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Sterilized Solid-Propellant Rocket Motors For Mars Landing Missions

(Revision No. 1)

L. C. Montgomery
H. E. Marsh, Jr.

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FOREWORD

JPL Technical Report No. 32-725, dated March 30, 1965, contained information which required that the Report be classified and published as Confidential. To permit wider dissemination of the unclassified propellant-sterilization information, the classified sections were deleted and the remainder of this Report reprinted herein as Revision No. 1.

ABSTRACT

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In the initial phase of the program to develop a sterile solid-propellant motor for planetary and lunar landings, the chemical approach was taken. Also, the chemical sterilization of a state-of-the-art propellant has been demonstrated. Current objectives, however, require the heat-sterilization approach. The ultimate test criterion for the heat sterilizability of a spacecraft component is the ability of the component to survive three cycles of exposure to 145°C for 36 hr. "Off the shelf" propellants from seven U.S. manufacturers were included in the initial tests. Three candidates were eliminated in initial sterilization cycle slump tests which were performed in both air and nitrogen atmospheres. The remaining four propellants having retained some integrity in the slump test are evaluated for the physical and ballistic changes that occur because of the sterilization treatment. The significant crusting of the propellants and its related physical effects are evaluated. The development of a silicone propellant for heat-sterilization application is also included.

Author

I. INTRODUCTION

The objective of obtaining fundamental information on the origin of life from the exploration of the surface of Mars requires that the ecology of Mars be protected from Earth micro-organisms delivered by landing spacecraft. For this purpose a program was initiated at JPL for the development of sterilization techniques for Mars-landing space vehicles. To support this program, the Laboratory has undertaken the development of the technology necessary to provide sterile or sterilizable solid-propellant motors. Of the two general approaches to sterile spacecraft, (1) sterile assembly of previously sterilized components and (2) dry heat sterilization of assembled and encapsulated spacecraft, the latter approach is favored as having a lower probability of contaminating the planet.

The NASA criteria (Ref. 1) for acceptance of a spacecraft which meets sterility standards are based on the probability of one chance in 10^4 of contaminating the planet. In other words the probability of one viable spore being aboard a landing craft must be no higher than 10^{-4}. Since the capability of sterile assembly techniques to meet this severe requirement has not been demonstrated, the dry heat approach has been adopted for current projects. The relative risks of the several approaches to sterile spacecraft are discussed by Dr. Leonard Jaffe (Ref. 2). The objectives of the present effort are (1) to assess the durability of selected available propellants to the severe sterilization heating conditions, and (2) to develop new propellants for heat-sterilization application. Prior to the adoption of the dry heat approach, however, JPL had undertaken the sterile component approach and developed a chemically sterilized state-of-the-art polyurethane propellant.

II. CHEMICAL STERILIZATION

In the initial phase of the program to develop a sterile solid-propellant motor for planetary and lunar landings, the chemical approach was taken. It was first determined that the propellant did not have bactericidal characteristics, as speculated that it might have, by virtue of the toluene di-isocyanate used as an ingredient in the binder. This being the case, a search was made to find a bactericidal chemical that could be used as an ingredient in the propellant. The most effective liquid bactericides were found to be beta-propiolactone, ethyleneimine, and ethylene oxide. All of these chemicals are very active chemically, and the third one listed has been used as a liquid monopropellant.

The ethylene oxide (C_2H_4O) (*EtO*) was found not to be reactive with the polyurethane binder ingredients. Therefore, it was selected as a possible sterilizing agent for that propellant.

Initially the *EtO* gas with 88% Freon-12 was bubbled through the propellant. This mixture of 12% ethylene oxide and 88% Freon-12 is a nonexplosive mixture commonly used as a gaseous sterilant. The operation was found to be quite successful in its sterilization qualities as well as being nondetrimental to propellant properties. During the mixing process the propellant absorbed the *EtO* gas readily under 10- to 12-psia pressure, and was released as the pressure was reduced to 0.07 psia for casting.

This process produced an extra benefit to the propellant since the *EtO* Freon mixture purged the propellant of trapped gases as it bubbled through the propellant during casting. Therefore, the finished grain was without voids.

Further investigation revealed that the liquid ethylene oxide could be added to the propellant without deleterious effects to the propellant. This simplified the procedure for measuring the amount of ethylene oxide that is added to the propellant mix, and gave greater assurance that the *EtO* reached all ingredients to be sterilized. In addition to the boiling, purging action given to the propellant mix at low pressures, the liquid *EtO* gave the propellant greater fluidity for easier, better mixing action.

For this sterilization process, the proportion of *EtO* used was 6% by weight of the propellant binder. The *EtO* was added to the toluene di-isocyanate, then this mixture was added to the propellant mix. This was done to reduce the boil-off of the *EtO* in the process of handling and to provide added safety.

Finally, to produce a sterile propulsion unit the igniter, nozzle, case and liner were dry heat sterilized at 295 ±2°F for 36 hr prior to sterile assembly into a propulsion unit. The oxidizer was dry heat sterilized to assure elimination of viable organisms inside the crystals. Since the *EtO* does not enter the *AP* crystals, it only sterilizes the binder ingredients and oxidizer crystal surfaces.

A. Propellant Investigations

Propellant batches containing *EtO* were made in a one-quart Sigma mixer, a five-gallon vertical Planetex mixer, and a ten-gallon Beken mixer. The propellant samples from these batches were used for bacterial analysis, impact sensitivity tests, burning rate tests, physical property tests, and in making static test motors.

B. Results of Tests

The sterilization treatment of the polyurethane propellant with the ethylene oxide did not measurably affect the impact sensitivity nor the burning rate of the *SYN*-3-3 *SYNCOM*-type propellant.

The physical characteristics of the propellant were tested after it was treated with various amounts of *EtO*, running from 3 to 16% of the binder by weight. As shown in Fig. 1 and 2, the ultimate tensile strength was reduced from about 170 psi with no *EtO* added and with 65% elongation to about 100 psi with 80% elongation with 14% *EtO* added during the final mixing operation. Any of these physical characteristics would be acceptable in a propellant. The physical characteristics can be altered considerably by adjustment of the oxidizer grind or ratio of the other ingredients.

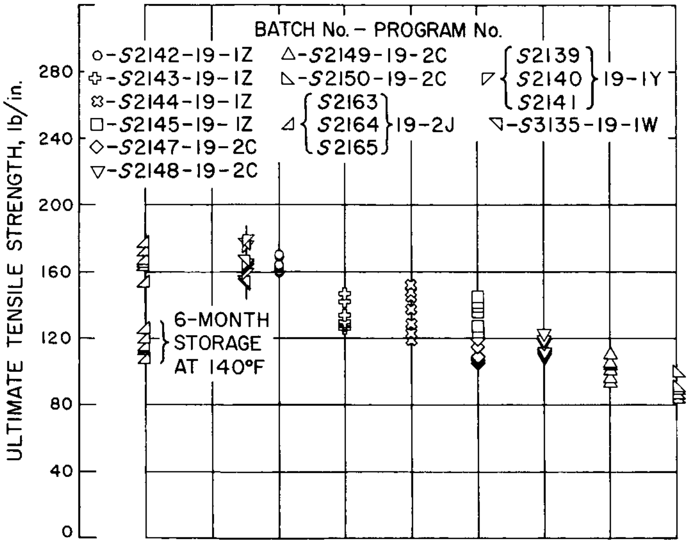


Fig. 1. Chemical sterilization of propellant—ultimate tensile strength, psi

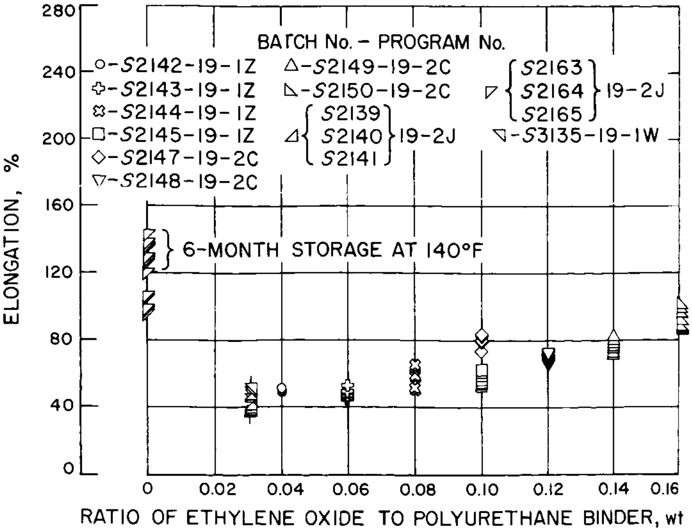


Fig. 2. Chemical sterilization of propellant—elongation, %

Bacterial analysis of the propellant was made by JPL and the Dynamic Science Corporation. The data obtained indicated that the viability of the inoculum, 1 × 10^6 of Bacillus subtilus var. niger spores per cubic centimeter, had been destroyed in specimens sterilized with 3% *EtO*. To assure that all other types of bacteria were also destroyed, it was decided to use 6% *EtO* by weight of the propellant binder.

