

## COMBUSTION STUDIES OF JET PROPELLANTS

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Final Report on Aerojet Contract P. O. #410386  
June 1991

### Objectives:

The general goal of this research was to achieve high combustion efficiency and improved burning rate characteristics of aluminized propellants with nitrate oxidizers, particularly of solution propellants under development by Gen Corp Aerojet.

### Approach:

The approach was to study combustion of small samples in laboratory scale burners, including combustion window, quench, and particle collection "bombs" and CO<sub>2</sub> laser pyrolysis, along with optical and SE microscope studies of quenched samples. Such studies, in combination with systematic modifications of propellant formulation, provide a quick route to qualitative understanding of combustion and propellant optimization.

### Summary of Research:

The research is described in the body of the report in three phases, which emerged as a result of two extended interruptions in the study due to discontinuities and reorientations of the parent Gen Corp Aerojet project.

In the first phase (July 1987 to February 1988), studies were made of model propellants prepared by dry-pressing mixtures of AN, AP, polymer and aluminum powders (no Aerojet propellants were available yet). It was found that AN:AP ratios higher than 25:60 gave poor combustion behavior (1000 psi), with irregular burning and minimal aluminum ignition. Use of combustion aids and optimum binder resulted in AN/AP ratios greater than 25:60 with regular burning and fair aluminum ignition. Work was suspended before optimization of combined aids was attempted.

In the second phase (August 1989 to December 1989), studies were made of combustion of propellant samples supplied by Gen Corp Aerojet (solution propellants). This phase of the studies was relatively nonproductive because of several features of combustion that impeded photographic observation (samples that would not burn, burning down the sides of end-burning samples, accumulation of residues (char) on the surface, and clouds of aerosol from the surface). These are all significant findings regarding combustion of this novel propellant, but singular, unexpected, and not particularly helpful in getting to the target of controlling burning rate and aluminum combustion. In particular, observation of the aluminum combustion was obstructed by residue and smoke obscuration. The propellant apparently burns with substantial release of undecomposed oxidizer from the surface, formation of char on the surface, and intense combustion of accumulated aluminum in the char layer. In most samples, a column of residue was left after the sample was consumed, with some unburned aluminum remaining. The practical significance of these novel features of the combustion, or their relevance to combustion in a motor environment remain uncertain.

In the third phase (June 1990 to September 1990), recourse was taken to atmospheric pressure laser pyrolysis tests in order to simulate combustion under conditions where less obscuration would be present. Samples were observed by video photography in a nitrogen flushed test chamber with incident infrared surface heating at about  $320 \text{ watts/cm}^2$  by a  $\text{CO}_2$  gas laser. Tests were run on all the propellant in the first shipment from Aerojet (Table 1) and all samples of a second shipment (Table 2). Full information on formulation was not supplied; however, each set of samples consisted of an unaluminized sample and a range of aluminum concentrations. In the laser pyrolysis tests, the details of surface behavior and aluminum combustion were relatively observable.

### Experimental Methods

Evaluation of the performance of nitrate based propellants was conducted using facilities in the combustion and microscopy laboratories in the School of Aerospace Engineering. The combustion lab contains: (1) a high pressure window bomb with lighting, video, and motion picture cameras; (2) a high pressure quench bomb; (3) decomposition equipment (DTA, DSC, TGA); (4) a 1000 watt  $\text{CO}_2$  laser with beam optics and optical table; and (5) sample preparation, handling, and storage

facilities. The adjacent microscopy laboratory consists of scanning electron and optical microscopes with associated heating stages.

These laboratories have been used extensively for studying propellant (primarily ammonium perchlorate based) combustion as well as the high temperature decomposition of individual ingredients. These studies of nitrate based propellants concentrated on the well established tools of propellant research: combustion photography and microscopic examination of quenched surfaces, as well as a relatively new procedure: laser assisted heating.

