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Technical Notes

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Mechanisms and Methods of Suppression of Combustion Instability by Metallic Additives

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Introduction

THE problem of unstable burning has been recognized in solid-propellant rockets since 1941. With the advent of pressure-measuring systems having adequate frequency response, it was discovered that unstable burning was associated with pressure oscillations in the motor having frequencies corresponding to acoustical modes of the cavity.

In the 1950s, when this work was conducted, much of the work in the investigation of unstable burning was of a "quick fix" nature; significant theoretical analyses were not conducted until late in the decade. Owing to the complex species and conditions that exist in a burning solid propellant, these theories necessarily involved a number of simplifications and assumptions that experimental results often tended to refute. Therefore, an experimental study was undertaken to investigate possible mechanisms for unstable burning and to determine various means of suppressing the oscillations.

Mechanism of Suppression

So that studies of suppression may be made, it is necessary to consider the various theories of oscillatory burning and the accompanying reactions. The general theory is that random noise may be amplified through some feedback path yielding acoustical waves, in accordance with the possible modes outlined by Lord Rayleigh. It may be shown that suppression of oscillatory burning may result from two sources: 1) attenuating the acoustical wave by absorption, reflection, or scattering; and 2) altering the feedback path by changing the physical or chemical requirements for reaction. The latter source may be further subdivided by considering the site of the controlling feedback reaction as either the condensed phase or the gas phase.

During the course of this study, a mechanism for suppression according to source 1 was proposed by Neustein and Altman,[1] based on the theoretical work of Epstein and Carhart[2] and the experimental findings of Zink and Delsasso[3] on the effect of solid particles suspended in a gas. According to both theory and experiment, considerable sonic energy can be absorbed by solid particles suspended in a gas through viscous drag, with the particle diameter of the solid being a major parameter. Because the amount of energy involved in the oscillations is only a minor portion of the total energy generated, such a reduction of the sonic energy would have a marked effect on the reinforcement of oscillations.

Following source 2, consideration of the reactions occurring in the feedback path leads the investigation to altering the endothermicity of the condensed-phase reactions by coolants or by heat-producing additives, as well as altering the thermal diffusivity of the condensed phase. Additives that burn in the condensed phase to liberate energy would eliminate the feedback path by removing the effect of heat transfer on the endothermic reaction. Additives that absorb large quantities of energy in the condensed phase should also affect the gain of the feedback path by requiring a larger amount of heat transfer for a given mass vaporized. For gas-feedback paths, additives that release significant energy in the gas phase would provide a means of decoupling the oscillations in heat transfer related to the condensed phase resulting from the pressure oscillations. This mechanism could be tested through the application of high-speed photography of the combustion zone. At the same time, it must be remembered that later studies of the combustion of some types of aluminum particles indicated that combustion would yield "smoke," which was determined to be submicron aluminum oxide. The extent to which the particulate-damping effectiveness of the oxide is difficult to quantify without a detailed knowledge of the particles produced.

Instrumentation

The motor used in the tests of oscillatory burning to be described was a standard piece of test equipment, fabricated from 4130 steel seamless tubing with a 6-in. i.d. and a length of 11.4 in. A 5-in. cylindrical mandrel was used because the acoustics of a cylindrical perforation are fairly well known. It was quickly found that the oscillations generally had the frequency of the first tangential mode, which changes from about 4800 Hz to about 4000 Hz during the course of a firing.

Regular range equipment was used with only a slight modification. Motors were mounted in a horizontal thrust stand and supported by two sets of ball-bearinged Y yokes. The pressure transducers were flush mounted into a special head designed for these experiments. Pressure measurements were made with a Baldwin transducer of the SR-4 strain gauge type, which has a flat dynamic response (within 5%) to about 3 kHz. This transducer is quite linear, has little or no hysteresis, and can withstand considerable abuse. In addition, a special gauge was fabricated at the Rohm & Haas Company, expressly for detecting high-frequency oscillations. The sensing element was a barium titanate crystal, $\frac{1}{2}$ in. in diameter and $\frac{1}{10}$ in. thick, of the Gulton Manufacturing Corporation's Glennite Body 103. The crystal was held in the case and protected from the flame by a $\frac{3}{8}$ in. thickness of Rohm & Haas Company's Paraplex Resin P-13. It was found that some temperature drift occurred, but because no integrations were made from this gauge, no cooling element was added, thereby giving a rugged, simple, and inexpensive (less than $50) transducer with excellent frequency response. The signal from this gauge was fed to a high-input-impedance, cathode-follower preamplifier whose output was divided and fed to 1) a Consolidated Magnetic Oscillograph, model 519, by way of a galvanometer-driver amplifier; and 2) the 307 channel of an Ampex model 311 magnetic tape recorder. The galvanometers on the

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former had a frequency response flat within 2% to about 3 kHz. The signals from the Baldwin transducer and the thrust gauge, a Baldwin load cell, were fed to Kintell chopper-stabilized dc preamplifiers, which are flat to about 40 kHz. These signals were then fed to the oscillograph through galvanometer-driver amplifiers.