Results from the static test firing of 5- × 6-in. motors having a cylindrical perforation showed no measurable change in the propellant ballistic characteristics as a result of the *EtO* treatment.

As a final demonstration of the capability of this system to produce a state-of-the-art sterile propulsion unit, one dummy and two live *SYNCOM*-type motors were made under sterile conditions. The 10-gallon horizontal Beken mixer with a flush bottom dump valve was used. The casting chamber and motor hardware with casting funnel were assembled to the mixer, sealed and surface-sterilized by a flow of *EtO*-Freon mixture under ½-in. water pressure for a 24-hr period. This assembly without the upper part of the casting chamber is shown in Fig. 3. The valve was actuated during the sterilization period to assure sterilization of all of its seals and exposed surfaces. After the 24-hr period the bottom valve was closed to seal the *EtO*-Freon gas in the casting chamber. The mixer was then contaminated by addition of the nonsterile propellant ingredients. At the completion of the fuel mix the chamber was again opened to add the mixture of toluene di-isocyanate liquid *EtO*. The propellant was mixed and sterilized for 45 min before the sterile propellant was cast into the motor chamber under vacuum. A vacuum was held on the motor for 30 min to boil off the *EtO* and purge the propellant of entrained gases.

The outside of the motor and exposed surface of the propellant became contaminated when the motor was moved from the casting chamber to the cure oven. These surfaces would need to be resterilized by *EtO*-Freon gas for assembly into the final sterile unit. The sterile motor elements are shown in Fig. 4.

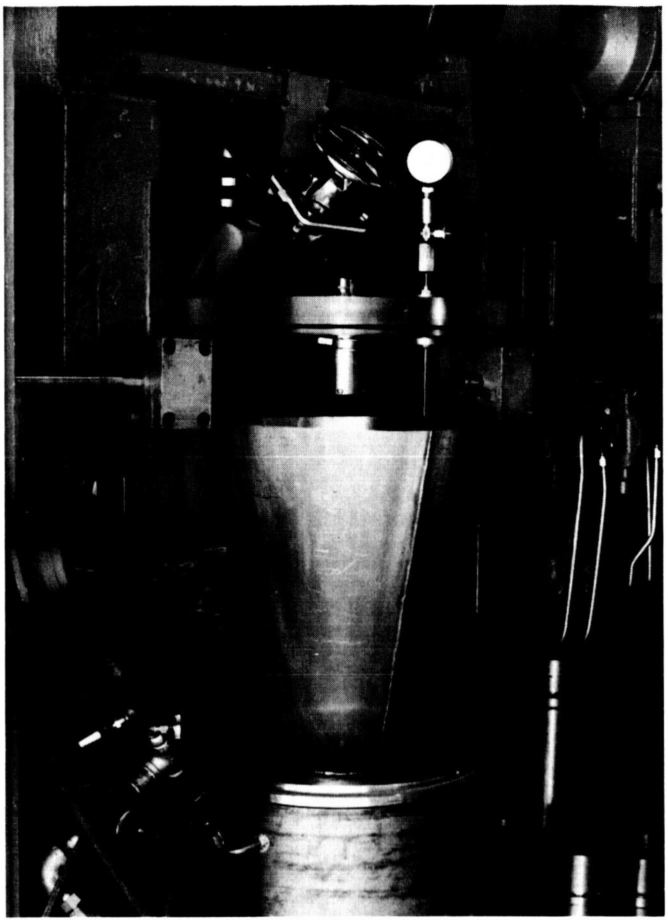


Fig. 3. Casting chamber and motor hardware with a casting funnel

Fig. 4. Motor sterile elements

One of the *SYNCOM*-type motors was fired approximately one month after being cast. The second motor was reinspected and X-rayed and fired after 10 months of storage at ambient conditions. Data from these two motors confirm that the chemical sterilization treatment had not adversely affected the motors' physical or ballistic properties.

If one has problems in propellant grains or ingredients with mold, jungle rot or other bacterial contaminants, this sterilization method could be a consideration for solving such problems and is ready, of course, when chemical sterilization is again used for spacecraft.

III. HEAT-STERILIZABLE PROPELLANTS

Since JPL's adoption of the dry heat sterilization approach to producing a sterile landing capsule, the Propulsion Division has taken three approaches to the problem. The prime approach is to find an off-the-shelf propellant that would satisfy the immediate needs of planetary landing programs. The second approach is to develop a "backup" propellant from known heat-resistant ingredients. The third approach is to develop a higher-energy heat-sterilizable system to upgrade the propulsion system for future requirements.

The heat-sterilization requirements, as given by NASA in Ref. 1, state that each component must reliably operate after being subjected to sterilization temperatures of 145°C for a period of 36 hr. Three cycles at this temperature are required to accommodate component changes and subsequent sterilization that may be required at the launch site.

Present Mars landing-mission propulsion studies indicate the possible use of two solid-propellant systems.

A small capsule deflection motor will be used to move the landing capsule from the initial fly-by trajectory of the bus to an impact trajectory. The second motor is a retro motor for avoiding communication blackout due to ionization of the heat shield during atmospheric entry.

This size of the small motor is dependent upon (1) motor performance, (2) initial trajectory and time of capsule separation from the carrying vehicle, (3) weight of the capsule, and (4) attitude control for the capsule and/or pointing error. Initial studies indicate the motor will contain between 1 and 5 lb of propellant to achieve the small ΔV required. Because of the relative size of this motor and the capsule, the variation in specific impulse or mass ratio will have only a secondary influence on the over-all weight of the capsule and is therefore not of prime concern.

The weight of the solid-propellant motor, needed as a retro to avoid the communication blackout problem, will be in the range of one to three times the weight of the capsule being landed. Thus, the performance of the propellant and mass ratio of the motor will have a great influence upon the weight of the capsule and therefore is of prime importance. Optimizing the retro's mass ratio and specific impulse and meeting sterilization criteria will require engineering design concepts yet to be explored.

A. Motor Design

The motor design is one that must be specialized to meet the heat-sterilization requirements. Prime concerns are those required for the heat-sterilization aspects, such as thermal expansion and interfaces, and those required for space-storage survival and reliability.

The thermal expansion becomes of prime concern during heat sterilization in the area of motor-to-capsule attachment, nozzle-to-motor attachment, and in the propellant-to-case interface. This latter aspect may very well dictate a cartridge-loaded motor, as indicated by the following calculation of the thermal differential expansion for case and nozzle:

$$\beta = \frac{L}{V}\frac{dV}{dT}$$

$$\delta\beta\, dT = \delta \frac{dV}{V}$$

$$\beta T\Big]_{T_1}^{T_2} = \ln V\Big]_{V_1}^{V_2}$$

where

β = volumetric coefficient of thermal expansion, in.^{3}/in.^{3}/°F

L = length, in.

