Heat Sterilizable Propellants for Planetary Missions

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Dry-heat sterilization, a requirement of all planetary lander missions, places severe requirements on solid rocket propellants that will be used on them. In an ongoing program, which has a goal of producing heat sterilizable motors with 130 kg of propellant, numerous insights into the problems associated with developing dry-heat sterilizable propellants have been gained. The one most significant means of increasing propellant stability at sterilization temperature (125°C) is to decrease the ammonium perchlorate (AP) particle size. One possible explanation is that some of the AP crystals larger than 250 μ in diameter are unstable at sterilization temperature. Another important findings is the effect grain diameter has on survivability at sterilization temperature. As the grain diameter increases, the time to failure decreases. This is probably due to the increased stress that results from the thermal gradients, which occur during grain heat up or cool down. In this work, 7-cm-diam grains have been made that survived 70 sterilization cycles (the requirement is eight); however, 71-cm-diam grains from the same propellant batch have survived only seven cycles.

Introduction

IN future planetary landings, it is required that all spacecraft components, including solid rocket motors, which could possibly impact another planet, be dry-heat sterilized. The ongoing effort described in this paper has as its goal the production of a sterilizable solid-propellant motor that will fulfill the requirements of the Mars ascent vehicle, which will be employed in a possible Mars sample-return mission. The solid propellant rocket motor requirements envisioned for this mission are[1]: motor sizes, 81 and 129 kg of propellant; motor mass fraction, 0.88; and propellant vacuum specific impulse, 2793 N-S/kg. The current sterilization requirements, as outlined for the project Viking,[2] are three temperature cycles, ranging in length from 25 to 40 hours at 113°C. However, in order to be accepted as flight worthy and sterilizable, each component must be capable of surviving a set of type-approval sterilization cycles. These are five 54-hr plus three 40-hr cycles at 125°C.

Two of the major problems yet associated with the development of a high-performance, heat-sterilizable motor are: ammonium perchlorate stability within the propellant, and grain stability as a function of its diameter. This paper will treat both of these subjects.

Experimental

Throughout, all the propellant batches were prepared from single lots of ingredients. The basic propellant formulation used is shown in Table 1.

All propellants were vacuum mixed and vacuum cast. They were cured in Teflon-coated cylinders, 7 or 30 cm in diameter. After cure, the propellant was removed from the cylinder and sterilized as a free standing grain. One exception to this was a 71-cm-diam grain. In this case, the propellant was cast, cured, and sterilized in a defective flight weight stainless steel motor chamber, which had been Teflon coated on its interior. Physical property measurements were made on separate samples prepared for that purpose, or cut from cylinders after sterilization.

All propellant failure determinations were made by radiographic inspection of the samples. Inspections were made before cycling, and after every other cycle on the 7-cm grains, after every cycle on the 30- and 71-cm grains. In all cases, cycling was continued until the sample failed. Failure generally appeared as many small voids that were located in the center of the grain. The key observation is that failure propellants, a crack would form. Failure is defined as the first appearance of voids in the grain. Cycling to failure is an imperative test procedure if differences between samples are to be found. A typical failure is shown in Figs. 1 and 2. Figure 1 is a photograph of a sample cut in half after six cycles at 135°C; no failure is evident here, or was evident in radiographs taken before it was cut. Figure 2 is another grain, cast from the same batch as the one in Fig. 1, after nine cycles. Here a gross failure has occurred, and many voids can be seen. These voids began to be observed after 7 cycles in radiographic inspections; however, they usually are not visible in cut samples until the failure has been allowed to progress further. The sample is also slumped, however it had not slumped at the onset of void formulation after seven cycles.

All sterilization cycling was done in monitored, forced-convection ovens. All 7-cm-diam samples were cycled 56 hours per cycle, 30-cm-diam samples 74 hours, and 71-cm-diam samples 150 hours. Separate tests determined the time required for the center of the various diameter grains to reach sterilization temperature; they indicated that it took 1, 20, and 96 hours for the 7-, 30-, and 71-cm-diam grains to heat up, respectively.

