective catalysis by carbon black is evidenced by no known observations of carbon black catalyzing AP decomposition at low temperatures similar to that which has been widely reported for Cu0202.[11]

The minimum pressure at which steady, stable deflagration was observed is plotted in Fig. 4. The important observation to be made from this figure is that a maximum value of P_{DL} exists at some intermediate value of f_m and that at higher carbon mass fractions the radiative loss at the propellant surface is somehow substantially offset.

One possible reason for the enhanced burn rates and depressed P_{DL} values at high carbon mass fractions is the change in the thermochemistry of the flame. At 68 MPa (1000 psi), the equilibrium flame temperatures of AP pellets with 0, 1, and 16% carbon added (by mass) are, respectively, 1404, 1600, and 2928 K. Thus, there is the definite possibility that carbon participation in the flame chemistry could be playing a role in the observed trends of Figs. 2-4. However, similar behavior is noted in AP/Cu0202/carbon pellets, as discussed in the following sections, even at much lower carbon mass fractions (0.1-1%). These amounts of carbon (0.1-1%) are so small that the change in the flame chemistry due to carbon could not be a factor. This suggests the possibility of radiative heat feedback from the flame offsetting the radiative heat loss from the propellant surface.

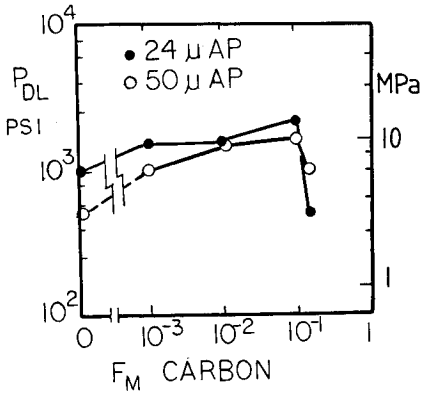

Fig. 4 Lower pressure limit vs carbon black mass fraction (strand burner).

Emission/Transmission Measurements

To characterize the radiative characteristics of the flame zone above the propellant samples monochromatic emission and transmission measurements were carried out in a window bomb. The optical system is pictured schematically in the plan view in Fig. 5.

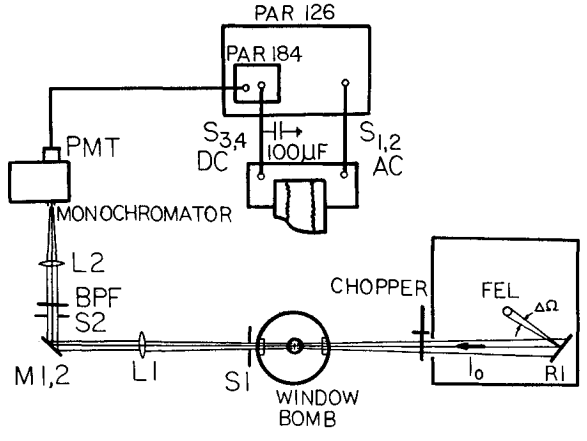

Fig. 5 Plan view of emission/transmission measurement system.

The 0.25 mm vertical monochromator entrance slit is imaged as a horizontal slit at the center of the flame zone by lenses L1 and L2 and mirrors M1 and M2. Between mirrors M1 and M2 the optical path is vertical, perpendicular to the plane of the paper. The first stop S1, with diameter of 0.635 cm (0.25 in.) insures that all rays originating at the FEL light source and transmitted to the detector actually pass through the flame and not around it. The second stop S2, with a diameter of 1.07 cm (0.42 in.), minimizes entrance of stray light. The bandpass filter BPF has a bandpass of 15 nm centered at 725 nm and is used to eliminate higher-order wavelengths, which are passed by the grating monochromator, from reaching the detector. The monochromator, a 1.4 m Spex is centered at 725 nm with a 1200 groove/mm grating which gives a resolving power of 40 Å/mm. Combined with the 0.25 mm slit, this gives a bandpass of 1.0 nm.

The wavelength of 725 nm was chosen according to three criteria: 1) it had to be within the range of reasonable detector response; for the PMT used, the peak response was in the neighborhood of 550 nm, dropping off at longer wavelengths; 2) the wavelength needed to be as large as possible to be near the maximum of the Planck function for the temperatures of interest, in this case, approximately 1400 K; and 3) the wavelength selected had to be away from any strong spectral emission lines due to gaseous species in the flame. This was so that the emission could be assumed to be due to particle incandescence (blackbody radiation) only. The wavelength of 725 nm was selected because it satisfied all three of these criteria. The flame was scanned with an EG&G PAR optical multichannel analyzer to insure that 725 nm was in the flat portion of the emission curve. It was thereby verified that the nearest spectral lines were those attributable to potassium at approximately 760 nm, which is well outside the bandpass of the monochromator.