T = temperature, °F

V = volume, in.^{3}

Furthermore,

$$\ln V_2 - \ln V_1 = \beta(T_2 - T_1)$$

$$\frac{V_2}{V_1} = \epsilon^{\beta(T_2 - T_1)}$$

where

1 indicates initial conditions

2 indicates final conditions

For homogeneous material of a typical propellant and steel case:

β_c ranges from 1.8×10^{-5} to 2.7×10^{-5}, in.^{3}/in.^{3}/°F (Ref. 3)

β_p ranges from 1.3×10^{-4} to 2.0×10^{-4}, in.^{3}/in.^{3}/°F (Ref. 4)

where

p indicates propellant

c indicates case

Assuming that the propellant is cured at 140°F and the stresses at that condition are zero, then $T_1 = 140$°F. Also, we can assume that the volumetric loading for a case-bonded propellant is 0.90. The sterilization temperature $T_2 = 293$°F. Therefore,

$$\frac{V_{c_2}}{V_{c_1}} = \epsilon^{(1.8\times 10^{-5})(293-140)}$$

$$\frac{V_{c_2}}{V_{c_1}} = 1.00275$$

$$\frac{V_{p_2}}{V_{p_1}} = \epsilon^{(1.3\times 10^{-4})(293-140)}$$

$$\frac{V_{p_2}}{V_{p_1}} = 1.0207$$

Letting V_{c_1} = unity, then $V_{c_2} = 1.00275$ which is the final volume of the case. The volume of the propellant initially $= V_{p_1} = 0.90\ V_{c_1}$. Substituting for V_{p_1},

$$\frac{V_{p_2}}{0.90\ V_{c_1}} = 1.0207, \quad \text{with } V_{c_1} = 1$$

$$V_{p_2} = 0.9186$$

The final volumetric loading is

$$\frac{V_{p_2}}{V_{c_2}} = \frac{0.9186}{1.00275} = 0.9161$$

The results are:

1. Minimum case and propellant expansion = 0.9161 or 1.79% change.
2. Maximum case and propellant expansion = 0.9236 or 2.62% change.
3. Maximum case and minimum propellant expansion = 0.9148 or 1.64% change.
4. Minimum case and maximum propellant expansion = 0.9249 or 2.77% change.

Making this calculation for the maximum and minimum values of β for the case and propellant shows a range of volumetric changes from 1.64% for the maximum case expansion and minimum propellant expansion to 2.77% for the minimum case expansion and maximum propellant expansion. The results of these changes, which increase rapidly with increased volumetric loading, are high compressive stresses in the propellant, which increase through the web from the wall of the case to propellant surface. Such stresses can cause failure of the propellant by "buckling" in the hoop direction and associated cracking of the grain.

Since the motors for space application have to have a very high reliability after sterilization and space storage, the motor configuration must take into account the stresses imposed by thermal expansion. Therefore, heat-sterilized motors will not allow the use of standard case-bonding techniques with the present propellants. Cartridge loading designs may be the solution. The use of a fiberglass case gives an even worse volumetric loading condition because the coefficient of thermal expansion for the glass is even less than that for steel. The coefficient for titanium is also less.

B. *Testing Program for Seven Commercial Propellants*

In July of 1963 inquiries were directed to U.S. solid propellant manufacturers, requesting information on propellants having the following characteristics:

1. High temperature stability (at 145°C for 36 hr in a sealed container—3 such cycles from ambient).
2. Vacuum ignition capability.
3. Long-term stability after heat sterilization.
4. Solid-free exhaust products.
5. Good physical properties.
6. Reasonable specific impulse (other requirements overshadow the desire for a high specific impulse).

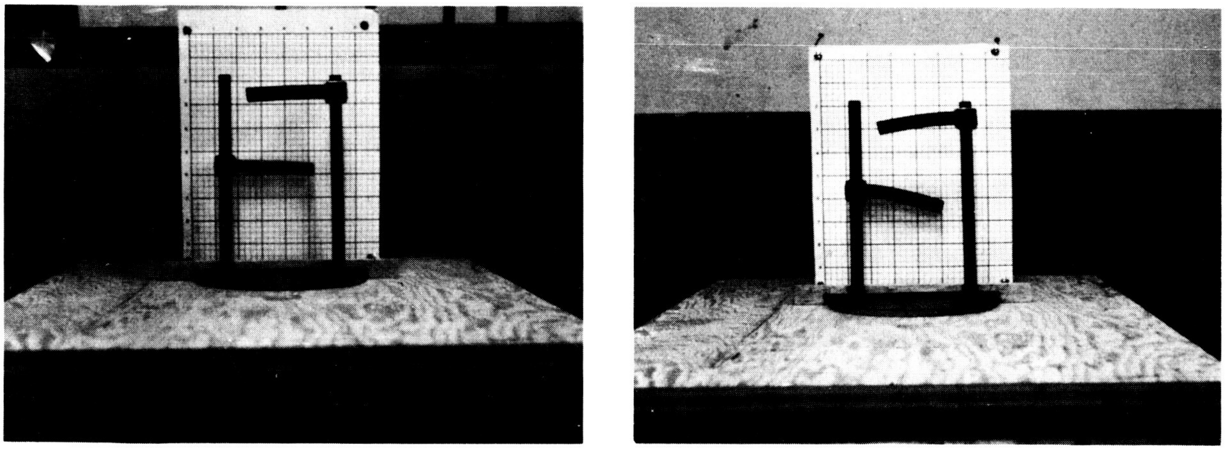
In response to this inquiry, seven companies indicated they had candidate propellants capable of meeting these requirements. These companies supplied JPL with samples of propellants for sterilization evaluation. The propellants were: (1) Aerojet-General, Sacramento, propellant AN 583 AF; (2) Atlantic Research Corporation propellant 413A; (3) Naval Propellant Plant propellant PVC-A; (4) Rocketdyne, McGregor propellant RDS-510-2A; (5) Thiokol Alpha propellant TP-H-8162; (6) Thiokol Elkton propellant TP-H-3105; and (7) United Technology Corporation propellant UTX-5113A. The propellants TP-H-3105, TP-H-8162, RDS-510-2A and UTX-5113A are based on a polybutadiene binder system; the propellants 413A and PVC-A are plasticized polyvinylchloride systems and the propellant AN 583 AF is a polyester styrene binder system.

The planned test program consisted of initial screening of the propellants by slump testing of cantilevered specimens. The propellants surviving this test were then subjected to a more comprehensive physical evaluation test program consisting of heating and testing of tensile specimens, torsion specimens, and 3-in. × 3-in. × 6-in. block specimens used for tensile tests. All the data are referenced to similar data taken from nonheated specimens.

The equipment items used in these tests were disposable ovens, an Instron tester and a Gehman torsion tester. Sterilization heating of specimens was done in both air and nitrogen atmospheres. Heating under an atmosphere of nitrogen was accomplished by maintaining a flow of nitrogen gas through the oven. The nitrogen exhaust from the oven was bubbled through water to assure a slight positive pressure inside the oven. The disposable ovens were constructed using a cylindrical commercial metal can which was wrapped with electrical heating tape and then insulated. The temperature of the oven was controlled by precise temperature controllers operating on an iron-constantan thermocouple signal.

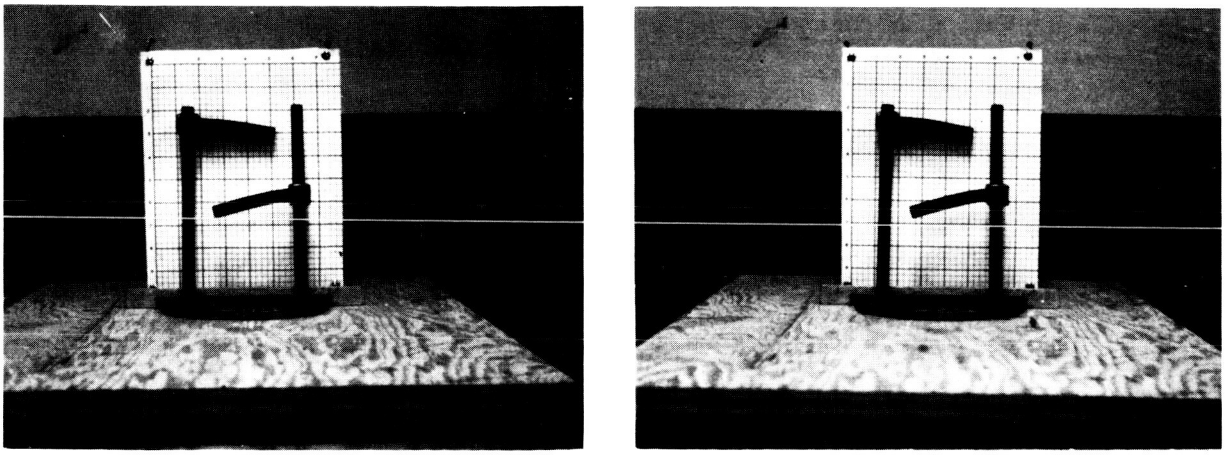
The initial screening evaluation tests consisted of heating cantilevered ½-in. × ½-in. × 4-in. specimens suspended with a 3-in. overhang. The specimens were heated to 145°C, maintained at that temperature for 36 hr, and then returned to ambient. Those specimens surviving the first heating cycle were then subjected to a second cycle at this temperature and then a third cycle. The tests were performed in atmospheres of both nitrogen and air.