### I. Video and Cine Photography

The most powerful and convincing available method of evaluating the combustion of solid propellants is cinephotography. All of the old saws: "seeing is believing" and "a picture is worth a thousand words" apply to this method. Burning rates as well as the uniformity of burning rate can be measured and qualitative features such as the combustion behavior of aluminum (accumulation, agglomeration) can be determined. The ability to witness the event and observe unanticipated processes is a valuable research tool.

The normal combustion facility photographs a small parallelepiped of propellant ignited on one end. In an actual rocket motor, the burning surface will experience a cross flow of propellant gases ranging from low in the head end to high at the aft end. This cross flow leads to higher burning rates (erosive burning) and is dependent on the actual location within the motor. Thus, it is important to note that standard combustion photography provides "non-erosive" or end burning. Thus, in an actual motor the local burning rate and aluminum behavior will depend on the character of the cross flow and thus will vary from point to point within the motor. The end burning results provide only a baseline.

Photography of propellants has traditionally been done by high speed (1000 to 10,000 frames/sec) 16 mm motion picture (cine-) photography. Unfortunately, the convenience of video has all but eliminated the amateur motion picture industry. Film processors are limited to a handful of national services with attendant shipping delays. High speed and high resolution have given way to

instant replay and low cost. Useful videos are limited to exposure times of 1/1000 sec but are adequate for measuring burning rate and observation of gross behavior. High magnification is still accomplished by lens extension tubes and close-up (macro-) lenses. Resolution is limited with the current generation of television monitors.

Propellant samples are mounted in a stainless steel chamber with quartz windows for external illumination and photography. Illumination is provided by a 2500 watt Xenon lamp. Nitrogen is used to pressurize the chamber and to provide a flushing flow parallel to the sides of the sample for removal of the smoke. As previously noted, this flushing flow is not parallel to the burning surface and does not provide a cross flow to affect the burning surface.

## II. Surfaces of Quenched Samples

Another useful tool for investigating combustion behavior is optical and electron microscopy of quenched samples. A quench bomb is similar to a window bomb except that the top is sealed with a stack of thin mylar disks trapping a nichrome wire. The chamber is pressurized, the sample is ignited, and after a brief delay the nichrome wire is heated by electrical resistance. The mylar diaphragm bursts, the chamber is depressurized in milliseconds, and the burning sample is quenched. The sample is then examined in a scanning electron microscope to obtain details on the microstructure of the burning surface.

For a heterogeneous propellant, the surface consists of partially burned ammonium perchlorate regions, divided by mounds of binder coated aluminum. Many details can be inferred by the surface structure of the AP, the size of the aluminum accumulates, and other microscopic features.

## III. Laser Pyrolysis

An alternative to the high pressure window bomb is pyrolysis with a CO<sub>2</sub> laser. Radiation from these lasers is in the infrared (10.6 micron) region and is thus an effective heating source. High power CO<sub>2</sub> lasers (about 1000 watts) can produce heat fluxes on the same order as a burning propellant. The lower density at atmospheric pressure reduces the smoke density and thus the

obscuration. Since the laser flux must enter the atmospheric chamber perpendicular to the burning surface, the flushing flow is removed from the side producing a cross flow parallel to the regressing surface. Previous tests heating a solid polymer revealed a strong shearing force on the pyrolyzing surface. Thus, the laser heating tests will permit clearer observation of the burning surface and thus the behavior of aluminum on the burning surface.