The source for the reference intensity I_0 was an FEL coiled-coil tungsten filament quartz halogen spectral irradiance standard lamp manufactured and calibrated for spectral irradiance (SI) $= I\Delta\Omega$, (see Fig. 5) by Eppley Laboratories. The lamp operated at the calibration current of 7.9 A d.c. and had an effective temperature of 3200 K. Since the lamp was calibrated in terms of the SI at a distance of 50 cm from the lamp, the light was reflected off of a diffuse surface R1 (Fig. 5) with high reflectivity to obtain the absolute reference intensity (or radiance) I_0 with units of W/cm^2·nm·sr. A conversion was performed to obtain intensity from the calibration quantity SI. The radiant energy per unit area, time and wavelength incident on the reflector plate located 20 cm from the lamp is given by the expression, SI (W/cm^2·nm)$(50/20)^2 = I\Delta\Omega$. The flux reflected from the plate is then $\rho(\mathrm{SI})(50/20)^2$, where ρ is the spectral directional-hemispherical reflectivity, assumed to be equal to the spectral bidirectional reflectivity (lambertian surface). The reflected intensity is then given as

$$I_0 = \frac{\rho(\mathrm{SI})(50/20)^2}{\pi} \tag{1}$$

The diffuse reflector plate was prepared by painting a 10 cm (4 in.) square aluminum plate with Kodak white reflectance coating, a high reflectance barium sulfate paint. The reflectance of the coating at the measurement wavelength of 725 nm was $\rho = 0.992$. The lamp was enclosed in a plywood box $0.67 \times 0.67 \times 1$ m tall painted black.

The reference beam I_0 after exiting the protective lamp housing box was chopped at approximately 100 Hz to discriminate between the times when the detector signal was proportional to the emitted plus transmitted intensity at the flame (chopper open) and the times when the signal was proportional to just the emitted intensity (chopper closed). The intensity I_0 was thus used as both a known reference intensity for emission measurements and as an incident intensity for transmission measurements.

Transfer Equation

For purposes of this study, the flame was assumed to be a homogenous, isothermal, nonscattering medium. The transfer equation along the optical axis is then

$$\frac{dI}{ds} = -a_g I + a_g I_b, \quad I(s=0) = I_0 \tag{2}$$

and the intensity after passing through the flame is

$$I(s=D) = \epsilon I_b + \tau I_0 \tag{3}$$

where

$$\epsilon = 1 - \exp(-\kappa) \quad \text{and} \quad \tau = \exp(-\kappa) \tag{4}$$

$$\kappa = a_g D \tag{5}$$

Here, D is the diameter of the flame, taken to be the diameter of the pellet, 1.27 cm (0.5 in.); κ the optical depth; and a_g the absorption coefficient in the gas above the propellant given by

$$a_g = N C_a = 1.5 f_{vg} (Q_a/d) \tag{6}$$

where f_{vg} is the particle volume fraction in the gas, Q_a the effective monodisperse particle absorption efficiency, and d the effective monodisperse particle diameter, assuming spherical particles.

The output from the photomultiplier tube was fed into a PAR 184 current sensitive preamplifier connected to a PAR 126 lock-in amplifier (see Fig. 5). Two signals were recorded, a d.c. signal at the output monitor of the preamp and an a.c. signal at the output of the lock-in amplifier. These two signals were recorded on a strip-chart recorder and used to determine the flame emissivity (equivalent to transmissivity) and I_b (equivalent to T_f through Planck's equation).

Table 2 Emission/transmission results window bomb

Run	Carbon, %	Cu0202, %	P, MPa	τ	κ	T_f, K	Q_a/d, μm^{-1}
1	1	1	0.42	0.656	0.421	1406	4.1
2	1	1	0.42	0.664	0.409	1420	4.1
3	2	1	0.76	0.209	1.57	1428	4.1
4	2	1	0.76	0.178	1.72	1449	4.8