Photographs showing typical specimen conditions before and after heating are shown in Fig. 5. Four propellants from these initial tests qualified for further evaluation in this program. These were the polyester styrene based propellant (AN 583 AF) and three polybutadiene based propellants (RDS-510-2A, TP-H-3105 and TP-H-8162). The AN 583 AF propellant showed no change due to heating during any of the temperature cycles except for a slight discoloration. The RDS-510-2A, TP-H-3105, and TP-H-8162 softened on the first heating



PROPELLANT RDS-510-2A
INITIAL CONDITION

PROPELLANT RDS-510-2A
AFTER 36 hr AT 300°F



PROPELLANT RDS-510-2A
AFTER 72 hr AT 300°F

PROPELLANT RDS-510-2A
AFTER 108 hr AT 300°F

Fig. 5. Photographs of propellant slump test specimens showing conditions after various sterilization heat cycles in nitrogen atmosphere

and showed a drop of approximately 1 in. at the free end of the bar. Subsequent cycles showed no further change except for further darkening of the samples. Identical tests, except for a nitrogen atmosphere, were made on identical samples. The results of the nitrogen atmosphere tests could not be distinguished from those of the air atmosphere tests.

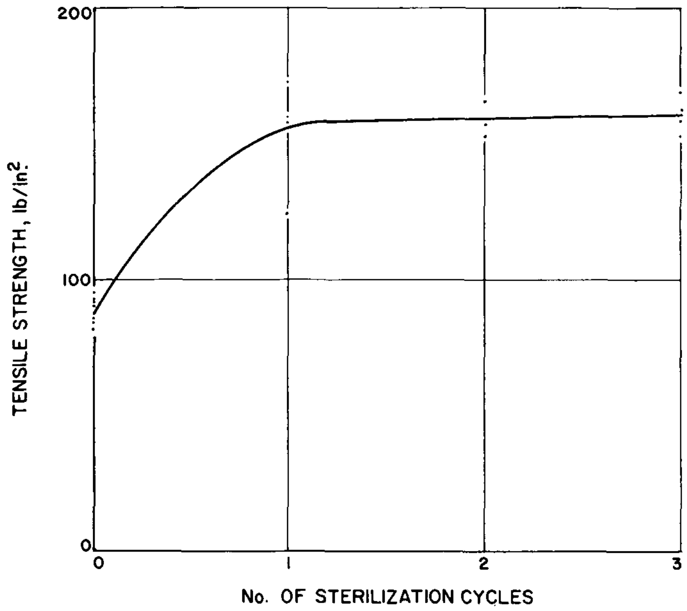


Fig. 6. Tensile strength of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr

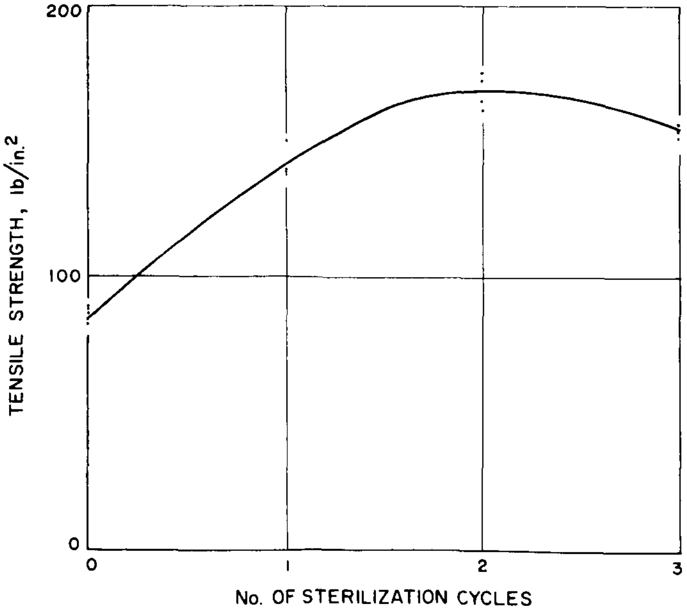


Fig. 7. Tensile strength of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr, heated in N_2

A carboxyl terminated polybutadiene propellant (UTX-5113A) and both plasticized polyvinyl chloride propellants (413A and PVC-A) did not survive the initial heating cycle of the slump tests in air or nitrogen gas. In air the polybutadiene softened to the point that it dropped off the holder into the bottom of the oven; in nitrogen it "wilted" and hung straight down. The polyvinylchloride propellant broke off at the point of maximum stress. The break indicated the propellant started to slump before a "brittle" fracture occurred.

The next series of tests were for determining more precisely the effect of the sterilization heat cycles on the physical properties of the four propellants which survived the slump test. In these tests, precut JANAF tensile specimens and 3-in. × 3-in. × 6-in. blocks of propellants were heat cycled and tested.

The tensile samples were heated both in atmosphere of air and nitrogen. Typical results of the tests of the propellants are shown in Fig. 6 through 9.

Although the amount of data taken is minimal, some interesting trends have been noted. In the TP-H-3105 propellant the ultimate tensile strength increases to a maximum with the first heat cycle in air and shows no further change in subsequent heating. However, a slightly

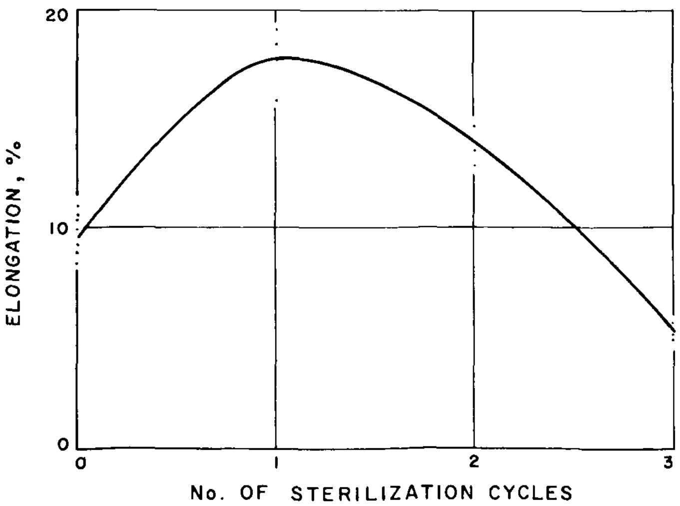


Fig. 8. Elongation percent of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr

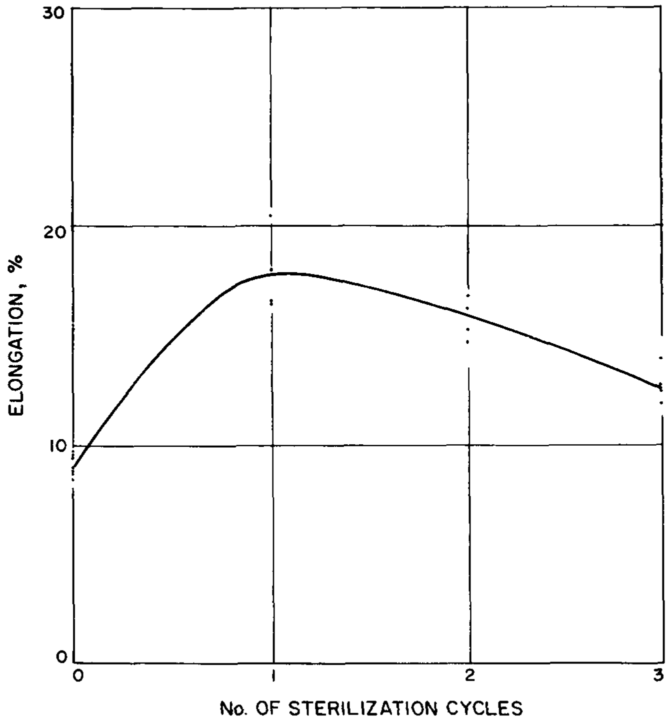


Fig. 9. Elongation percent of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr, heated in N_2

higher maximum is reached on the second heat cycle in the N_2 atmosphere and then the tensile strength drops back in agreement with the air-heated specimens. The percent elongation at ultimate tensile strength is approximately the same in both cases.