The original motors fired contained petrin-acrylate propellant and used only the Baldwin pressure gauge placed in a head that had a grease-filled line 1 in. in length between the motor chamber and the sensing element to prevent any undue heating. The grease attenuated the oscillations to some extent, so that definite comparisons of magnitude could not be made from these tests. However, this system could detect the presence or absence of oscillations having moderate amplitudes.

Results

The first tests were conducted with petrin acrylate propellants having the composition: petrin acrylate = 16.4%, NH_4ClO_4 (35 μ) = 59.1%, triethylene glycol dinitrate (TEGDN) = 19.5%, $P = 920$ (Polyester 920, a product of Barrett Division, Allied Chemical and Dye, Incorporated) = 1.0%, 2-ethyl hexyl acrylate = 1.8%, ethyl centralite = 0.2%, and test additive = 2.0%.

Six different grades of aluminum and eight other additives were tested in this formulation, and immediate improvement was shown with some of these formulation changes. Where peak-to-peak oscillations of over 500 psi magnitude had been observed with the nonaluminized formulation, adding 0.5% Alcoa 123 aluminum lowered the magnitude to 30 psi; 1% gave barely visible oscillations; and 1.5% completely eliminated oscillatory burning. However, further experiments indicated that not all types of aluminum were effective.

The first additive-evaluation tests compared the results obtained with different grades of aluminum. Four tests were conducted for each formulation at a temperature near 70°F. It was found that Alcoa 123 (14 μ) was successful in suppressing oscillations, whereas Alcoa 120 (26 μ) was not successful. It was also found that two grades of flake-type aluminum–Alcoa 408 (5% oxide, 3% grease) and 606 (3% oxide, 1% grease)—did not suppress oscillatory burning (see Table 1).

As a result of these preliminary results, an ancillary experimental technique was introduced, viz., high-speed cinemicrography. Quarter-inch strands of each propellant were burned in a window bomb at 1000 psi. Initial studies of propellants in the polypetrin acrylate family disclosed that the controlling factor for aluminum was whether or not the additive burned at or very near the surface, the spherical aluminum showing superior combustion properties. This behavior is probably due to the coating on the flake aluminum (characteristic of the manufacturing process) that deters the combustion reaction.

(Note that tests made at Thiokol Chemical Corporation in the Hawk motor disclosed that Reynolds 400 (5 μ) aluminum was effective in suppressing oscillations, but Alcoa 120 was not. Cinemicrographs showed, once again, that the Reynolds 400 was burning at the surface, but the Alcoa 120 was not. Later tests with the Subroc motor indicated identical behavior, i.e., only fine aluminum particles that burned near the surface would suppress instability.)

Table 1 Results with petrin acrylate

Additive	Result
Heat addition	
Aluminium	
Alcoa 123, degreased MD-105	Successful suppression
Alcoa 120, 408, 606, "greasy" MD-105	Unsuccessful suppression
Magnesium	
3% wax-coated Mg	Almost complete suppression
Boron	
80% B	Good amount of suppression
92% B	Little or no suppression
KDNAN	Very little effect
Solids damping	
Carbon black	No effect
Silon S	Almost complete suppression

The results with the petrin-acrylate system implied that thermal diffusivity of the aluminum was not the factor controlling its effectiveness as a suppressant. If the diffusivity was controlling by means of heat absorption in the boundary layer, then flake aluminum should be superior to spherical aluminum because the surface offered for heat absorption by the thin platelets of the flake is larger than the surface of the spheres for the same particle size. The web thickness of the platelets should not be a limiting factor, due to the short residence times involved.

Experiments with another type of aluminum, MD-105, having a particle size of 7 μ, were very significant. The first batch of the material tested suppressed the instability; however, the second batch of material (received in a different shipment) did not suppress combustion instability. Movies of the combustion of propellant samples made with the two batches of MD-105 showed a definite difference, viz., the original batch of MD-105 ignited and burned near the surface, whereas the second batch demonstrated a significant ignition delay. Chemical analyses showed that, although the two batches had the same particle size, the second one had a coating, which was probably stearic acid. When the greasy MD-105 material was washed with solvent, the "degreased" MD-105 ignited and burned quickly, and static tests demonstrated that it was completely effective in suppressing the combustion instability.

