Nonacoustic Combustion Pulsations of Ammonium Perchlorate Containing Aluminum

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The inherent, nonacoustic combustion pulsations of ammonium perchlorate propellant strands containing varying amounts of fine (~6 μ) aluminum powder have been determined over a range of pressures, based on frequency analyses of radiation pulsations. Each formulation usually showed a single, prominent frequency in the region below 300 cps. Such peaks appear to be associated with the aggregation of a fixed amount of aluminum on the surface, which protrudes ultimately into higher temperature regions of the flame zone, where ignition occurs and a light pulse is produced. Strands containing up to 30% molybdenum powder (~7 μ) showed no preferred pulsation frequencies, reflecting the very low ignition temperature (~920°K) reported for this metal, and suggesting that this is the minimum surface temperature. At very low aluminum content [or with larger (~40 μ) particle size], prominent, discrete pulsation frequencies are not observed, and this is attributed partly to the reduced opportunity for aluminum aggregation because of the increased interparticle distance.

Introduction

In previous work,[1] low-frequency, combustion pulsation behavior of a nonacoustic nature was observed with certain aluminum-containing solid propellants. This was inferred from both infrared and visible radiation emitted from the vicinity of the burning propellant surface, as well as through the direct detection of thrust pulsations. There was considerable indirect evidence that agglomeration of aluminum at the propellant surface was mainly responsible for the observations. However, it was considered desirable to investigate the phenomenon in more detail, using a simple propellant system, under controlled conditions. The system chosen was ammonium perchlorate, containing aluminum powder.

The pulsating behavior of such ammonium perchlorate-aluminum strands is readily observed in a simple, qualitative way by direct contact with a glass-blowing, hand torch at atmospheric pressure. (None of the formulations would sustain combustion at atmospheric pressure.) The strands are observed to "flash" with great regularity under these conditions, the frequency increasing with increasing aluminum content. The strand surface recedes in a normal, linear manner. The flash is largely due to a single pulse of burning aluminum, and an aggregate network of aluminum is observable on the surface with a microscope when heating is stopped just prior to a flash.

In the experiments to be described, the combustion pulsations were characterized by observing the radiation from the "flashes" just noted. For the most part, the effects of fine aluminum powder content (~6 μ) and pressure were investigated, although some limited data were obtained on one other aluminum particle size (~40 μ). In addition, the study was extended to molybdenum-ammonium perchlorate to illustrate the characteristics of a metal whose ignition temperature is lower than aluminum and corresponds as closely as possible to the ammonium perchlorate surface temperature.

Experimental Procedure

A technique similar to that described by Friedman[2] was used to prepare the metallized perchlorate strands. Metal powder was intimately mixed with carefully sized ammonium perchlorate (37–44 μ fraction), and the mixture was pressed into a pellet (approximately 4 × 4 × 50 mm) at a pressure of about 26,000 psi. A sieved fraction (37–44 μ) of Alcoa 120 and "as-received" Alcoa 140 aluminum powder was used. Determination of the particle size distribution with a micromerograph showed that, for Alcoa 140 aluminum powder, about 50% by weight of the particles had diameters less than 6 μ (see Fig. 1). For experiments requiring molybdenum, relatively coarse molybdenum powder (Fisher Scientific Company) was ground with an agate mortar and pestle until the particle size distribution corresponded approximately with that of Alcoa aluminum powder (Fig. 1).

The pressed perchlorate pellets (sides inhibited with "fluorolube") were ignited with a piece of solid propellant placed on

Table 1 Effect of aluminum concentration, pressure, and burning rate on peak pulsation frequencies[a]

Aluminum,	Peak pulsation frequency, cps			Burning rate, cm/sec		
wt. %	1000 psig	1500 psig	2000 psig	1000 psig	1500 psig	2000 psig
15.0	81	135	178	0.58	1.04	1.35
12.5	77	121	155	0.63	1.05	1.28
10.0	72	108	145	0.56	0.98	1.28[b]
5.0	40,80	60,122	72	0.97[c]	1.40[c]	1.75[b]
3.5	Broad	40,75	55,110	...	1.53[c]	1.90[b]
2.0	Broad	75	Broad	...	...	...
0.5	Broad	Broad	Broad	...	...	...
0.0	Broad	Broad	Broad	...	...	...

[a] Matrix: 37–44 μ ammonium perchlorate; additive: ~6μ aluminum.
[b] Values taken from previous studies.
[c] Estimated values.