In the case of the RDS-510-2A propellant, there appears to be no differences in the ultimate tensile strength if the propellant is heated in air or N_2 and little change occurs. Even though there is little change in the ultimate tensile strength, a great change occurs in the elongation in the two tests. The elongation drops from the 20 to 30% bracket to around 7.5% on the first heating cycle and continues a downward trend to under 5% on the third cycle. Little deviation from these trends occurs with the samples heated in N_2.

The ultimate tensile strength data for the TP-H-8162 propellant heated in atmospheres of air and N_2 showed a slight trend down on the first cycle, an increase to a maximum tensile strength on the second cycle, and a drop to a minimum just under the tensile strength for the non-heated specimens on the third cycle. However, the propellant elongation acted similarly to the RDS-510-2A propellant and dropped drastically from around 20% elongation to 5% on the first sterilization cycles in both atmospheres and continued down with each successive heating.

The AN583AF propellant indicated even more unexpected trends. The ultimate tensile strength and the elongation both increased. The elongation at ultimate tensile strength was improved very slightly by sterilization heating in both atmospheres. The ultimate tensile strength of the propellant when heated in air increased from 250 to 430 psi, to 540 and to 600 psi on the successive heatings in air. The nitrogen atmosphere caused the ultimate tensile strength to level off at just about 500 psi on the second two heating cycles.

Since the tensile bars just discussed were precut for heating, a large surface area was exposed to the surrounding environment. Therefore, to get a better picture of heating effect on the internal propellant, blocks of propellant, 3 in. × 3 in. × 6 in., were subjected to sterilization heating in an atmosphere, then cut into JANAF tensile specimens and tested. Typical results of these tests are shown in Fig. 10 and 11. The figure at the top of the chart indicates the position each tensile specimen had occupied in the 3-in. × 3-in. × 6-in. block. The surface crust was left on specimens numbered 1, 4, 5, and 8. Specimens numbered 2, 3, 6 and 7 were cut from internal sections of the block with the test section being no closer than ¼ in. from the outside edge of the block. Specimens 9 and 10 were also supposed to be internal specimens. However in some cases, not enough material remained to allow for the heated crust to be taken-off of the specimen. Therefore, data from these specimens are shown on the plots but are not used in the analysis. It should be noted that the specimens 1, 4, 5, and 8 have only one side of crust and therefore the data from these specimens will not necessarily agree with the data from specimens heated in the form of precut JANAF specimens. However, trends from the specimens containing crust should be similar. Hereafter in this Report, precut heated JANAF tensile bars will be referred to as the "heated JANAF specimens," and the term "block specimens" refers to those tensile specimens cut from the 3-in. × 3-in. × 6-in. block after heating.

The ultimate tensile strength data from the TP-H-3105 propellant block specimens show the same trends as the heated JANAF specimens, but lower values. Surprisingly, the specimens having a crust show a slightly lower ultimate tensile strength than do the center cut specimens. The elongation shown by the block specimens

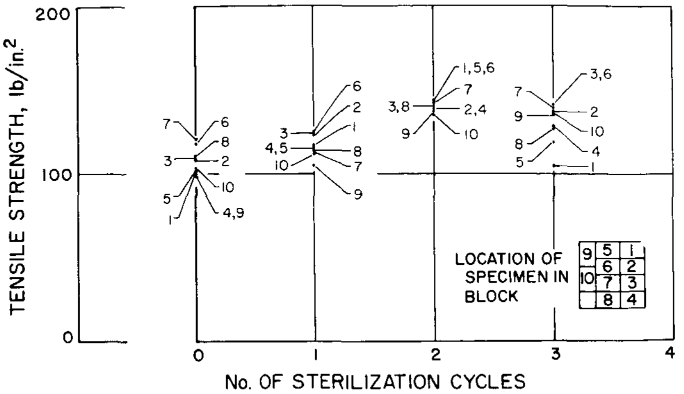


Fig. 10. Tensile strength of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr—block specimens

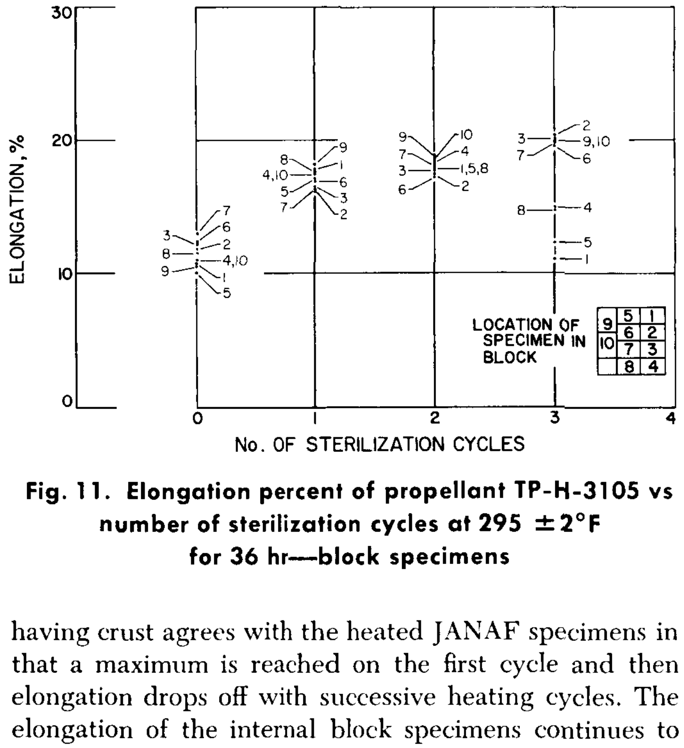


Fig. 11. Elongation percent of propellant TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr—block specimens

having crust agrees with the heated JANAF specimens in that a maximum is reached on the first cycle and then elongation drops off with successive heating cycles. The elongation of the internal block specimens continues to increase.

The ultimate tensile strength from the block specimens of RDS-510-2A propellant does not agree with that from the heated JANAF specimens on the first sterilization heat cycle, but tests of specimens from the last two heat cycles do show agreement. No explanation is found for this anomaly. The internal block specimens show a trend to decrease in ultimate tensile strength on the first heat cycle and an increase on subsequent cycles, while ultimate tensile strength of the crust samples decreases with each heat cycle. The downward trend in elongation of the external block specimens agrees with the heated JANAF specimens, but the initial block specimens show an increase in elongation on the first heat cycle and then drop to just below the initial elongation condition on cycles 2 and 3.

For the AN583AF propellant, the trends indicated by the heated JANAF specimens hold true in the outside block specimens as well. The ultimate tensile strength at the internal part of the block shows a slight decrease on the first two cycles but drops from about 290 to 230 psi on the third cycle. Again the elongation shows a very slight tendency to increase, which is a very important factor for this study. The propellant strength and elongation are sufficient to accommodate the strains imposed by the thermal expansion.

The block of TP-H-8162 propellant cracked internally when heated. Figure 12 shows a cross-section of this block. No external evidence gave indication that internal cracking was occurring although it was measured, weighed and examined after each heat cycle. However, when it was cut for fabrication of JANAF bars, it was found to be permeated by small cracks. The reason for this seems to be associated with the loss in elongation characteristics.

In the initial sterilization treatments of the 3-in. × 3-in. × 6-in. block specimens, the length of the heat cycle was measured from the time the outside surface of the specimen reached the 293°F sterilization temperature. This did not take into account the time for the internal part of the specimen to reach this maximum temperature. It was assumed that the estimated 5% additional time required to raise the internal propellant to 293°F would have little effect on the propellant physical properties. However, in the second set of tests of block specimens, a ⅛-in. hole was drilled 2 in. deep in the propellant and a thermocouple inserted. The additional time required for heating the entire grain was between 1½ and 2½ hr, depending upon the particular propellant.

The three specimens (AN 583 AF, TP-H-3105, and RDS-510-2A), that were subjected to this longer time at sterilization temperature, failed to withstand the three sterilization cycles.