Results and Discussion

This section will be broken into two broad areas: oxidizer stability and grain diameter effects. A very significant increase in propellant stability at sterilization temperature can be made by reducing the oxidizer particle size. Selected data, representative of the many propellant batches that were

Table 1 Basic propellant formulation

Binder: 19%	Relative amount of equivalents in the binder
Saturated hydroxyl terminated polybutadiene[a]:	0.7-0.8
Trimethylolpropane:	0.2-0.3
DDI[b]:	1.1-1.3
Aluminum: 16%[c]	
Ammonium perchlorate: 65%[d]	

[a] Telagen, General Tire and Rubber Co.
[b] DDI Brand Diisocyanate 1410, General Mills Chemical Div.
[c] Reynolds Aluminum Co., LSA-765, 18-micron special order; iron content < 20 ppm.
[d] Kerr McGee Chemical Co., purchased to JPL Spec GMO 50043, Analysis, AP 99.7%, NH_4Cl 0.008%, NH_4ClO_3 0.009%, Nonalkali metal oxides 0.002%, water insolubles 0.003%, moisture after drying <0.005%.

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Fig. 1 12-cm grain cut in half after six sterilization cycles at 135°C.

Fig. 2 12-cm grain cut in half after nine sterilization cycles at 135°C.

prepared and tested, are presented in Table 2. All of the batches included in Table 2 were prepared with the identical lot of ammonium perchlorate (AP). Several observations can be made from these data. First, the modulus of each propellant is high. A high modulus is necessary to have the propellant survive more than just a few cycles, regardless of AP stability. The goal of being able to prepare a lower-modulus sterilizable propellant remains, but to date it has not been reached. The second observation is the significant increase in the number of sterilization cycles the 7-cm-diam cylinders will survive as the AP particle size is reduced. Simply sieving out the coarser fraction doubles the number of sterilization cycles survived. Reduction of the AP particle size by grinding in a hammer mill, further increases the stability of the propellant. A comparison of batches 143 and 8 shows an order-of-magnitude increase in the number of sterilization cycles survived, the result of grinding the AP. Data from numerous other propellants, not tabulated here, also support this finding.

The obvious questions are, what occurs and why does it happen? Chemically, no changes of any type have been made; the sole difference is the AP particle size. Previous work,[3] using time lapse photography to observe propellant samples between microscope slides at sterilization or slightly higher temperatures, indicated that failure began at, and propagated from, a few discrete points. Typical sterilization failures also begin with tiny void formations at a few points located near the center of the grain. The key observation is that failure initiation is not general, but only at a few separate points. It has been previously determined[3,4] that the propellant failure initiates with the oxidizer. These observations indicate that failure initiation is associated with only a small percentage of the oxidizer crystals, estimated to be on the order of less than one AP crystal in a thousand. Figures 3 and 4 show a magnified view of propellant surfaces before and after exposure to sterilization temperature (125°C). Before exposure the large unground AP particles are translucent and difficult to see. Prolonged exposure (the time varies with different AP lots) to sterilization temperature causes 1) the larger crystals to become opaque and white; and 2) a few of them break, as shown in Fig. 4. During this exposure the small (ground) AP particles remain translucent. The exposure of neat AP to 135° C for long periods of time, generally 200 to 1000 hours depending upon the lot of AP, will also result in fractured crystals.[3] Continued exposure of propellant samples, sealed under vacuum in glass ampules, will result in the formation of surface voids (Fig. 5). It is assumed that these voids form in a manner similar to those formed within propellant samples. The back surface, which is not in focus, appears much like the remainder of the propellant surface.

Table 2 Sterilization of 7-cm-diam grains

Batch No.	$\frac{NCO}{OH}$[a]	$\frac{OH_{triol}}{OH_{total}}$[b]	Physical properties before cycling, 22°C: E_i'[c] N/cm²	S_m'[d] N/cm²	ϵ_m'[e] %	121°C: E_i' N/cm²	S_m' N/cm²	ϵ_m' %	Cycle temperature, °C	Cycles to failure
Unground AP, average particle size: 180 microns										
128	1.11	0.20	-	145	51	245	40	33	135	2
143	1.15	0.19	-	171	31	514	53	18	135	3-4
Sieved AP, <150 microns										
211	1.12	0.20	-	-	-	-	-	-	135	7
Ground AP, average particle size: 12 microns										
6	1.15	0.15	2800	186	12	558	70	18	135	16
7[f]	1.15	0.15	2800	221	14	1310	110	16	135	14
8	1.15	0.20	2100	187	16	724	76	14	135	34
9	1.20	0.15	2800	177	10	690	79	19	135	36
31	1.15	0.20	2400	159	13	614	70	16	125	73
32	1.15	0.30	3000	177	10	1100	85	8	125	70

[a]Isocynate/hydroxyl ratio in binder. [b]Hydroxyl from triol/total binder. [c]Initial modulus. [d]Maximum stress. [e]Strain at maximum stress. [f]Contained 0.3% HX-868 (Three M) as a bonding agent.