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Table 2 Examples of relationship between peak pulsation frequency and burning rate of aluminized ammonium perchlorate strands[a]

Aluminum, wt. %	r_{2000}/r_{1500}	f_{2000}/f_{1500}	r_{1500}/r_{1000}	f_{1500}/f_{1000}	r_{2000}/r_{1000}	f_{2000}/f_{1000}
10.0	1.31	1.34	1.75	1.50	2.28	2.01
12.5	1.21	1.28	1.68	1.57	2.04	2.01
15.0	1.30	1.32	1.78	1.67	2.31	2.20

[a] Subscripts refer to pressure.

the 4- × 4-mm surface and burned in an optical bomb at nitrogen pressures of 1000, 1500, and 2000 psig. The radiation from the burning strand was observed with a 929 phototube (spectral response, 3000–7000 Å; maximum spectral response, 4000 Å) operating at 200 v with a 1-meg load resistor. The phototube was placed 24 in. from the sample. The phototube output was tape-recorded, and this recording (closed-loop) was then fed into a frequency analyzer (Hewlett Packard 302A) to obtain the output as a function of frequency.

In addition to these measurements, the burning rate of several compositions was determined at the noted pressures.

Results

Frequency spectra obtained from the analysis of the radiation pulsations are illustrated in Fig. 2 for various weight fractions of 6μ aluminum in ammonium perchlorate. The notable feature shown by these figures is the presence of fairly well-defined peaks occurring at low frequencies (<300 cps), particularly in the spectra for highly aluminized strands burned at high pressures. Reproducibility of the peak frequencies was excellent in repeat experiments. The most prominent peak-frequency values and strand burning rates are tabulated in Table 1.

It will be noted that the peak pulsation frequencies tend to increase with increasing burning rate for a given aluminum content. This effect is an anticipated one, since higher burning rates imply a correspondingly higher shedding rate of aluminum from the surface. The correspondence between peak frequency f and the burning rate r is quite satisfactory within experimental error, as illustrated by the data tabulated in Table 2.

Discussion

The good correspondence between peak frequency and the burning rate for a given aluminum concentration suggests

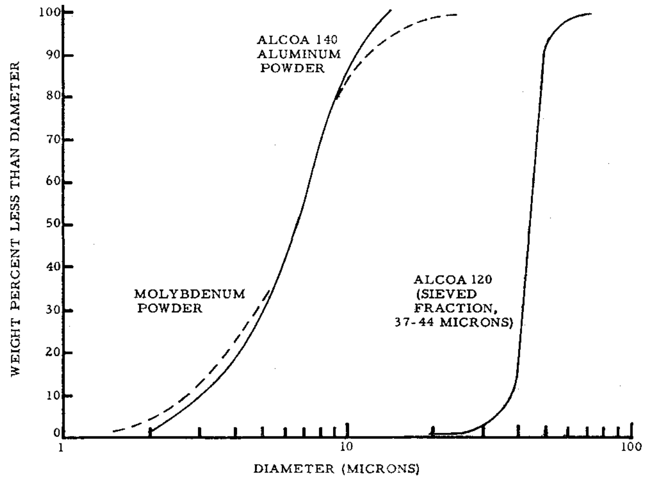


Fig. 1 Particle size distribution analysis (Sharples micromerograph).

that the formation of a pulse is associated with the collection of a fixed quantity of aluminum on the surface of a burning strand. This concept is strengthened by directly observing the pulsation behavior of aluminized ammonium perchlorate strands when they are contacted with a torch flame at atmospheric pressure. When heat is first applied to the surface, a mound is observed to grow there (presumably, aluminum oxide collecting). Further heating results in the sudden ejection of the mound, accompanied by a bright flash. Recent high-speed cinematography taken by Crump[3] on burning aluminized ammonium perchlorate strands reveals the identical behavior in very striking fashion. These observations and the data in Table 2 suggest that a critical (roughly constant) amount of aluminum-aluminum oxide collects at the surface before ejection takes place.