Particle and Matrix Continuity

In order to relate the particle volume fraction in the gas f_{vg} to that in the propellant f_{vs}, the particle and matrix (nonparticle) continuity equations were utilized. The particle continuity equation is

$$\rho_p f_{vs} r = \rho_p f_{vg} U \tag{7}$$

where ρ_p is the particle density, r the linear burn rate of the propellant, and U the particle velocity in the gas phase, assumed equal to the gas velocity (no slip). Since the particle density is constant the particle continuity equation reduces to

$$f_{vs} r = f_{vg} U \tag{8}$$

Similarly the continuity equation for the matrix (nonparticle) phase is,

$$(1 - f_{vs})\rho_s r = (1 - f_{vg})\rho_g U \tag{9}$$

where ρ_g is the gas density and ρ_s the AP density. Assuming that

$$f_{vs} \ll 1 \quad \text{and} \quad f_{vg} \ll 1 \tag{10}$$

the particle continuity, matrix continuity, and ideal gas equations can be combined to relate the gas-phase particle volume fraction to that in the "solid" propellant phase as

$$f_{vg} = f_{vs}\left(\frac{PM_g}{\rho_s \bar{R} T_f}\right) \tag{11}$$

where P is the pressure, M_g the mean molecular weight of the gaseous species (taken here to be 28.4, see Ref. 12) and $\bar{R}$ the universal gas constant, 1206.2 psia·cm^3/mole·K. The AP density was taken as 1.95 g/cm^3.

Using Eqs. (5), (6), and (11), an effective value for the particle absorption efficiency over diameter Q_a/d was calculated.

Emission/Transmission Results

The results for the flame transmissivity τ, optical depth κ, temperature T_f, and effective particle absorption efficiency over diameter Q_a/d are listed in Table 2. Not all of the window bomb runs made were used to calculate these flame radiative properties. Video recordings of the burning process indicated that a heavy condensate often formed that the nitrogen flow was unable to purge from the bomb. The higher the concentration of copper chromite, the greater this tendency seemed to be. Two further difficulties encountered were 1) excessively fast burn rates, which caused the bomb to be filled with a dense smoke cloud, and 2) inability to burn some pellets at all. The pellets with high Cu0202 concentration had a greater tendency for high burn rates, while those with pure carbon black were extremely difficult to burn. As a result, it was not possible to obtain emission/transmission

measurements for any of the samples with either Cu0202 or carbon black only in the AP. The only successful runs exhibiting a slow, steady burn with a clearly defined luminous flame (as verified by the video tape) were those for a mixture of Cu0202 and carbon black with AP, as listed in Table 2.

There are several checks on the validity of the results in Table 2. First, the flame temperatures measured, 1406-1449 K, are in good agreement with generally accepted values for AP monopropellant flames. If anything, they are slightly higher, which may be due to oxidation of the carbon particles. Second, the Q_a/d value of 4.1 μm^{-1} is consistent with what would be expected for submicron carbon black particles. For comparison, Q_a/d was also determined from a histogram of the size distribution of thermax carbon particles obtained from scanning electron micrographs.[13] The observed size distribution $N(r)$ was used together with an assumed complex refractive index[13] of $n-ik=1.7-0.7i$ and a Mie property computer program to calculate Q_a/d from Eq. (12),

$$\frac{Q_a}{d}=\int_0^\infty r^2 Q_a(2\pi r/\lambda,n,k)N(r)\,dr \Big/ 2\int_0^\infty r^3 N(r)\,dr \qquad (12)$$

The resulting value of $Q_a/d=3.3$ μm^{-1} is fairly close to the 4.1 μm^{-1} value obtained from emission/transmission measurements. The difference is probably due to an error in the assumed optical constants and the neglect of scattering in the emission/transmission result. Finally, the predicted value of $Q_a/d=4.1$ μm^{-1} seems to be fairly consistent for two particle loadings f_{vs}. Two factors change between runs 1-2 and 3-4: the particle concentration in the propellant doubles and the pressure doubles. The measured optical depth quadruples, indicating correctly that the particle concentation in the gas phase also quadruples. (This assumes that Q_a/d remains constant from the propellant condensed phase to the gas phase just above the surface, which should be a reasonable approximation.) That the gas-phase particle concentration quadruples follows from two factors. One factor of two comes from twice the particles being added to the propellant. The other factor of two comes from the matrix continuity equation. Since the pressure also doubles, the gas velocity U is halved and therefore the particle number density doubles. These two factors of two result in a quadrupling of the gas-phase particle concentration and hence the optical depth.