The purpose of the laser heating tests is to investigate the combustion behavior of the aluminum in these propellants. This is important because unlike the oxidizer and fuel which react at the burning surface (within several hundred microns), the aluminum is ignited at the surface but normally continues burning in the gas flow through the rocket motor. The transition from a single aluminum particle in the propellant to an ignited mass in the gas flow is important in determining combustion efficiency, slag formation, acoustic damping, and other parameters. Before describing the behavior of the aluminum in each of the samples, it is worthwhile reviewing the possible scenarios for aluminum combustion in solid propellants and their efficiencies. From an analytical viewpoint, the simplest path would be for an isolated aluminum particle (in a lightly loaded composition) to arrive at the burning surface, detach from the surface, ignite and burn in the gas flow. This is a simple and efficient path, but it is not common. In practice, when an aluminum particle arrives at the burning surface it is in contact with other aluminum particles (more so as the aluminum content is increased) and the relatively high temperatures cause the particles to sinter together to form an accumulate.

The accumulate is basically an irregular chain of sintered particles which eventually begins a slow, exothermic oxidation and thus increases in brightness. The accumulate may linger on the surface feeding heat back to the surface and/or may detach to burn in the gas flow. If the surface (or gas) temperature is high enough, the oxide shells defining the original particles will collapse (possibly melt) and all of the aluminum will coalesce into a large sphere called an agglomerate. The agglomerate will usually detach at some point and burn in the gas flow. The ignited agglomerates are extremely bright and comet-shaped with a convective trail.

In summary, in video coverage of the laser sustained combustion, the

simplest (and possibly ideal) case of single particle detachment would appear as numerous small, very bright streaks above the surface. In the more realistic case of ignited agglomerates, bright spheres would move across the burning surface (as the sintered accumulate draws up into an agglomerate), detach and be convected slowly away from the propellant surface. If the aluminum does not agglomerate it will appear as less bright irregular shapes on the surface and possibly in the gas flow. Aluminum combustion by this path is less efficient since combustion may not be complete by the time the accumulate leaves the rocket motor. Finally, the aluminum may not detach at all but rather form a sintered glowing bed on the surface. This has the worst efficiency and the self heating may cause the propellant to continue "burning" even after the laser heating is removed.

## Results

### I. Phase I: Investigation of Dry Pressed Nitrate Propellants

The first phase of this investigation involved attempts to produce in-house propellants using ammonium nitrate, powdered binders, and aluminum. Due to the poor performance of ammonium nitrate, ammonium perchlorate was added to produce a mixture of AP and AN capable of sustaining combustion. Established methods of coating AN to reduce the hygroscopicity as well as burning rate stabilizers were also investigated.

#### A. Oxidizer Self Deflagration

Initial experiments attempted to establish a baseline for the combustion of ammonium nitrate. Ammonium perchlorate will burn as a monopropellant in nitrogen at pressures above 300 psi. Ammonium nitrate (dry pressed into a parallelepiped) would not burn at 1000 psi in nitrogen or methane (a fuel). A dry pressed mixture of 90% AP and 10% AN burned irregularly at 1000 psi in nitrogen while an 85/15 mixture did not burn.

#### B. Combustion of Dry-Pressed Oxidizer-Fuel Combinations

In order to avoid problems associated with small scale propellant mixing

(inaccurate mixtures, trapped air bubbles, long curing times), pressed mixtures of dry powdered ingredients were used. While the oxidizers and aluminum are dry powders, a solid powdered hydrocarbon is substituted for the normally liquid binder to produce a dry mixture. The dry powders are measured, mixed and poured into a stainless steel die. The die is hydrostatically pressed at 19,700 psi and held for several hours to produce a compact sample. The sample is mounted in the window bomb, pressurized (with nitrogen to 1000 psi except as noted) ignited and recorded on video tape.

#### Variation of Oxidizers

The initial mixture consisted of 85% oxidizer, 10% aluminum and 5% carnauba wax (a dry powder binder substitute). Tests at 500 psi and 1000 psi indicated that a 60% AP and 25% AN mixture burned unevenly while a 50/35 mixture would not. Results of this series of tests are shown in Table 3. Switching to a mixture of 90% oxidizer, 9% binder (with 1% aluminum just to indicate ignition performance), gave a formulation closer to stoichiometric without the heat sink associated with heavy aluminum loadings. This mixture required a 70% AP, 20% AN ratio to sustain combustion.