Silon S, which is essentially sand having a diameter of 0.2 μ, is an additive that would find its effectiveness in the gas phase of the reaction. For the frequencies used, this diameter is nearly the optimum size for maximum damping, according to the formulas of Epstein and Carhart,[2] and would give about 25-dB attenuation with the test motor. When added to petrin acrylate, nearly complete suppression resulted; however, when the more sensitive gauge system was used with the material in the plastisol propellant, it appeared that more attenuation was needed, as may be seen in Table 2.

A total of 21 additives was then evaluated in a plastisol nitrocellulose propellant system. The basic composition was as follows: ball powder = 22.10%, NH_4ClO_4 (35 μ) = 34.84%, TEGDN = 41.06%, and test additive = 2.00%.

As a result of the tests in the petrin-acrylate system, emphasis was placed on additives that burn to liberate large quantities of energy. Because these additives must burn near the propellant surface to decouple the effects of pressure oscillations from the heat transfer to the burning surface, this is the region where the use of cinemicrography assumes its greatest importance.

The heats of formation of the oxides of the elements tested are given next: 1) element = Al, B, Mg, and Zn; 2) ΔH_f (kcal/g) = 3.91, 3.99, 3.57, and 1.04; and 3) assumed oxide = Al_2O_3, B_2O_3, MgO, and ZnO.

Cinemicrographs show that there is a large difference in the mechanism and region of combustion for these additives. The data listed in Table 2 show that substantial differences were observed in their ability to suppress combustion instability. The first finding to be noted is that fine aluminum was as effective as a suppressant in the plastisol system as it had been in the petrin-acrylate system.

Because boron theoretically liberates the most energy during combustion, it would be expected that this element would be effective in suppressing instability. However, cinemicrographs show that the boron does not burn at the surface, leading to the experimentally verified prediction that this would not be effective as a suppressant of oscillatory burning. Four different types and grades of boron were tested, and only one was successful to any extent. This particular grade had significant impurities (80% B), with the major impurity being nearly 15% magnesium. Boron only gives an overall green hue to the film, with a few flashes that are probably due to the magnesium impurity. In any case, boron does not appear to burn with sufficient efficiency to be used as an additive to suppress combustion instability.

Zinc very definitely flashes when heated, particularly the 5-μ zinc dust tested in these studies. In fact, experiments at the Jet Propulsion Laboratory showed that zinc particles almost exploded when passed

Table 2 Additive evaluation in the plastisol system

Additive	Particle size, μ[a]	Film results	P_b, psi	P_{osc}, psi[b]	Amplitude reduction, %
		I. Control			
None	——	——	700–1100	250–500	——
		II. Particle damping			
Silon S	0.2	No flashes	750–900	0–60	85–100
Al_2O_3 (A-10)	6	No flashes	800–900	200–500	0
Al_2O_3 (A-14)	3	No flashes	875–950	100–300	40–60
Al_2O_3 (A-3)	1	No flashes	750–850	50–300	40–80
Fe_2O_3	0.5	No flashes	950–1025	0	100
		III. Thermal conductivity			
Silver	4	No flashes	100–1150	300–400	0
		IV. Endothermal phase change			
Wood's metal	20–44 (Ref. 1)	No flashes	800–1000	175–200	30–60
		V. Heat addition			
Alcoa 1230	12	Definite flashes at the burning surface	600–1000	0	100
Fine Mg	40 (Ref. 1)	Flashes, but some induction period	850–950	30–60	85–90
Coarser Mg	90 (Ref. 1)	A shorter induction period	1000–1270	0–25	90–100
1% wax-coated Mg	8	A slight induction period	900–1000	25–60	85–90
3% wax-coated Mg	12	Burned nearly at the surface	850–900	0–40	85–100
Zinc dust	5	Flashed at the surface	800–900	60–150	75
KDNAN	53–75 (Ref. 1)	A few flashes, but away from the surface	1000–1500	100–400	30–60
80% Mg–20% Al	14	Flashed at the surface	1050–2100	0	100
60% Mg–40% Al	12	Decreasing numbers of flashes	1100–1175	0–75	85–100
40% Mg–60% Al	11	Decreasing numbers of flashes	900–1100	0–70	85–100
20% Mg–80% Al	20	Decreasing numbers of flashes	825–1000	0–300	40–100

[a] Particle size determined by Fisher Sub-Sieve Sizer, except on samples marked.[1]
[b] P_{OSC} = amplitude of the oscillations.

through a flame. This information led to the selection of zinc as one of the additives to be tested. The table of heats of formation shows that less heat is available from zinc than from aluminum. When zinc was added to plastisol at the 2% level, a large amount of suppression was affected, but not as much as that accomplished by the "hotter" additives that burned at or near the surface. It is quite possible that more zinc would succeed in liberating enough energy to remove the effect of heat transfer completely, rather than partially, as it appeared to have done.