It should be noted that the values for Q_a/d were obtained by neglecting the presence of Cu0202 particles, even though 1% Cu0202 was present in the propellant. This procedure is felt to be justified due to the lack of luminosity observed for the Cu0202/AP flames. The reason for the lack of luminosity is probably that the Cu0202 particles are larger and more dense. The density of copper chromite is 5.27 and that of carbon black 1.9-2.1. The Cu0202 is probably at least twice as large in effective diameter as the carbon black; so, taken together, the size and density differences will result in at least an order of magnitude difference between the optical density due to carbon black and that due to Cu0202 for runs 1-4 in Table 2.

Since a mixture of 1% Cu0202 with carbon black was the only combination found that produced successful emissivity/transmissivity results, further tests were conducted in which the concentration of Cu0202 was held constant at 1% and the concentration of the carbon black was varied to see the effect on P_{DL}. Figure 6 displays these results. As the mass fraction of carbon black increases from 10^{-3} to 10^{-2}, P_{DL} drops from 1000 to 50 psig. Since the concentration of the catalyst Cu0202 is constant, the lowering of the pressure limit must be due, at least in part, to the increased radiative feedback. It cannot be attributed to more efficient gas-phase catalysis by Cu0202, since the gas-phase particle concentration is decreasing due to the lower pressure and higher gas velocity.

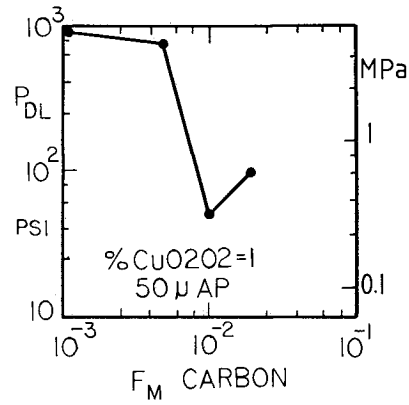

Fig. 6 Lower pressure limit vs carbon black mass fraction (window bomb).

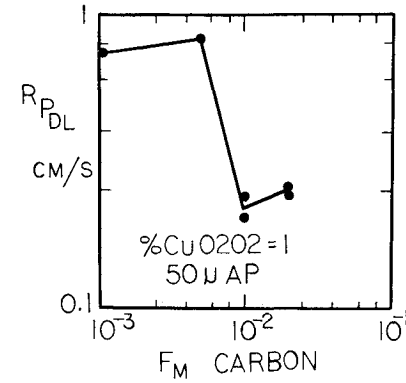

Fig. 7 Deflagration rate at lower pressure limit (window bomb).

Comparing the results in Figs. 4 and 6, it can be seen that the concentration of carbon needed to substantially drop P_{DL} without Cu0202 is 16% as compared with 1% with Cu0202. The effect of Cu0202 alone in a concentration of 1% is known to be that of augmenting the burn rate and decreasing P_{DL} (Fig. 1). Since the Cu0202 is apparently playing such an important role in the flame chemistry, it seems logical that the pellets without Cu0202 would require a much higher concentration of carbon than the pellets with Cu0202 before radiative feedback from the flame could compensate for the radiative loss from the pellet surface.

Figure 7 gives the results for the burn rate measured at the lower pressure limit in the window bomb. The burn rate follows approximately the same trend as P_{DL}.

Finally, Fig. 8 shows some results for burn rate as a function of pressure for a limited number of pressures above the lower limit. These results were also obtained in the window bomb for AP pellets containing mixture of Cu0202 and carbon black. Both the 1 and 2% carbon mixtures show rather large pressure exponents of 0.93 and 0.95, respectively. The somewhat surprising result, however, is that the 2% carbon pellets are harder to burn, as evidenced by lower burn rates in Fig. 8 and a higher lower pressure limit (Fig. 6). A possible explanation is that the carbon particles are not participating in the flame chemistry, but are simply acting as a heat sink.

Radiative Analysis

To determine if sufficient radiative feedback is available for that to be the cause of the observed augmentation of AP deflagration at high particle concentrations, an approximate radiative analysis is performed on the flame zone and thin propellant surface layer, using the radiative parameters obtained from the emission/transmission measurements. Two isothermal, homogenous, nonscattering regions are considered. One is the thin liquid/solid surface layer of thickness H at temperature $T_s=900$ K containing particles with volume fraction f_{vs} and an effective absorption efficiency over diameter Q_a/d of 4.1 μm^{-1}. This region is assumed to be an in-

finite slab with a mean beam length of 1.8 H (see Ref. 14). The other region is the gas zone above the surface, which is taken to be a right cylinder of diameter D and height L. Based on review of the video tapes taken during the bomb window studies, L/D is taken to be 2. The mean beam length for the gas radiating to the surface[14] is thus 0.6 D. The temperature in the gas region T_f is assumed to be 1400 K.