#### Variation of Fuels

Powdered carnauba wax has been used extensively as a dry binder and produces good ignition of aluminum. Substitutes including ABS (Acrylonitrile/-Butadiene/Styrene) resin, Acrylonitrile/Butadiene Copolymer and Polyacrylonitrile were also used as dry binders. ABS was available in a more desirable particle size range and the 50% AP/25% AN/10% ABS/5% Al sample burned more evenly (but with greater aluminum agglomeration) than did the equivalent sample with wax.

#### Variation of Ammonium Nitrate

Due to the hygroscopic nature of ammonium nitrate, it must be kept desiccated. Sample preparation is delayed by inclement weather and quenched samples often deteriorate before examination in the scanning electron microscope. In an attempt to create a moisture barrier, Silane, a standard protective coating for AN, was used to coat a batch of AN. The coated AN was marginally better at

resisting clumping and dissolving in high humidity and produced slightly more even combustion. The most notable improvement came with the use of NiO phase stabilized AN. Although only preliminary work was carried out using NIOPSAN (because it was received after the stop work notice, it showed substantial improvement with regard to AN/AP ratio for good combustion and aluminum ignition.

#### Burning Rate Stabilizers

Sodium barbiturate is reputed to be a necessary additive in some applications for obtaining consistent, uniform burning of AN. The addition of 1% sodium barbiturate to the formulations with marginal burning characteristics gave improved results, but this line of investigation was also terminated by the stop work order.

Results from video recording of early emulsion propellants supplied by Aerojet were of acceptable quality, but revealed poor performance. Early samples did not burn (at 1000 psi) while later samples burned with a measurable burn rate but without aluminum ignition. The combustible sample (C728-46C) retained aluminum filigrees which were coated with a black carbonaceous residue. Substituting air for nitrogen as a pressurizing and flushing gas removed the carbonaceous residue and aluminum detached but did not ignite.

#### Phase II.

The primary objective of Phase II was burning rate measurement and evaluation of aluminum ignition behavior of the A3L series of propellants from Aerojet General Corp. using combustion photography. The composition of these samples is listed in Table I. Unfortunately, observation of all samples photographed in the window bomb was limited due to "smoke" produced by these propellants. Combustion was superior to the original emulsion propellants, but the A3L leaves a fine ash residue which accumulates on the burning surface, deflecting the products of combustion and filling the volume between the window and the sample with a dense smoke. Sides of the sample were coated with various inhibitors in an effort to eliminate side burning, but the surface was usually concealed by the inhibitor. The aluminum did not ignite and leave the surface



but remained trapped in the residue, glowing due to exothermic oxidation.

While viewing the details of combustion of A3L propellants was impossible due to smoke and residue, it was often possible to measure the rate of advance of aluminum self luminosity through the sample. These rates were close to the measured burning rates supplied by ASPC. Unfortunately, the residue did not permit the identification of a clearly definable surface (such as the gas-solid interface normally seen in AP-based solid propellants) and subsequent measurement of the regression rate of this surface. Thus, while measurement from most cinephotography is unambiguous, the actual surface is subject to speculation in the A3L combustion photograph and thus its regression rate is uncertain. High speed motion pictures of the combustion in place of video photography increased both time and spatial resolution of clear areas. The actual burning surface was still obscured, but the dense smoke was observed to be emitted in small unsteady jets. It is probable that this residue would be swept off by the cross flow in a real motor and would not be a significant factor in propellant combustion. It is simply an impediment to observation. The effect of the residue on aluminum behavior could not be evaluated in these tests.

In summary, the visual recording processes, both cinematography and video, which were effective in evaluating the combustion of dry pressed propellants with AN and AP propellants were not capable of producing unambiguous burning rates or evaluation of the accumulation and agglomeration characteristics of aluminum. They did reveal a tendency for the A3L propellants to form a surface residue in an end burning or cigarette configuration and to emit dense "smoke" from the surface, possibly oxidizer aerosol.