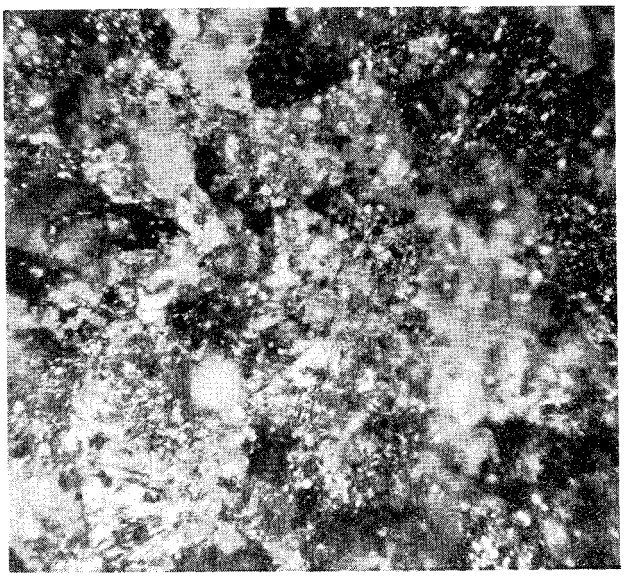

Fig. 3 Magnified propellant surface before exposure to sterilization temperature (125°C).

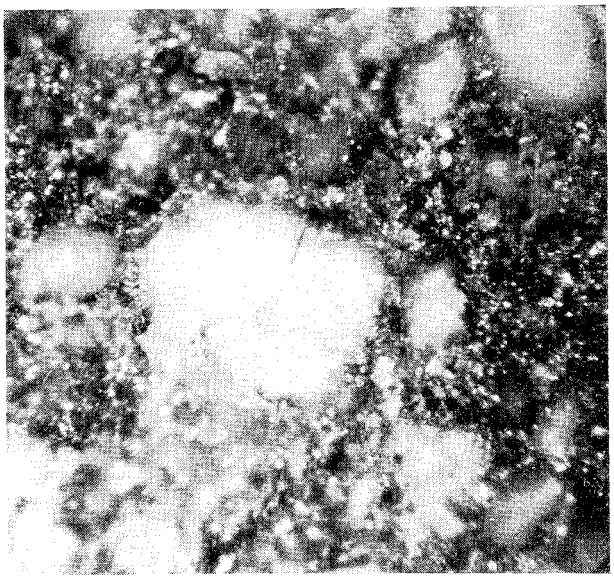

Fig. 4 Magnified propellant surface after prolonged exposure to sterilization temperature (125°C).

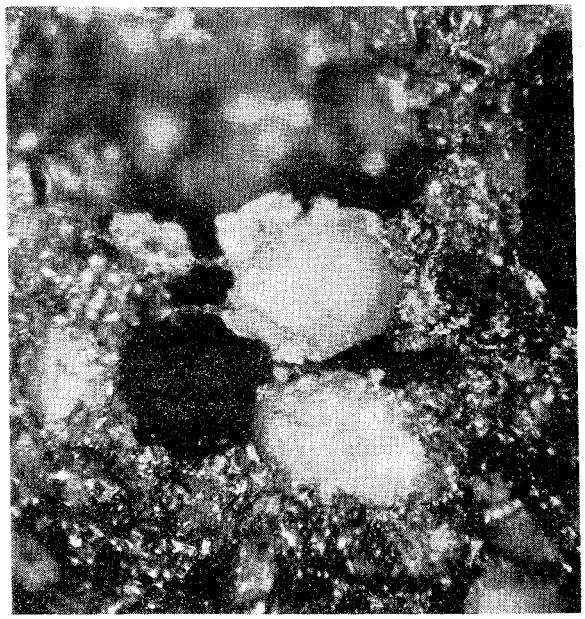

Fig. 5 Surface void formed in propellant after prolonged exposure to 125°C in an evacuated glass ampule.