Weight data from this second series of tests of the TP-H-3105 propellant showed no change from those from the first series. Weight changes were not measurable, and dimensional changes were negligible (less than 1%). The

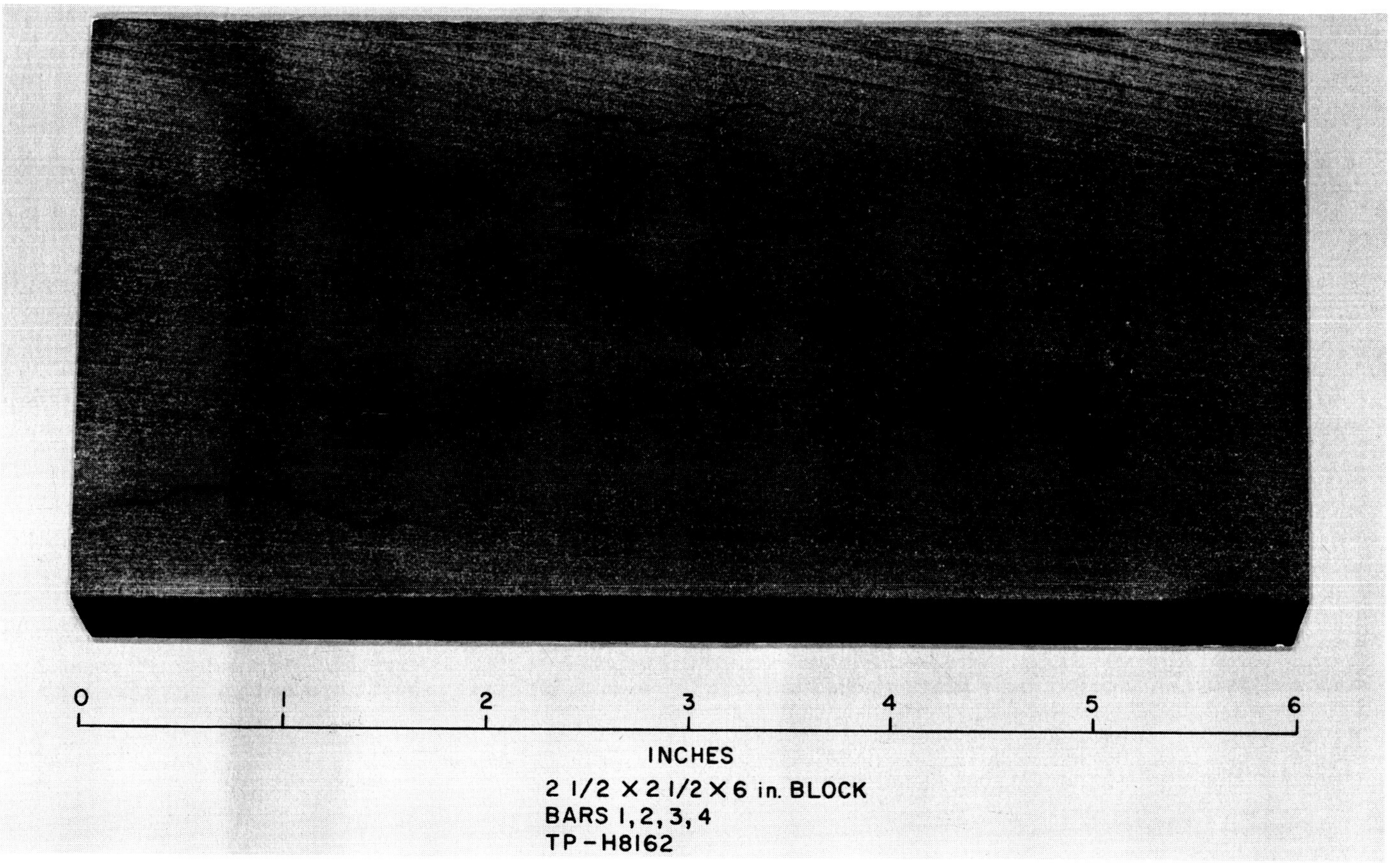


Fig. 12. Three 36-hr sterilization cycles at 295 ±2°F

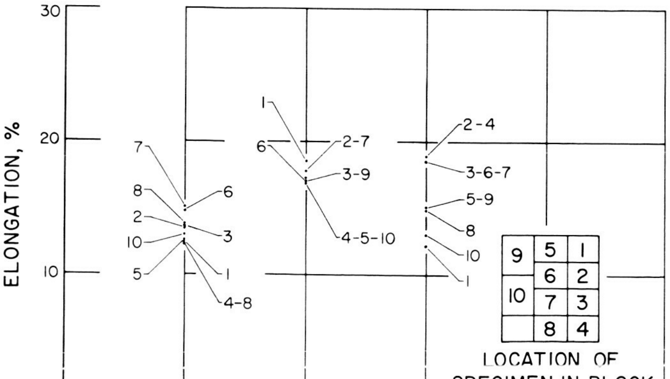


Fig. 13. Elongation percent of Thiokol Elkton TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr, 2nd check

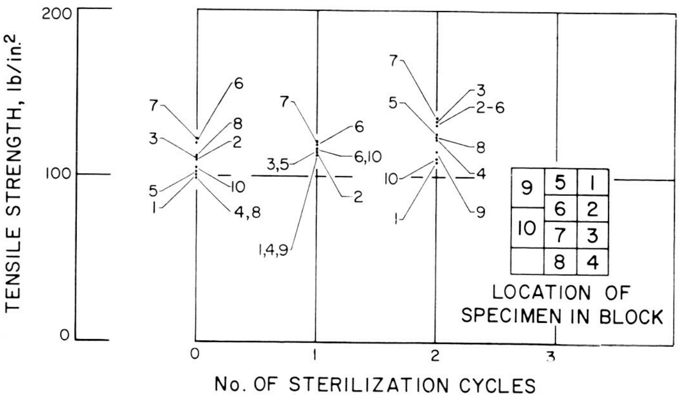


Fig. 14. Tensile strength of Thiokol Elkton TP-H-3105 vs number of sterilization cycles at 295 ±2°F for 36 hr, 2nd check

tensile data for these block specimens show agreement with data from the first block specimens except that elongation of the internal block specimens made a marked drop on the second cycle instead of the third, as shown by the first block specimens. Comparison of Fig. 10 and 13 and Fig. 11 and 14 will show these differences. On the third cycle, the specimen split longitudinally; the fracture appeared to be caused by a differential thermal expansion of the internal and external parts of the grain and a reduced elongation in the outer crust.

The RDS-510-2A propellant showed no changes on the first sterilization cycle, but an 8.4% swelling of the propellant started with the second cycle. However, the grain appeared to retain its integrity until the third cycle when the formation of many small gas bubbles in the center of the grain caused it to change its shape. Figures 15 and 16 show (1) a cross-sectional view of the propellant block and (2) a magnification of a sector of the block by a factor of 34, respectively. The tensile data from the blocks subjected to 1 and 2 heat cycles show similar trends for the external block specimens as those in the first tests; however, comparison of the same data for internal specimens shows a reversal; i.e., the first test at the shorter heat cycle shows a decrease which was initially a subsequent increase in tensile strength, while the second test at the longer heat cycles shows initially an increase and subsequent decrease in tensile strength. This trend is probably a continued curve for this propellant, but shows an undesirable sensitivity to the heat duration. The elongation trends are similar for both tests, with the outside surface elongation dropping drastically on the first heating. The physical data on this propellant indicate it as not being suitable as a candidate for heat-sterilizable motors.

The physical data from the second series of heat sterilization tests of block specimens of AN 583 AF propellant show the same results as those in the initial tests with one exception: the tensile strength of the internal specimens dropped 25% on the first sterilization cycle; after the second cycle, X-ray revealed internal cracking had occurred. The additional heating had evidently reduced the internal strength of the grain until it could no longer withstand the internal stresses. Therefore, this propellant in this configuration could not survive but one cycle of sterilization heating.

It should be noted that the mode of failure was different for each of the propellants; i.e., one cracked externally, one cracked internally, and one formed bubbles.