Quench testing of the A3L samples was not hindered by the smoke or residue (which was stripped by the rapid depressurization) but was limited by the near homogeneity of the samples. The Aerojet propellants are only heterogeneous because of the aluminum. During the rapid depressurization, the surface residue and accumulated aluminum was stripped off. Optical examination of the burning surface revealed a liquid or glazed surface with patches of aluminum that appeared to be below the glazed surface. After coating with gold and examining in a scanning electron microscope, the liquid layer seems to have evaporated

leaving a fairly nondescript (but irregular) surface with areas of high concentration of aluminum. Whereas accumulates of aluminum are normally seen on the surface of a heterogeneous AP propellant, the aluminum is buried in the Aerojet propellants with only slight bumps to indicate their presence. Although a comprehensive SEM study of quenched nitrate propellants might reveal subtle but important characteristics, the lack of any obvious distinct features at this point forced our efforts toward methods with a higher guarantee of success.

### Phase III.

The objective of the final phase remained the evaluation of the combustion efficiency of the aluminum in the A3L series. Due to the lack of success with video and cine photography in the high pressure window bomb, video recording of laser assisted heating in an atmospheric chamber was pursued. Measurement of the regression rate of samples irradiated with 550 watts of power (700 watts at the laser) produced a regression rate value about 40% of the burning rate (as supplied by Aerojet) at 500 psi. Smoke and residue ash were often found in the exhaust, but did not obscure the observation of the pyrolyzing surface.

Laser heating tests were carried out in a thin walled test chamber with a nitrogen atmosphere and purge. The chamber is scavenged through a side port which creates a cross flow of nitrogen across the pyrolyzing surface of the sample. The laser flux enters through a Zinc Selenide window on the top while quartz side windows permit illumination and video. Laser power was set at 700 watts at the shutter for all tests, resulting in 550 watts over a 1.5 cm circle at the sample.

Multiple runs on each of the eight propellants in the C478-74-X series (Table 1) and a second shipment of samples labeled C494-29A to G and 652-81 and 652-82 (Table 2) have been analyzed and the results are listed below:

**C478-74-1:** Some small, fast burning particles (single particles or small agglomerates) convect with the gas flow. Some large agglomerates form and detach. Some glowing spherical agglomerates remain on the surface near the edges.

**C478-74-2:** A few small, ignited particles are seen in the gas flow but most aluminum is retained on the surface forming a large glowing bed of accumulated aluminum. This sample had the poorest efficiency.

**C478-74-3:** Small surface accumulates form and detach to burn as agglomerates.

**C478-74-4:** More surface accumulation. Detached aluminum does not appear to spheroidize, implying only limited aluminum reaction. Burning accumulates/agglomerates are larger than -3.

**C478-74-5:** Substantial surface accumulation. Accumulates ignite to form large agglomerates. Burning agglomerates leave the surface.

**C478-74-6:** Bright surface ignition, a few single particles or small accumulates are seen in the gas flow. Numerous large agglomerates ignite and detach.

**C478-74-7:** Large surface accumulates are formed. Accumulates change to large agglomerates on the surface and detach reluctantly. After the laser was switched off, a large surface accumulate continued glowing, feeding heat back to the surface and continuing to pyrolyze the solid. The sample continued burning several seconds before finally extinguishing.

**C478-74-8:** Basically good ignition with large agglomerates which detach and are convected away.

**C494-29A:** Burns with surface accumulation with vigorous aluminum combustion in the accumulation. Some agglomerates appear to escape the surface (not many). Burning seems to fade only slowly after laser cut-off.

**C494-29B:** Burns with surface accumulation and very large and bright aluminum combustion in the accumulation, with a little spewing of aluminum outward (fine streaks). Large Al reaction sites in accumulate fade only slowly after laser cut-off.