The thickness of the surface layer H is taken as the characteristic length for conduction into the propellant (assuming a nonradiative, convective diffusive zone), which can be calculated as

$$H = \lambda_s / r\rho_s C_s \tag{13}$$

where λ_s is the AP thermal conductivity (assumed to be 9×10^{-4} cal/cm·K), ρ_s the AP density (1.95 g/cm^3), and C_s the AP specific heat (0.33 cal/g·K). The resulting value for H, assuming a burn rate of 0.24 cm/s, is 59 μm.

The particle volume fraction in the gas region can be calculated from Eq. (11). Then, the net radiative heat loss from the surface q is given by

$$q = \{1-\exp[-a_s(1.8H)]\}\sigma T_s^4 - \{1-\exp[-a_g(0.6D)]\}\sigma T_f^4 \tag{14}$$

where

$$a_{s,g} = 1.5 f_{vs,g}(Q_a/d) \tag{15}$$

By assuming (arbitrarily) a constant radiative heat loss value at the minimum deflagration condition of $q_{DL}=0.1$ cal/cm^2·s (0.42 W/cm^2) and making use of Eq. (11), the preceding equation for q can be solved for P_{DL} as a function of particle volume fraction in the propellant f_{vs}. The resulting behavior is displayed in Fig. 9. In Fig. 9, at low particle loadings, as more particles are added the effective emissivity of the surface $\{1-\exp[-a_s(1.8H)]\}$ increases faster than the gas emissivity $\{1-\exp[-a_g(0.6D)]\}$. The radiative loss increases faster than the radiative gain back to the surface and the lower pressure limit increases. The opposite occurs at higher particle loadings. At intermediate concentrations (10^{-3} in Fig. 9), the surface emissivity is relatively high, but the gas emissivity is still low. Therefore, a higher pressure is required, according to particle and gas continuity, in order to maintain a sufficient number of particles in the gas phase above the surface so that the net radiative loss does not exceed the fixed (assumed) value of 0.1 cal/cm^2·s.

Although Fig. 9 does demonstrate that through proper consideration of particle continuity, matrix continuity, and radiative transfer the observed deflagration behavior can be predicted, the precise numerical values involved in this sample calculation are of little consequence. Furthermore, the assumption of a constant limiting value of radiative loss is questionable. It is more likely that as f_{vs} varies, and therefore P_{DL}, the necessary total heat flux back to the propellant also varies. Therefore, it is likely that q_{DL} is not constant, but is perhaps a fixed fraction of the total heat feedback requirement. The results of Fig. 9 are intended to have only qualitative—not quantitative—significance in that the trends are correctly predicted.

Finally, a comparison of the magnitudes of the radiative heat feedback and the total required heat feedback indicates that at minimum deflagration conditions radiation can indeed be a significant contribution. An AP pellet burning at 0.2 cm/s (the minimum deflagration value in the AP/Cu0202/carbon pellets) requires 50 cal/cm^2·s of total heat feedback (assuming $T_s=700$ K). The radiation flux emitted by a perfectly black AP flame at 1400 K is 5 cal/cm^2·s or 10% of the total required amount. For a 16% carbon flame ($T_f=2928$ K) the maximum radiative flux is

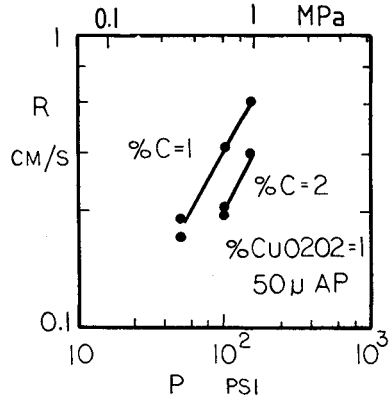

Fig. 8 Deflagration rate for carbon/Cu0202/50 μm AP (window bomb).

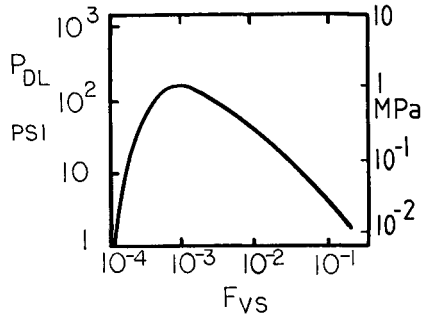

Fig. 9 Predicted lower pressure limit vs particle volume fraction.