Two differences were made in the second series of tests from that of earlier tests: (1) the ⅙-in.-D hole, 2 to 3 in. long, in the charge, and (2) the approximate 2-hr

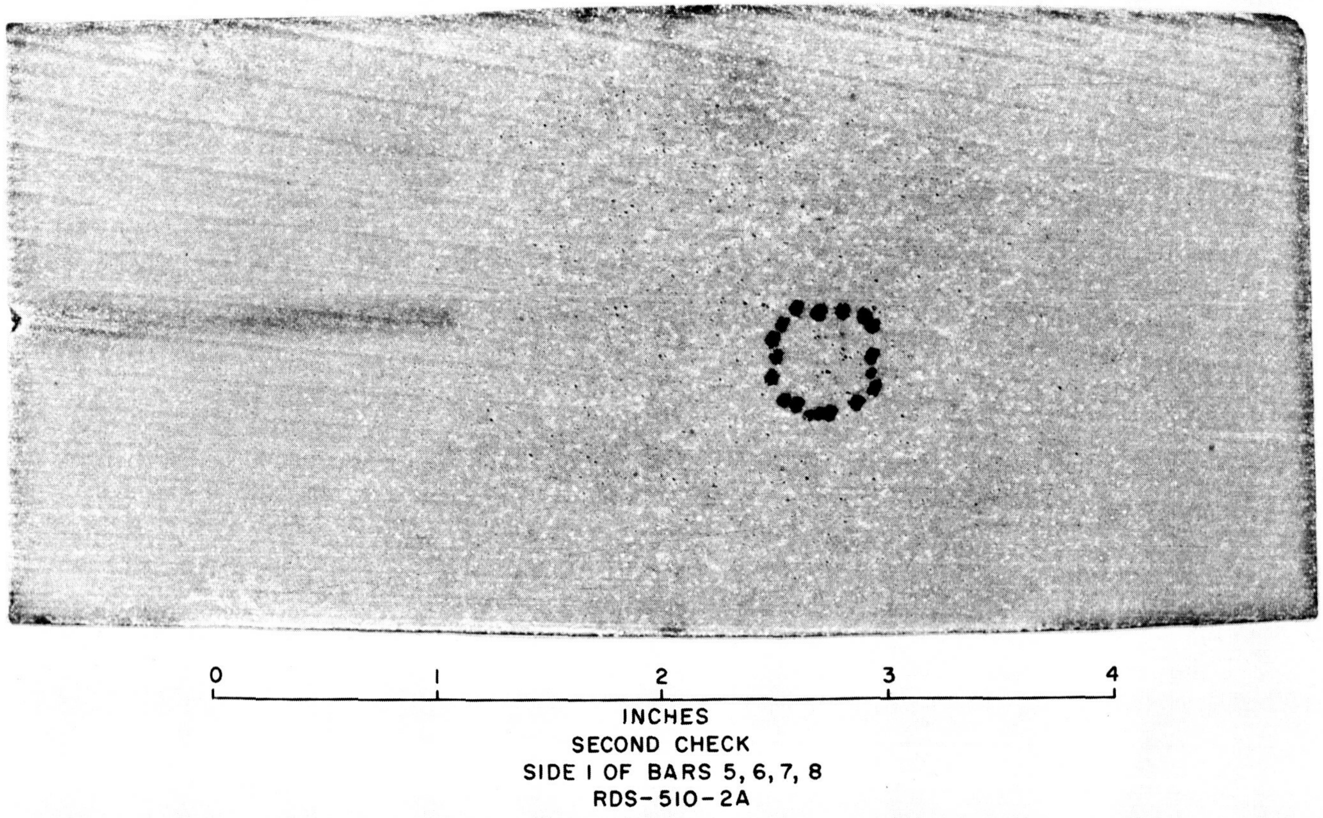


Fig. 15. Three 36-hr heat cycles at 295 ±2°F in 2½- × 2½- × 6-in. block form

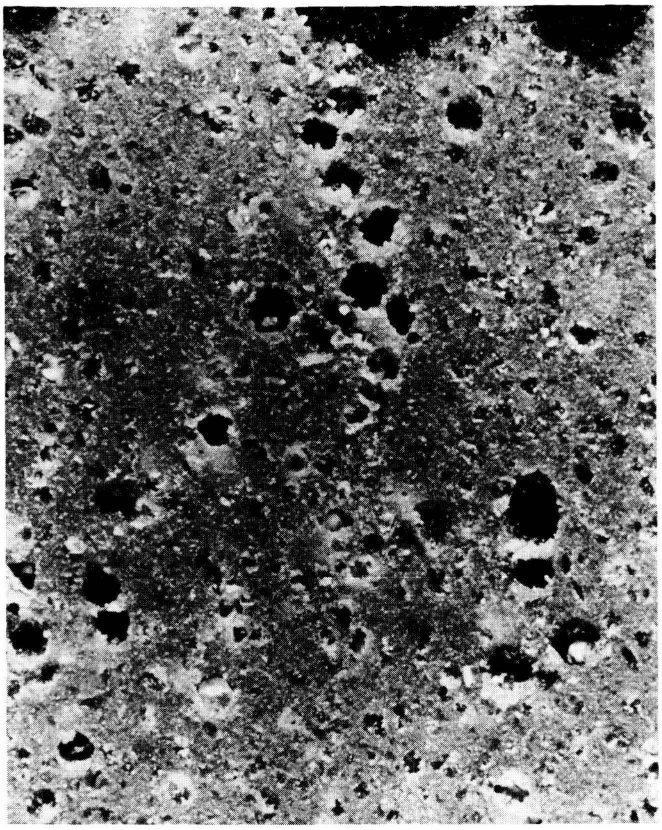


Fig. 16. A sector of the block magnified 34 times

longer time for keeping the charge at high temperature on each cycle. Very close examination was made, trying to relate the propellant failures to the drilled hole. However, there was no evidence to support this thesis, and it was concluded that the hole did not contribute to the failure. Therefore, the only conclusion that can be drawn from this small number of tests is that the test limits are right at the survival limits for these propellants.

Additional work is needed to determine the causes of the failures and the relationship of physical and chemical parameters to that of the failures.

C. *Test Summary*

The trends indicated in this portion of the Report are gleaned from data on propellants furnished by propellant manufacturers of candidate propellants for heat sterilization. The propellants were heat sterilized in small and large pieces and in air and N_2, and slump tests, tensile tests, and torsion tests were run.

The polyvinyl chloride propellants acted alike and broke in the slump test when heat sterilized.

Small changes in binder formulation have a profound effect on the way in which the polybutadiene binder responds to sterilization heat cycling. Of the two carboxyl terminated polybutadiene propellants, one "melted" under the sterilization treatment while the other showed little change in tensile strength and a drastic decrease in elongation, finally forming bubbles internally.

Of the two polybutadiene acrylic acid binders, one initially increased in tensile strength and elongation, followed by a decrease in elongation in the second and third cycles, while the elongation of the second one was drastically reduced on the first cycle while showing little change in tensile strength. This second propellant was found to crack internally when heated in a large block. These data emphasize the need for basic studies in the effects of formulation on propellant physical characteristics in regard to this problem and the need for basic studies in understanding the internal stresses of a grain under various temperature conditions.

The polyester styrene propellant showed a large increase in tensile strength from heat sterilization with a slight tendency to increase in percent elongation. However, with a slight increase in heating time, the tensile strength of the internal part of the grain was drastically reduced and failure occurred on the second heating cycle.

D. *Results*

None of the propellants examined have shown an unqualified capability of meeting the heat-sterilization criteria for a Mars landing mission. However, it has been considered that the shape of the block specimens (3 in. × 3 in. × 6 in.) used to make the majority of the tests may have induced extreme stresses in the propellant during sterilization, and that another shape of specimen might not do this. One test of another propellant (a JPL silicone) has shown evidence of this when it survived heat sterilization in the form of a perforated cylinder, but cracked open on the third heat cycle when heated in the 3-in. × 3-in. × 6-in. block. On this evidence, further studies and tests of grain and motor design are being formulated.

The propellants will be cartridge-loaded in the initial designs to avoid the problem of differential expansion of case and liner and/or case and propellant. The required design will allow for expansion of the propellant without interference with the case.

IV. SILICONE PROPELLANT DEVELOPMENT

As a backup program for a heat sterilizable motor, JPL undertook a feasibility program for development of a propellant composed of a siloxane binder and ammonium perchlorate. The siloxane binder was selected because of its known high temperature characteristics. In a period from September 1963 to August 1964, carried as a side project, this program progressed from hand-mixed impact specimens to the firing of three heat-sterilized 5-in. × 6-in. motors and three similar motors that had not been heat sterilized.

A. Propellant Development

In initial binder evaluation tests, it was determined that a product of Dow Corning, Sylgard 182 with Sylgard Catalyst 182, had sufficient properties for use as a propellant binder. This material was subsequently used as a fuel with ammonium perchlorate as oxidizer.