**C494-29C:** Burns with some conventional outward-moving agglomerates and some aluminum combustion in a surface accumulation. The brighter burning accumulates

were slow to fade after laser cut-off.

**C494-29D:** Similar to 29C, but with fewer detaching agglomerates, more surface accumulation and larger bright sites in the accumulation, reluctant to go out after laser cut-off.

**C494-29E:** (Non-aluminized) (The beam is centered to left side of sample top surface.) Massive accumulation of irregular structures.

**C494-29F:** Large accumulate structures, bright areas that appear to be mobile but are probably propagating through a relatively nonmobile accumulate structure. Brightness comparable to 29D, but spews some bright streaks. Fades quickly at laser cut-off.

**C494-29G:** Forest of surface accumulate with aluminum combustion in the accumulate with some spewing and  $Al_2O_3$  smoke. Fades fast on laser cut-off.

**652-81:** Forest of accumulates with bright aluminum reaction sites that propagate busily with some spewing and streaking. Very few agglomerates leave the surface. Bright sites fade only slowly after laser cut-off.

**652-82:** Similar to 652-81 except Al combustion sites in the accumulate are brighter, larger, and persist after laser cut-off (sample burns to completion).

## SUMMARY COMMENTS

### Limiting Conditions on Investigation and Experimental Problems

In this section, an effort is made to describe combustion of A3L propellants. This should be prefaced by a general comment on the character and limited success of the investigation and credibility of results. a) Because of the stop-start nature of the program (two extended "stop work" orders) and shifting propellant systems, there was only limited opportunity to study the final candidate propellants. b) Interpretation of results is hindered by the limitation of tests to a set of propellants provided by Aerojet, in which variation of formulation variables was chosen to meet total program goals, but

not well suited to a combustion mechanism study. c) There were a number of unique difficulties involved in testing this propellant, that frustrated the usual methods for studying combustion.

As a result of these frustrating (but unavoidable) circumstances, the picture of combustion of A3L propellant that emerged is incomplete and speculative. What is clear is that A3L propellant combustion is very different from that of other well-studied propellants.

### Combustion Photography Results

In window bomb tests of A3L propellants at 1000 psi, the combustion photography shows a dense cloud of aerosol, with relatively stationary areas of intense luminosity seen diffusively through this "fog," where aluminum is present in the propellant. Unlike other propellants, no view of the burning surface is possible because of the smoke. This was further complicated by a propensity for rapid flame spreading down the sides of the samples. After burnout there was usually a substantial amount of ash, sometimes still in place as a column where the sample had been. Residual ash occurred with both aluminized and non-aluminized samples, and a major part of the aluminum combustion occurred "in place" in the ash column. The residual ash did not appear to contain unburned aluminum (no quantitative analysis made). The window bomb tests revealed completely novel aspects of A3L propellant combustion (aerosol, ash, constraint of burning aluminum in the ash). The aerosol may have been a fog of HAN. It seems likely that ash concentration on the surface would be less in the flow environment of a motor. Also, it has been suggested that the propellant may have a second mode of steady state combustion in which the "ash" material is oxidized at (near) the surface, with heat release and corresponding minimization of surface accumulation of either ash or aluminum. While this possibility cannot be ruled out, there was nothing marginal about the ignition in the window bomb tests; and the burning was usually very intense due to aluminum combustion. It is worthy of note that, in Sandia studies of liquid gun propellants with the same oxidizer, the liquid burning was dominated by the oxidizer decomposition, with oxidation of the fuel ingredient occurring as a "fog" burning some distance from the surface. This was attributed to the low exothermicity of the oxidizer decomposition, along with low activation energy for the decomposition reaction.

In the solid propellant, the fuel is less easily convected away than the liquid fuel fog, leaving a complex, flow environment-dependent fuel burning process above the surface. There is an obvious need for much more detailed study of this unique combustion process.