100 cal/cm^2·s, which is a significant portion of the total required heat feedback of 150 cal/cm^2·s (assuming $r_{DL}=0.6$ cm/s from Fig. 2 and $T_s=700$ K).

Conclusions

1) In both strand burner and window bomb tests, augmentation of the deflagration rate of pressed AP pellets by the addition of relatively large amounts of noncatalytic carbon black is observed.

2) A decrease in the lower pressure limit for deflagration of AP is also observed upon addition of large amounts of carbon black.

3) The effects observed in conclusions 1 and 2 are attributed to the influence of thermal radiative feedback by the hot particles in the flame zone above the propellant.

4) Simultaneous monochromatic light emission and transmission measurements in carbon black/AP flames resulted in a flame temperature of approximately 1400 K and an effective particle absorption efficiency over diameter of $Q_a/d=4.1\mu m^{-1}$. These properties predict ample radiative feedback levels for altering the total heat feedback requirement.

Recommendations

1) The technique of simultaneous emission/transmission measurements used here should be expanded to multiple wavelengths and used to investigate aluminized propellants. Little or no information is currently available as to the effective emissivity or the effective temperature of aluminized propellant flames.

2) Future studies on propellant combustion modification using particle additives should include optical as well as chemical and physical properties of the particles among the potentially important factors influencing the combustion behavior.

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References

[1]Friedman, R., Nugent, R.G., Rumbel, K.E., and Scurlock, A.C., "Deflagration of Ammonium Perchlorate," *Sixth Symposium (International) on Combustion*, Reinhold Publishing Corp., New York, 1957, p. 612.

[2]Levy, J.B. and Friedman, R., "Further Studies of Pure Ammonium Perchlorate Deflagration," *Eighth Symposium (International) on Combustion*, Williams and Wilkens Co., Baltimore, 1962, p. 663.

[3]Munson, W.O. and Reed, R., Jr., "Effect of Additives Introduced by Spray Drying on Ammonium Perchlorate Decomposition," AIAA Paper 69-502, June 1969.

[4]Cohen, Nir., E., "An Experimental Study of the Low Pressure Limit for Steady Deflagration of Ammonium Perchlorate," *Combustion and Flame*, Vol. 20, 1973, pp. 419-435.

[5]Boggs, T.L., Zurn, D.E., and Cordes, H.F., "The Combustion of Ammonium Perchlorate and Various Inorganic Additives," AIAA Paper 75-233, Jan. 1975.

[6]Boggs, T.L., Price, E.W., and Zurn, D.E., "The Deflagration of Pure and Isomorphously Doped Ammonium Perchlorate," U.S. Naval Weapons Center, Rept. TP 4981.

[7]Hertzberg, M., "The Free-Laminar and Laser-Induced Combustion of Ammonium Perchlorate," *Combustion Science and Technology*, Vol. 1, 1970, pp. 449-460.

[8]Boggs, T.L., "Deflagration Rate, Surface Structure, and Subsurface Profile of Self-Deflagrating Single Crystals of Ammonium Perchlorate," *AIAA Journal*, Vol. 8, May 1970, pp. 867-875.

[9]Boggs, T.L., Zurn, D.E., and Netzer, D.W., "Ammonium Perchlorate Combustion: Effects of Sample Preparation; Ingredient Type; and Pressure, Temperature and Acceleration Environments," *Combustion Science and Technology*, Vol. 7, 1973, pp. 177-183.

[10]Spalding, D.B., "The Theory of Burning of Solid and Liquid Propellants," *Combustion and Flame*, Vol. 4, March 1960, pp. 59-76.

[11]Rosser, W.A., Inami, S.H., and Wise, H., "Thermal Decomposition of Ammmonium Perchlorate," *Combustion and Flame*, Vol. 12, Oct. 1968, pp. 427-435.

[12]Williams, F.A. and Guirao, C., "A Model for Ammonium Perchlorate Deflagration between 20 and 100 atm," *AIAA Journal*, Vol. 9, 1971, pp. 1345-1356.

[13]Eversole, J.D. and Hulsizer, S.C., "Particle Sizing in Two-Phase Flows from Scattered Laser Power Spectra and Laser Attenuation," *Journal of Applied Physics*, Vol. 54, July 1983, pp. 3704-3709.

[14]Siegel, R. and Howell, J.R., *Thermal Radiation Heat Transfer*, 2nd ed., McGraw-Hill Book Co., New York, 1981, p. 618.