The average amount (weight) of aluminum which may gather on the surface of a strand of unit cross-sectional area before a pulse is produced is estimated from the following expression:

$$W = (1000\rho \cdot F \cdot r)/f$$

where

W = weight of aluminum on unit square centimeter area, mg/pulse
F = weight fraction of aluminum
ρ = density of strand, g/cm³

Table 3 Weight of aluminum per pulse for aluminum-ammonium perchlorate strand of unit cross-sectional area

Weight fraction of aluminum F	Burning rate r, cm/sec	Density of strand[a] ρ, g/cm³	Pulsation frequency[b] f, pulses/sec	Weight of aluminum W, mg/pulse-cm²
0.035	1.53	1.97	40	2.6
0.035	1.90	1.97	55	2.4
0.050	0.97	1.98	40	2.4
0.050	1.40	1.98	60	2.3
0.050	1.75	1.98	72	2.4
0.100	1.28	2.01	145	1.8
0.100	0.98	2.01	108	1.8
0.100	0.56	2.01	72	1.6
0.125	1.28	2.02	155	2.1
0.125	1.05	2.02	121	2.2
0.125	0.63	2.02	77	2.1
0.150	0.35	2.03	178	2.3
0.150	1.04	2.03	135	2.3
0.150	0.58	2.03	81	2.2
			Average:	2.2

[a] Calculated using the densities of aluminum (2.70) and ammonium perchlorate (1.95).
[b] Most prominent peak selected.

f = peak pulsation frequency, pulses/sec
r = burning rate of strand, cm/sec

The results of such computations are given in Table 3.

It is seen that the amount of aluminum which corresponds to a single pulse is roughly constant, over a wide range of the burning rate and aluminum content of the strand. An alternative method of presenting the data in Table 3 is shown in Fig. 3. Here the prominent peak pulsation frequencies are plotted against the mass flow rate of aluminum through the surface of the particular burning formulation. It is seen that the data points cluster around a straight line passing through the origin; the slope of this line is, of course, the average weight of aluminum per pulse previously computed.

The aggregation and ignition of a constant amount of aluminum on the propellant strand surface raises the question of a mechanism by which this is possible. Clearly, the data demonstrate that the mean aggregation time of the aluminum on the surface differs widely from case to case. For example, consider the formulation where 15% aluminum is present; the residence time varies from 5.6 to 12.3 msec. If the ignition process ultimately occurred at the surface, we would not expect the same mass of aluminum to require such different times for ignition. In fact, if ignition were possible at the surface, we would hardly expect that an aggregate of particles would ignite more readily than a single particle. Hence, we are led to the conclusion that the surface temperature is so low that even such small particles do not ignite, although they may melt and undergo relatively slow oxidation.

The collection of an approximately constant amount of aluminum strongly suggests that the ultimate mechanism of ignition consists in the aluminum aggregating at the boundaries of the ammonium perchlorate grains and growing out from the surface in the direction of the higher temperature regions of the flame reaction zone. Ultimately, the outermost portions can ignite and propagate combustion through the whole aggregate, resulting in a combustion and light pulse. Such a loose network of aluminum particles has, in fact, been directly observed on the surface of a strand under a microscope where the strand has been contacted with a laboratory torch just short of obtaining a "flash."

The assumption that the ammonium perchlorate surface temperature is too low to effect ignition is not an unreasonable one. Surface temperatures have been reported as ranging between 900° and 1100°K,[4] which is probably insufficient to ignite the aluminum. This interpretation gains further support from the experiments with molybdenum-ammonium perchlorate strands. At the 30% (by weight)