#### Laser-Assisted Combustion at One Atm.

In an effort to gain a better view of the surface processes during combustion, tests were run in an atmospheric-pressure nitrogen-flushed test chamber with infrared CO<sub>2</sub> laser illumination to support combustion. This allowed a pyrolysis rate comparable to that in combustion at 1000 psi, but with less smoke obscuration. In these tests, smoke obscuration was minimal and the ash concentration was revealed as an extraordinarily complex sponge-like structure. With the unaluminized propellant, the accumulation appeared to "flow" laterally on the surface under the influence of a mild lateral cross flow due to side-venting of the flushing gas. Since the material is presumably vaporizing at its surface, it is difficult to be sure that the apparent motion is really "flow."

With aluminized formulations, the surface accumulation did not have this appearance of flow. It was clear that aluminum burning occurred in the char layer. In fact, the luminosity was so bright that other features of the surface layer were difficult to resolve (because of low luminosity). In the motion pictures the luminous material appears to exhibit local, more or less random, motions, but careful examination suggests that the sponge-like structures are not moving, but the luminous processes are. It seems likely that portions of the structure are sintered aluminum accumulations, and that combustion spreads through these structures. Unlike conventional propellants, this does not lead to formation of detaching aluminum agglomerates. The aluminum seems to usually burn in place, with the intense reaction sites probably being governed by extent of aluminum concentration, extent of the local oxidizer flow, and heat-up by the laser beam.

The detailed description in the test characterizes these surface features for each formulation. These descriptions do not allow much insight into formulation effects because a) the extraordinarily complex behavior was not

conspicuously different for the different propellants, and b) it is difficult to rank the propellants according to specific formulation variables because formulation variables were generally changed more than one at a time. Aside from the features mentioned above, the most distinctive behavior was with formulations C-652-82 and C-494-29C. C-652-82 exhibited very large and persistent accumulate structures on the surface. It continued to burn after laser cut-off. the top of the surface structures became less bright, while the under side continued to glow brightly, apparently due to continued aluminum combustion. Formulation C494-27C burned somewhat more like conventional propellants, with aluminum agglomerating and moving away from the surface when first ignited. Some surface accumulation developed as burning continued, but to a lesser degree than most of the aluminized samples.

Unfortunately, the laser experiment became operational so late in the program that it was not fully exploited (most of the tests were run after the end of the contract). It would be desirable (at the very least) to do a chemical and microscopic study of the residue on sample surfaces remaining after laser cut-off.

### Summary

Combustion of A3L propellants appears to proceed by an exothermic oxidizer decomposition at the surface with possible emission of an oxidizer aerosol as well. It is not clear how the polymeric fuel decomposes, but it appears to accumulate on the surface as a porous structure, through which the oxidizer or its products must pass. In our tests it could not be determined whether the accumulation oxidized in place or broke away from the surface.

In metalized formulations the aluminum was impeded from leaving the surface by the surface concentration, and burned instead in this layer (and probably added aluminum oxide structures to the layer). Because of the high temperatures associated with the aluminum combustion, the polymeric fuel structures would be decomposed and then oxidized. The remaining surface structures would then presumably be aluminum oxides, carbides, and nitrides. These energetic reactions must contribute to the heat flow that sustains burning, but probably in a very pressure dependent way, presumably modified on the motor environment also by the combustor gas flow.

To the extent that surface concentration occurs in a motor environment, it has several practical implications:

- a) Ignition is not fully achieved until the layer is built up.
- b) Because the layer is the site of energetic reactions, processes that modify accumulation and reaction there should affect burning rate.
- c) If, as seems likely, accumulated material "tears away" from the surface, it may not react fully in small motors.
- d) Formation of aluminum concentrations may lead to relatively slow combustion of the aluminum, and to a larger than usual size of particles or droplets in the two-phase flow, with correspondingly modified two-phase flow problems.