Batches of this propellant were made in a one-quart Sigma mixer from which impact samples, tensile bars, and burning-rate strands were made. Subsequent tests indicated the propellant had acceptable characteristics. The impact sensitivity was found in a Bruceton test to be 24 kg-in. The burning rate of this siloxane propellant was found to be 0.60 in./sec at 500 psi, and 0.90 in./sec at 1000 psi. The burning-rate exponent of 0.57 appears to be a little higher than many current composites, but it was decided for this program that the propellant would be usable. A study of the exponent changes as a function of heat sterilization cycles indicated no change occurred. Typical tensile strength data are shown plotted in Fig. 17, and the elongation in Fig. 18. As those data show, the ultimate tensile strength increases until the third heat cycle, when there is a reduction in strength. Note that the bars which were heated in the mold showed a loss in tensile strength greater than those heated after being removed. The reason for this is believed to be the differential thermal expansion of the mold and the propellant, causing local high strain in the propellant near the mold wall. This combined with the reduced elongation from the heating would weaken the propellant specimen. The elongation begins at 65% and is reduced to about 40% on the first two heating cycles. On the third cycle it is reduced to about 5%. These physical characteristics were sufficient for the unrestrained cartridge-type change.

Ten motors containing the siloxane/AP propellant have been made. Because of the limited mechanical properties

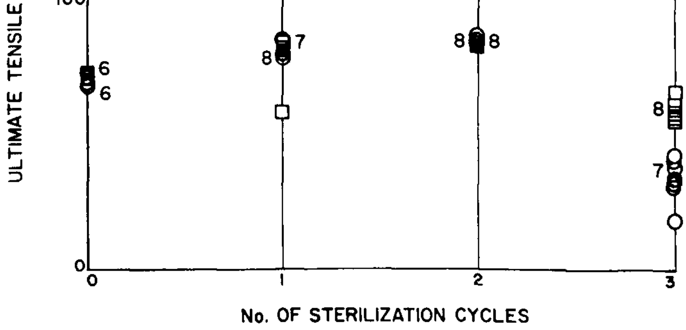


Fig. 17. Heat-sterilized siloxane-propellant ultimate tensile strength vs sterilization heating cycles at 145°C for 36 hr/cycle

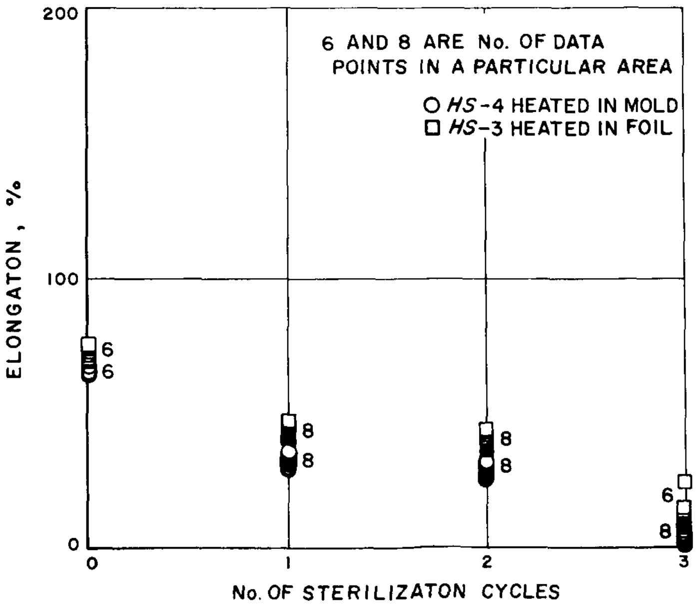


Fig. 18. Heat-sterilized siloxane-propellant percent elongation at ultimate tensile strength vs sterilization heating cycles at 145°C for 36 hr/cycle

of this propellant, the severe thermal cycling required by sterilization, and the inability of the propellant to bond to steel or to the several liners tried, the cartridge-loading technique was employed. Propellant was cast into molds with teflon-coated walls and cylindrical-core mandrel. Cured charges with dimensions of a 4½-in. D by a 5-in. length and a 2-in.-core D were potted in 5-in. × 6-in. test chambers with Dow Corning RTV-11 room-temperature vulcanizing silicone rubber.

Propellant charges potted in chambers before heat cycling suffered severe stresses due to differential thermal expansion; whereas, grains heat-cycled before potting were unaffected. The first set of three charges was heat-cycled at 145°C (293°F) after potting. At this temperature, considerable extrusion of potting liner was observed. One charge survived one 36-hr cycle without damage. A second charge showed no discernible defect until after the third cycle, at which time pull-aways appeared between propellant and liner as well as between liner and case. Examination of propellant after removal from the case revealed small transverse cracks in the outer cylindrical propellant surface. The third charge exhibited a liner-case pull-away after two cycles; however, the propellant was found to be sound. The two good grains, one and three, were cleaned up, repotted and successfully static tested.

The second set of three charges was heat sterilized before it was potted in the test chambers. One charge was subjected to 36 hr of 145°C; the second had two cycles of the sterilization temperature and the third had three. X-ray and manual examination revealed all charges to be sound, so they were potted in the test chamber with RTV-11 and all successfully static tested.

The pressure vs burning rate and K_n data, respectively, from four of the static tests are shown in Fig. 19 and 20. Examination revealed that the performance was higher than had been estimated.

B. Results

To compare the performance of this siloxane propellant with the other nonaluminized propellant systems, an approximation of specific impulses at 1000 psia expanded at 14.7 psia was made. These data indicate the performance of this propellant in an acceptable range for a nonaluminized system.

Concern was expressed before tests that the "burned" solids might remain in the motor or plug the nozzle. It was surprising to find that the SiO_2 in the exhaust assumed the form of "snow flakes." Since the charges had a cylindrical perforation and were inhibited on both ends, the pressures progressed from about 100 psi to about 900 psi in the 2.6-sec burning time.

This propellant has been found to be heat sterilizable and was developed as a backup propellant. However, complete characterization has not been done. Work on this propellant has been discontinued until such time as a need arises for its further development.

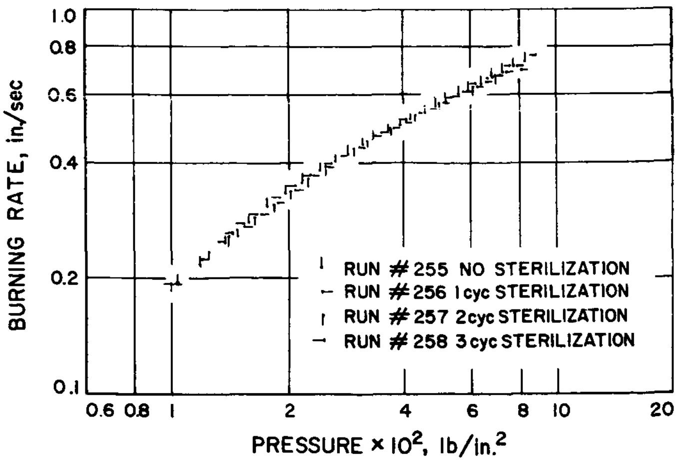


Fig. 19. Burning-rate data from batch check (inhibited burning)

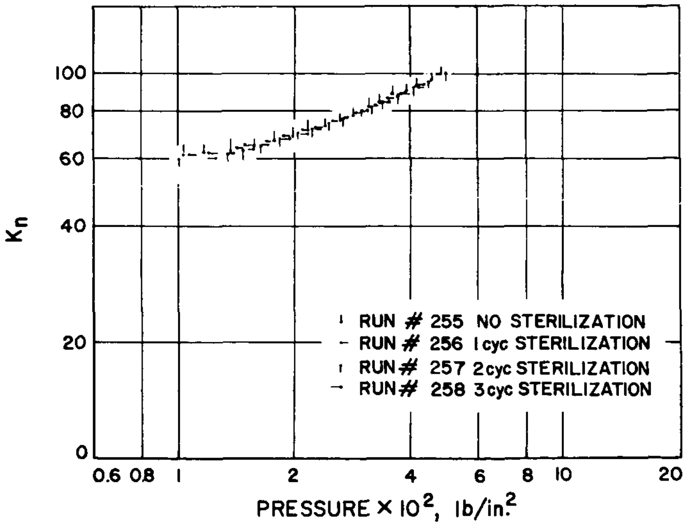


Fig. 20. K_n data from batch check (inhibited burning)

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