A large number of types of magnesium and magnesium-containing alloys were tested, mainly in the plastisol system. Because of the extreme reactivity of fine magnesium, particles that will pass even 270 mesh are difficult to obtain commercially and present several hazards in propellant processing. Results with uncoated magnesium showed that care must be taken in using this material. The finer (40 μ) grade was over 5 years old, whereas the coarser (90 μ) material was relatively fresh. The 40-μ material was less effective, suggesting that some oxidization had occurred during storage, and photographs of combustion showed a longer induction period. The other two magnesium samples were coated by Dow Chemical Company with FT-300 wax at the 1 and 3% levels. These samples were finer (8 and 12 μ by Sub-Sieve Sizer), but tended to clump slightly to form larger particles in some cases. Micromerograph readings showed a d_m of over 30 μ for both samples. Both coated materials were relatively effective in suppressing oscillations, the 3% more so than the 1%. It is quite possible that the 1% coating was not sufficient to protect the metal from forming some kind of surface coating.

The results with these metals agreed with the conclusions drawn from the studies with various grades of aluminum, namely, that heat release near the surface was a significant factor in the effective suppression of instability. Insufficient studies of the combustion of the other metals have been made to enable any statements to be made concerning the generation of fine oxide particles by combustion with the associated particulate damping.

To test the hypothesis that thermal diffusivity was important, 4-μ silver, which should have the approximate thermal conductivity of aluminum, but would not burn, was used. The results shown in Table 2 indicate that combustion instability still persisted, indicating that the change in diffusivity was not sufficient to suppress the reaction. This experiment tends to corroborate the aluminum results because the possibility of an insulating grease coating does not have to be considered here, as was the case with the flake aluminum.

The effect of an additive that would absorb energy in the condensed phase was studied by the addition of Wood's Metal (20–44 μ); this would affect the gain of our feedback path by requiring more heat transfer for vaporization of a unit mass. This material should melt before the first decomposition reactions, which would take place at over 200°C, a temperature nearly 150°C above the melting point of the eutectic. The results in Table 2 indicate that the gain of the feedback path was apparently affected, but not to a very large extent.

Five ingredients that would suppress the oscillations through particulate damping were evaluated in the plastisol system: Silon S, fine iron oxide, and three grades of aluminum oxide. Films of the combustion of propellants containing these additives showed no sign of reaction near the surface. Once again, Silon S was quite effective (see Table 2). Fine (0.5 μ) Fe_2O_3 is also close to the optimum particle size for particle damping, which is about 0.48 μ for the 4000-Hz frequency range, and was almost completely successful as a suppressant. The grades of aluminum oxide evaluated ranged in size from 1 to 6 μ; hence, all were slightly too large for maximum effectiveness in this motor. Although only minimal suppression was observed, as shown in Table 2, the degree of suppression varied with the particle size in a manner agreeing with the particle-damping theory.

Further credence has been lent to the mechanistic hypotheses related to the effectiveness of heat addition by results obtained on test samples kindly furnished by Aerojet-General Corporation as part of their concurrent major study of combustion instability in a polyurethane binder.[4] The compositions were not specified, and, on the basis of cinemicrography, predictions were made of the tendency for combustion instability, with heat addition being considered as the major suppression mechanism. Good agreement was found between predictions on the basis of cinemicrography and motor results for a propellant class that was quite different from either of the propellants used in the evaluation of additives at the Rohm & Haas Company. Such agreement tends to support the mechanisms of the suppression of oscillatory burning that have been set forth in this paper.

Aerojet-General Corporation also found that fine (1 μ) Al_2O_3 would suppress unstable burning, and that the fine material was more effective than larger (3 and 6 μ) grades of the oxide.[4] Once again, calculations made using the Epstein and Carhart formula[2] showed some correlation with particle-size optimization effects in the Aerojet-General Corporation test configuration.

The importance of optimum particle size has been demonstrated with other materials. For example, carbon black has shown some effectiveness. However, the only material tested at the Rohm & Haas Company in the petrin-acrylate system had an average diameter of 0.03 μ, and was ineffective, undoubtedly because this size was too small for the motor geometry tested. Other sizes tended to inhibit polymerization.