Of course, these singular effects would be absent if no surface concentration occurred in the flow environment of a motor. Then burning would be more fully dominated by the primary reactions.



Table 1  
Composition of C478-74-X Series of Propellants

<u>Component</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>
AL MDX-65	15.0	7.5	18.0	9.0	22.0	11.0	26.0	13.0
H-60	--	7.5	---	9.0	---	11.0	---	13.0
PVA	13.0	16.0	13.0	16.0	16.0	13.0	16.0	13.0
Burning Rate Add.	2.0	3.5	3.5	2.0	2.0	3.5	3.5	2.0
Oxidizer	70.0	65.6	65.5	64.0	60.0	61.5	54.5	54.0

Table 2  
Composition of C494-29 and 652-81 Series of Propellants

	<u>C494-29A</u>	<u>29B</u>	<u>29C</u>	<u>29D</u>	<u>29E</u>	<u>29F</u>	<u>29G</u>	<u>652-81</u>	<u>652-82</u>
S-HAN-5	65.3	62.0	65.0	65.0	81.0	70.0	75.0	62.0	65.3
GNX	3.7	4.0	--	--	--	--	--	4.0	3.7
A1 MDX-65	18.0	15.0	15.0	10.0	--	5.0	2.5	15.0	18.0
A1 H-60	--	5.0	5.0	10.0	--	5.0	2.5	5.0	--
PVA HT	12.0	13.0	15.0	7.5	9.5	18.0	18.0	13.0*	12.0*
PVA	1.0	1.0	--	7.5	9.5	2.0	2.0	1.0	1.0

\* PVA HT from Cone Dryer

Table 3  
Results for Dry Pressed AP/AN/AI/Wax Samples  
at 500 and 1000 psi in Nitrogen

AN	AP	AI	Wax	500 psi	1000 psi
				*	*
85	0	10	5	NB	NB
75	10	10	5	NB	NB
65	20	10	5	NB	NB
55	30	10	5	NB	NB
45	40	10	5	NB	NB
35	50	10	5	P	P
25	60	10	5	B (Uneven)	B (Uneven)
15	70	10	5	B	B
5	80	10	5	B	B

\* NB: No burn  
P: Partial ( 3 mm or less) burn  
B: Burned to completion

## Appendix A

### EXPLANATION OF VIDEO RECORDS

In the experimental set-up, the test sample is arranged relative to the camera as in Fig. A-1, with external illumination from the upper right and mild  $N_2$  flushing flow from the bottom, vented to the left. The sample is tilted relative to the focal plane so that the image is in focus across the middle of the surface ignited by the laser beam. The camera is started before the laser exposure starts, runs until well after the laser beam shut-off. Multiple tests were made on most formulations for a variety of reasons.

- a. Poor laser beam positioning
- b. Camera problems
- c. Singular combustion behavior
- d. Run tests with and without neutral density filters to cope with extreme difference in brightness due to metal flame.

The descriptions of results in the text are based on review of all tests. The video tape provided gives short scenes from typical pictures of the propellants in Table 2.

In viewing the tape it should be understood that the scene is a diagonal downward view of a VERY complex surface, consisting of what is often a forest of "accumulate" structures. Sometimes there are aluminum agglomerates or bursts of fine droplets leaving the surface; the low video framing rate and  $N_2$  flow prevent tracking of the progress of this detached aluminum. However, most of the aluminum combustion (most formulations) occurs in the forest of accumulated surface material. The resulting bright sites seem to have high mobility. However, most of this "mobility" is actually spreading of inflammation through the structure of a relatively stationary accumulate forest.

Comments in the text pertain to such features as brightness of combustion, presence or absence of detaching aluminum agglomerates or spewing of fine droplets, extent or structure of surface accumulation, and behavior after laser cut-off (the top of the accumulate forest darkens quickly, but active aluminum combustion sites sometimes continue to burn, so that the under side of the surface accumulation remains luminous after the top has turned dark.