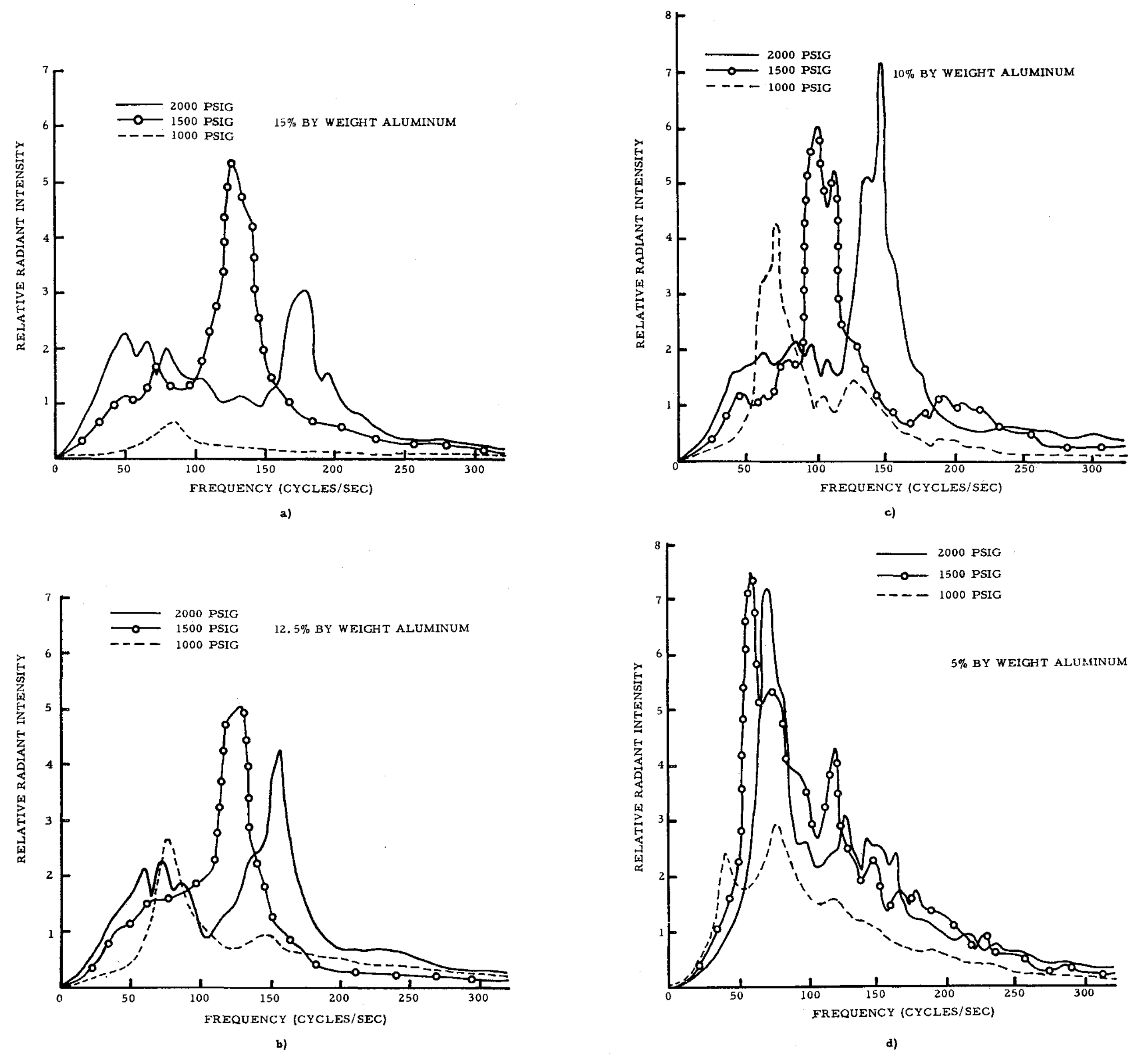


Fig. 2 Radiation pulsation frequencies of burning ammonium perchlo-

level (~7 μ), no indication of discrete pulsation frequencies was observed. The over-all light intensity was very low and similar to pure ammonium perchlorate. Molybdenum is reported to have an "ignition temperature" of about 900°–1000°K, and it is postulated that individual particles are able to ignite at the surface and be expelled before any aggregation is possible. (Note: the molybdenum concentration chosen corresponds approximately to the same number of additive particles per unit volume as an 8% aluminum composition.)