Conclusions

A number of experiments showed that there are several mechanisms by which high-frequency oscillatory burning may be suppressed or its magnitude substantially decreased. The most significant finding is that the results of motor firings correlate well with photographs of the burning process of those additives that liberate large amounts of energy. It appears possible to make predictions of the effectiveness of these additives.

It has been shown that certain additives, e.g., Silon S, Fe_2O_3, and carbon black, can absorb sufficient sonic energy to eliminate high-frequency oscillations. However, the speculation that the nucleation of the Al_2O_3 formed from burning aluminum gives particles of the optimum size for damping by the particle-drag mechanism is not supported, because the region of the additive's burning appears to be the determining factor.

Increasing the heat required to vaporize a unit mass of propellant can decrease the magnitude of oscillation, and the effect of an additive with high thermal conductivity has been investigated, but a higher concentration is required before much of an effect will be realized from either of these approaches.

Because the extent of the attenuation of sound by a suspension is affected by motor geometry and the resulting characteristic frequencies, incorporation of an additive that suppresses oscillations by releasing energy appears to be a more practical method of eliminating combustion instability than one based solely on particle damping. Moreover, the photographic method similar to that employed here offers an excellent method of predicting the ability of a specific additive to suppress oscillations in a given propellant system.

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References

[1]Neustein, I., and Altman, D., "Study of Detonation Behavior of Solid Propellants," Aeronutronics Systems, Rept. 4208-N, Newport Beach, CA, Sept. 1958.

[2]Epstein, P. S., and Carhart, R. R., "Absorption of Sound in Suspensions and Emulsions," *Journal of the Acoustical Society of America*, Vol. 25, 1953, pp. 553–565.

[3]Zink, J. W., and Delsasso, L. P., "Attenuation and Dispersion of Sound by Solid Particles Suspended in a Gas," *Journal of the Acoustical Society of America*, Vol. 30, 1957, pp. 765–771.

[4]Lou, R. L., "Suppression of Unstable Burning in Solid Propellants," Aerojet-General, Rept. 1250, Sacramento, CA, April 1957.

Early Investigations of Solid-Propellant Combustion Instability in Russia

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Nomenclature

A	= oscillation amplitude
c	= heat capacity
K_1	= coefficient of increment per unit burning area
K_2	= coefficient of oscillation absorption
P	= pressure
q	= heat of chemical reaction in reactionary layer of condensed phase
S	= initial combustion area
T_o	= starting temperature
T_s	= the temperature of condensed phase surface
t	= time
t_c	= relaxation time of condensed phase
t_g	= relaxation time of gaseous flame
u	= combustion rate
v	= combustion-product flow rate
x	= coordinate
α	= rate of decrease in burning area
β	= temperature coefficient of combustion rate, $1/T_0(\partial u/\partial T_0)_P$
ρ_g, ρ_c	= densities of gaseous and condensed phases, respectively

Introduction

DESIGNING and improving solid-propellant rockets, both before and during World War II, resulted in the discovery of phenomena that were inexplicable within the framework of views and knowledge available at that time. These phenomena included 1) anomalous pressure rise when long charges were employed, known today as erosive combustion; 2) spontaneous combustion damping, known as anomalous combustion or low-frequency motor rocket combustion instability; and 3) secondary peaks of pressure that arise during propellant burning in the combustion chamber, today known to arise from high-frequency instability. To explain these phenomena, it was necessary to create new modern theories for propellant combustion and internal ballistics of solid-fuel rockets. Contrary to the classical theory that focused primarily on steady burning, these new theories required the study of unsteady burning and its interaction with gasdynamic and heat processes in a rocket motor. Russian scientists contributed significantly to developing these theories. In particular, during World War II, Zel'dovich elaborated a theory of unsteady propellant burning,[1,2] as well as theories for erosive combustion[2,3] and low-frequency combustion instability,[2,4] which retain much of their validity today. Experimental research on erosive and anomalous combustion (i.e., low-frequency combustion instability), which confirmed the Zel'dovich theories, were conducted by Leipunskii[5] and other Russian scientists. This Note describes some of the early experimental combustion studies in Russia on the third class of the previously noted phenomena of modern internal ballistics of solid-propellant rockets, that is, high-frequency unsteady propellant burning.

Discussion

Peaks in the pressure of a rocket combustion chamber, which appear some time after ignition, were detected in 1938 by Dernovoy.[6]

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