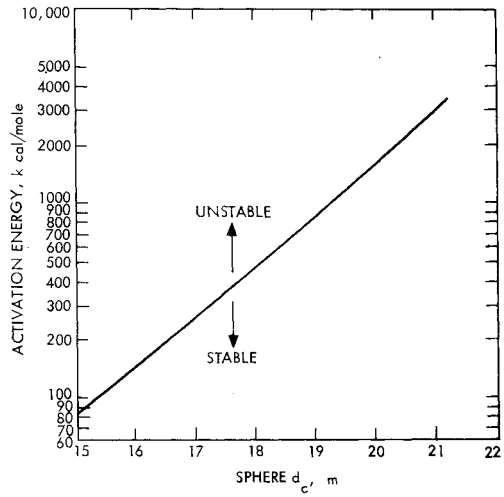

Fig. 6 Critical diameter versus activation energy at 135°C.

The mechanism of the initial failure and its subsequent propagation is not well understood. It has been determined that it begins with selected oxidizer particles, followed by growth of the failure in the surrounding area. This area has been studied by Schmidt[4] who suggests the following. "After initiation, on the oxidizer surface, the decomposition propagates by reactions at the binder-oxidizer interface," He further states, "The oxidation of the polymer most probably proceeds, or at least is initiated, by a radical attack. The experimental evidence suggests that the first step most likely involves a radical, from the oxidizer decomposition, abstracting a hydrogen atom from the hydrocarbon."

Another analysis, which yields a possible insight into the AP decomposition phenomena was made by Attar and McKay.[5] Their investigaiton included the examination of 22 separate lots of AP, each of which had been thoroughly analyzed chemically,[6] and also incorporated into propellants which were sterilized to failure. On the subject of AP decomposition and propellant stability they state, "We can markedly increase the stability of propellant made from any of the AP lots merely by grinding it. There is a theoretical explanation for this result as follows: The decomposition of AP is exothermic and will increase the temperature locally. The increase in the temperature in turn will accelerate the decomposition, and so on to completion. However, if sufficient heat is removed from the crystal by conduction to the surface, the reaction will be quenched. Following this hypothesis, the critical size was calculated for spherical crystals based on the surface temperature, the activation energy for decomposition, the heat of reaction, the Arhenius frequency factor, and the thermal conductivity of the AP."

In Fig. 6, from their report, the critical diameter, the diameter above which the crystal will become unstable at 135°C, is plotted against activation energy. As can be seen, at an activation energy of 17 kcal/mole, an accepted value for AP, the crystals whose diameter is greater than approximately 250μ are unstable at 135°C. Additional data, from the Attar and McKay report, show that any lowering of the activation energy will rapidly decrease the critical diameter for stable crystals. Impurities such as manganese, iron, or calcium in concentrations as low as 0.1, 2, or 150 ppm, respectively, will significantly decrease the critical diameter.

Other failure mechanisms could surely be envisioned. Crystal lattice defects are more likely to be found in larger AP particles, therefore causing them to fracture and possibly

begin to decompose preferentially. Sieving out the coarse particles would remove a majority of the less perfect crystals. Grinding would also fracture the AP crystals along imperfect planes, thus reducing the percentage of defective particles significantly. The grinding of AP does significantly reduce the weight loss rate of neat AP stored at 135°C from the weight loss rate of unground AP. However, AP weight loss alone cannot be correlated to stability in propellant. For instance, the most stable oxidizer (least weight loss after 1000 hours at 135°C) of 22 lots tested made the least stable propellant.[3] This observation is not understood yet. However, all the data gathered to date clearly point to decreasing the oxidizer particle size as possibly the one most significant means of increasing propellant stability at sterilization temperature.

Finally, the effect of temperature on stability is also clearly pointed out in Table 2. Samples from batches 31 and 32 were cycled at 125°C. As can be seen, they survived more than twice as many cycles as did similar samples cycled at 135°C, only 10° higher. This is a very encouraging result, since the actual sterilization of flight motors will be at 113°C. However, it makes the task of passing the type-approval cycles much more difficult.