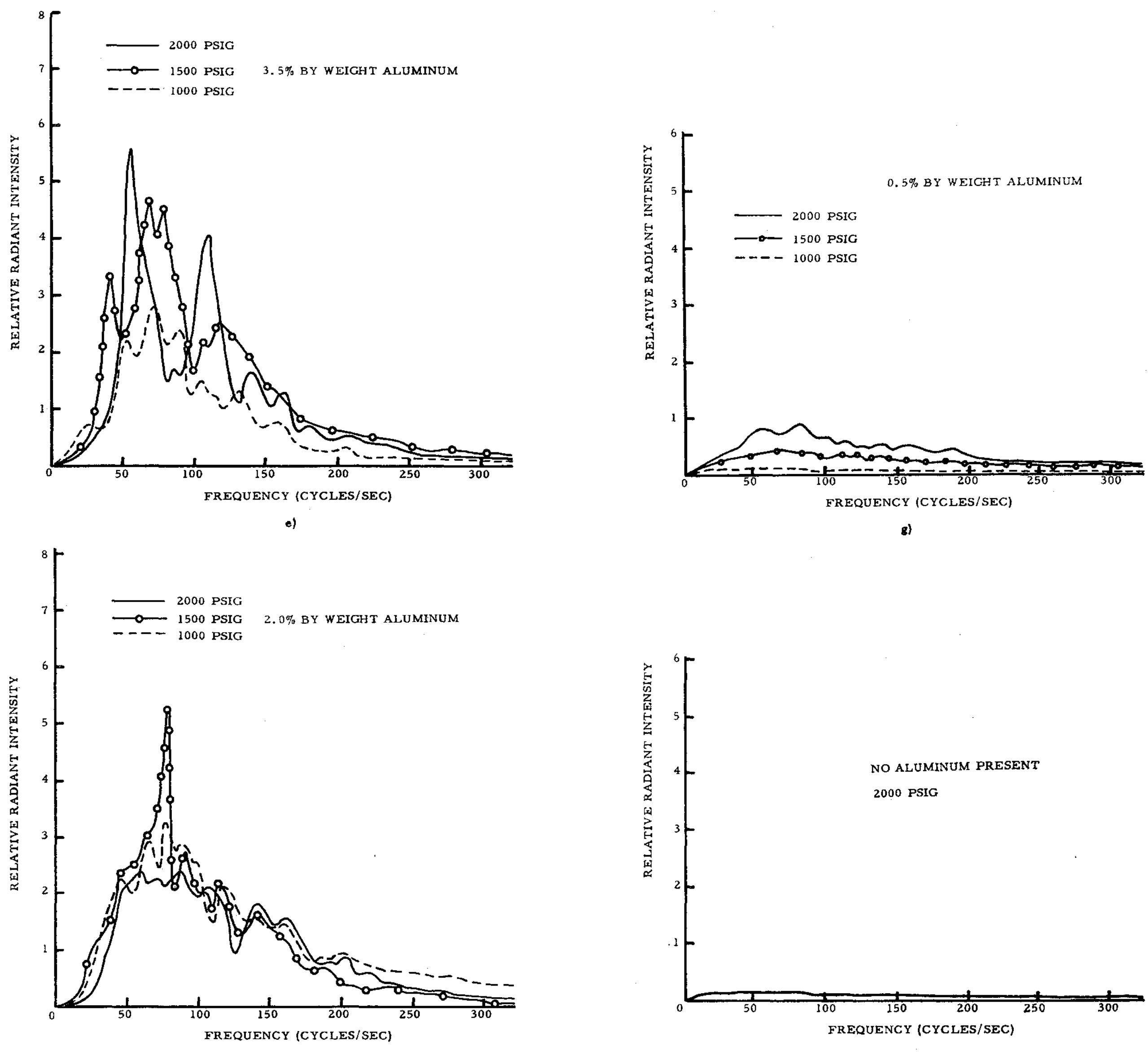
In the case of 0.5% aluminum content (Fig. 2g), no preferred pulsations were observed, and the general radiation intensity level was low (almost as low as pure ammonium perchlorate). This result is best understood by considering the interparticle distance as a function of aluminum concentration, illustrated in Fig. 4. We note that the interparticle distance increases very rapidly with diminishing concentration, and at the 0.5% level it is of the order of the ammonium perchlorate particle size. Thus the opportunity for aggregation rapidly diminishes at lower concentrations, and the particles probably lead a relatively isolated existence and undergo slow oxidation at the surface. This same tendency is illustrated at the 2 and 3.5% levels, particularly at the lower pressures. In these cases we also note that low pressures result in lowered burning rates and, hence, a longer residence time for an individual particle, which may undergo extensive flameless oxidation. This, coupled with diminished opportunity to collide with partners to form an ignitable network in the manner previously described, may account for the absence of well-defined pulsation frequencies. In some cases, there appears to be more than one peak frequency (e.g., 3.5% case); the origin of such multiple peaks is not clear at this time.

Finally, we note that 2 and 5% of 40 μ aluminum powder also fail to show discrete pulsation frequencies (Fig. 5). Once again, this is attributed mainly to the wide spatial separation of individual aluminum particles. Thus, at the 2% level, the interparticle spacing is about 108 μ, and at the 5% level, it is about 79 μ. It is noteworthy that, when these formulations were contacted with a torch, no "flashing" behavior was noted, and the strand receded completely, leaving behind a mound of reaction products of aluminum.

No attempt has been made to interpret the variation in amplitude of the observed peak frequencies at this time.

References

[1] "Study of resonance behavior in solid propellants," Aeronutronic Div., Ford Motor Co., Thirteenth, Fourteenth, and Fifteenth Quart. Repts. (1961); also First and Second



rate as a function of aluminum content (6-μ particles) and pressure.