One might say, if you can survive seventy 54-hour cycles at 125°C with a 7-cm-diam grain, then what is your problem? A quick look at the effect grain diameter has on survivability at 125°C will point out the problem. In spite of the fact that considerable understanding of the problem has been gained, there is still a long way to go. Tabulated in Table 3 are data from 7-, 30-, and 71-cm-diam grains, all cycled at 125°C. The cycle times, out of necessity, vary. As the sterilization requirement states, the most thermally remote portion must be at the sterilization temperature for the required number of hours. Recall that it requires 20 and 96 hours for the center of 30- and 71-cm-diam grains, respectively, to heat from ambient to 125°C. The reverse occurs on cooldown. Therefore, these grains spend from 37 to 178% more time at sterilization temperatures than do 7-cm grains, for the same number of cycles. Even more important is that the stress, resulting from the thermal gradient across the grain, is significantly higher in the larger grains. In a 38-cm-diam grain, the stress in tension at the center is approximately 8.3 N/cm^2 (12 psi) during heat-up. During cooldown, it does into compression. As can be seen from the data in Table 3, both the number of cycles and total hours to failure are significantly decreased as the diameter is increased. Why the 71-cm-diam grain survived as long as the 30-cm grain is not known. Possibly the effect levels off above some diameter; it is planned to repeat the 71-cm-diam test at a future date.

An effort aimed at gaining more insight into the effects of stress, as well as AP dopants and crystal particle size, was carried out by W. G. Schmidt.[7] He prepared propellant samples (with binders similar to those made at JPL) with double-recrystallized AP, some of which were then doped with chlorate, to accelerate decomposition, or with phosphate, to retard decomposition. The dopant level was on the order of 0.1%. A portion of Schmidt's data is presented in Table 4. Here it can be seen that increasing stress has a dramatic effect on the time to failure (break) of bars with a cross section of 1.2×1.2 cm. The stress levels of this test approximated those that would be experienced by larger grains due to thermal gradients. Increasing the stress from 2.8 to 6.0 N/cm^2 decreased the time to failure by a factor of five.

The effect of dopants is also significant. Workers at Aerojet have done extensive work in this area. The cocrystallization of phosphate with AP markedly increases the time to failure.

Schmidt's data also confirm our finding that reducing the AP particle size significantly stabilizes the propellant. Elimination of the coarse oxidizer increased the time to break by an order of magnitude, in one case from less than 0.5 hours to 5.5 hours, and in the phosphate doped case, from 1.5 to 14 hours.

Conclusions

The main conclusions that can be drawn from this work are:

1) Using AP of decreased particle size significantly increases the stability, at sterilization temperature, of solid propellant. This is possibly because the critical diameter for stable AP crystals is approximately 150 μ at 135°C. Elimination of these unstable crystals greatly enhances the propellant stability.

2) Increasing grain diameter decreases the time to failure of propellant at sterilization temperature. This is probably due to increased stress resulting from thermal gradients during temperature changes.

3) Cocrystallization of AP with phosphate increases propellant stability (Schmidt).[7]

4) The time to failure is quite temperature sensitive. Decreasing the temperature from 135 to 125°C will double the time to failure for a given propellant.

5) To properly ascertain a propellant's stability at sterilization temperature, it must be tested to failure.

Table 3 Time to failure, comparison of different grain diameters

Batch no.	$\frac{NCO}{OH}$	$\frac{OH_{triol}}{OH_{total}}$	Diameter, cm	Cycles to failure at 125°C	Hours to failure at 125°C
31	1.15	0.20	7	73	4088
			30	7	532
32	1.15	0.30	7	70	3920
			30	7	532
12	1.15	0.20	7	38[a]	2128
			71	6-7[b]	900-1050

[a] Possibly failed prematurely due to casting voids.
[b] Maybe voids after six cycles, difficult to tell from the radiograph.

Table 4 Time to break at two stress levels as a function of AP dopant and particle size at 170°C

Oxidizer	Oxidizer particle size, μ		Time to break, hours	
	60%	40%	2.8 N/cm^2	6.0 N/cm^2
AP·ClO_3	175-250	44-88	4.0	<0.5
	125-175	<44	–	5.5
AP	175-250	44-88	10	1.5
AP·PO_4	175-250	44-88	14	2.0
	125-175	<44	–	14

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