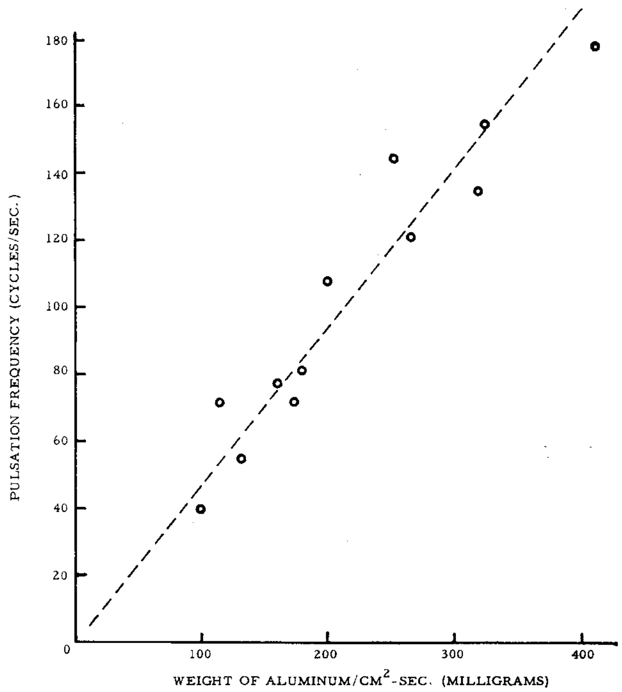


Fig. 3 Peak pulsation frequencies vs mass consumption rate of aluminum.

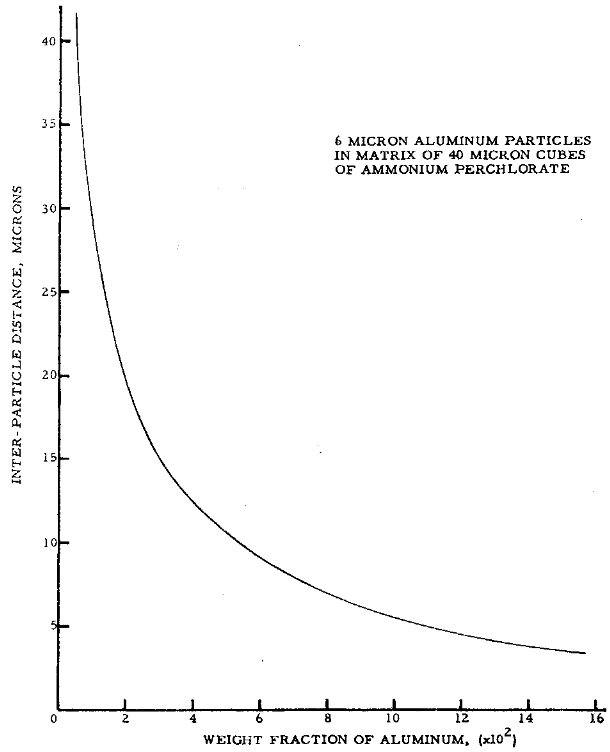


Fig. 4 Interparticle distance vs weight fraction of aluminum.

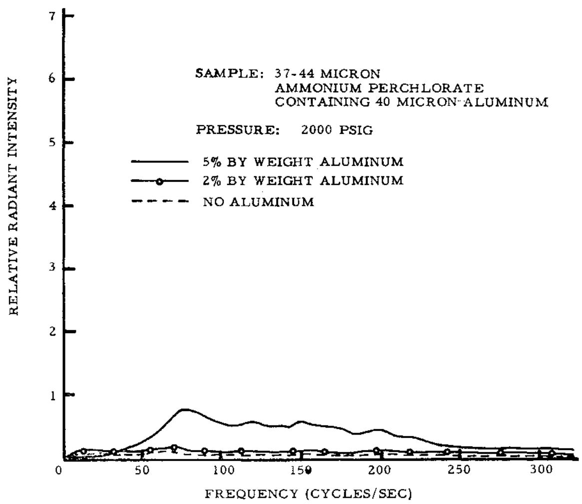


Fig. 5 Radiation pulsation frequencies of burning ammonium perchlorate strands containing 40 μ aluminum powder.

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[4] Levy, J. B. and Friedman, R., "Further studies of pure ammonium perchlorate deflagration," *Eighth Symposium (International) on Combustion* (Williams and Wilkins Co., Baltimore, Md., 1962), pp. 663–672.