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AFFDL-TR-65-29
Part III

FA Report R-1773
Part III

PAD PROPELLANTS FOR USE AT HIGH TEMPERATURES

III. Evaluation of Extrudable, Heat-resistant, Composite Propellant for -65° to 400° F Exposure

MARTIN VISNOV
(Frankford Arsenal)

TECHNICAL REPORT AFFDL-TR-65-29, Part III

March 1966

AIR FORCE FLIGHT DYNAMICS LABORATORY
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

NOTICES

DISPOSITION INSTRUCTIONS

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Philadelphia, Pa.

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AIR FORCE FLIGHT DYNAMICS LABORATORY
Research and Technology Division
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Wright-Patterson Air Force Base, Ohio

FOREWORD

The research work described in this report was performed by Frankford Arsenal, Philadelphia, Pennsylvania, for the Air Force Flight Dynamics Laboratory (AFFDL) under Project 1362, "Crew Escape for Flight Vehicles", and Task 136205, "Propellant Actuated Devices Research." The program was funded by MIPRs Number 33(616)60-17, 33(616)61-12 and 33(657)-2-R&D-111; its period of performance was March 1961 to January 1963. Captain D. S. Barron was the AFFDL (FDFR) Project Engineer, Mr. M. Visnov was the Frankford Arsenal Project Engineer. This is Part III of three parts.

Manuscript of this report released by the author 23 December 1965 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

CHARLES V. MAYRAND
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ABSTRACT

Heat-resistant potassium perchlorate/Hycar polyacrylic binder propellants, extrudable in small web geometries, were evaluated for application to propellant actuated cartridges to withstand temperatures from -65° to 400° F. Results of measurements of autoignition temperature, amount and nature of gas evolution, and retention of grain configuration showed these propellants to have thermal stability sufficient to meet the 400° F-4 hour high temperature objective.

Extensive firings in the M73 cartridge-M3 (or M5) initiator system from -65° to 400° F demonstrated the ability of these propellants to survive and function, as designed, in a typical propellant actuated device.

TABLE OF CONTENTS

List of Tables

List of Illustrations

INTRODUCTION

This is the third report on the program for the development of propellants for propellant actuated devices (PAD) to withstand temperatures up to 400° F. Previous work[1,2*] showed that the nitrate ester propellants would not meet the temperature objective and that composite propellants, as a class, had higher thermal stability. In the second report it was demonstrated that composite propellants could be substituted for nitrate esters in meeting the ballistic requirements of a typical propellant actuated device which utilized small web, extruded propellant grains (the M73 cartridge-M3 initiator system). However, in order to do this it was necessary to hand-tailor small disc geometry grains because major composite propellant sources were oriented to large, cast-and-cure propellants for rocket motors and had not developed the technology of producing small web, extruded grains of composite propellant. The best that were obtainable in diameters of less than 0.5 inch O.D. were experimental solid rod extrusions.

As a result of these studies, it was recommended that efforts be directed toward the development of heat-resistant composite propellants capable of being processed by commercially feasible means (i.e., extrusion) into small web gun-type grains, including both monoperforated and multiperforated geometries. A contract** was negotiated with Hercules Powder Company for this purpose.

A number of composite propellant formulations emerged from this contract which were processable via commercial solvent techniques, using the same equipment that is used for the manufacture of double base propellants.[3] These were based on extrudable fuel binders of fluorocarbon, polyacrylic, or polyacrylic/triallyl cyanurate origin, and perchlorate oxidizer. On the basis of ease of processing, thermal stability at 400° F, and ballistic performance, the most successful of these were propellants based on potassium perchlorate oxidizer and Hycar 4021 polyacrylic rubber employing various curing additives (Table I).[4]

Propellants which had been processed successfully were subjected by the contractor to preliminary screening via thermal stability and closed bomb tests. Those propellants which the contractor considered to have passed his tests were then forwarded to Frankford Arsenal for further evaluation. This report describes additional thermal stability study and ballistic firings.

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*See REFERENCES.

**Contract DA 36-038-507-ORD-3572M.

TABLE 1
Heat-resistant Propellants[a]

	HES 6468.1A	HES 6484.1A	HES 6573.1A
Ingredients (% by wt)			
$KClO_4$	84.00	84.00	84.00
Hycar 4021	15.55	12.00	15.00
DMP-30	0.35	-	-
Sulfur	0.10	-	-
Luperco ATC	-	-	-
Tryallyl cyanurate	-	0.20	-
Trimene base	-	3.80	-
	-	-	1.00
Observed H_{expl} (cal/gm)	1380	1425	1400 (est)
Observed density (gm/cc)	1.82	1.94	1.90
Closed bomb data[b]			
RQ (%) (equal wt basis)	82	86	92
RF (%) (equal wt basis)	57	51	54
RQ (%) (equal vol basis)	100	108	102
RF (%) (equal vol basis)	79	78	63

[a]Data from Reference 3.

[b]Fired against HES 5808.7C as 100% RQ and 100% RF standard.

NOTE: Extrusion die size for all three propellants - 0.202 inch O.D., seven perforations (0.014 inch I.D.); 0.510 inch grain length.

EXPERIMENTAL

Development of Test Equipment

Since this program required firings at 400° F after a soak period of four hours, the problem arose as to whether ballistic test components (in addition to the propellants being developed) could withstand this temperature schedule. Tests at 400° F verified that a number of the inert components in the M3 initiator and the test system did deteriorate. In addition the 72M percussion primer in the M73 cartridge became insensitive. A small scale materials program was then undertaken in order to conduct the 400° F firings of the propellant. The high temperature-resistant test firing system which resulted entailed a considerable number of changes, but retained the specified pressure-time requirements.

A major change was necessary in the M73 cartridge. Tests showed that the standard 72M percussion primer became insensitive after 400° F exposure; therefore a program was initiated to develop heat-resistant percussion primers.[5] However, experimental primers from this development did not become available until the 400° F firings of propellant were almost concluded.

In the absence of a completely developed 400° F-resistant percussion primer for the 400° F propellant firings, an electrically fired miniature glow plug was designed to fire the M73 cartridges in place of the primer. The glow plug cavity was packed with approximately 0.1 gram of boron-potassium nitrate igniter in a 14/35 Tyler mesh granulation around the bare bridge wire and was topped with a lead seal. The glow plugs were threaded into the cartridge primer head, using a copper washer seal, annealed to a "dead-soft" condition. The glow plug connector was silver-soldered to the end of asbestos-sheated electrical lead wire. The glow plug-cartridge assembly is shown in Figure 1. Due to the heavy bridge wire, the glow plugs were fired with a 375-microfarad capacitor charged to 300 volts.

Use of electric ignition for the 400° F firings resulted in a change-over from the M3 to the M5 initiator. The ballistic requirements were the same. The latter, due to its design, allowed a direct path for the electrical lead wire to the glow plug simply by removal of the firing pin.

In oven tests, the AN6227 rubber O-rings in the initiator and cartridge had become brittle and acquired a "set," and the petrolatum-based O-ring lubricant in the initiator had melted and run. These problems were solved with material changes. Silicone O-rings and a silicone-based lubricant were substituted and found to perform satisfactorily at 400° F for five hours.

Sections of the M28741-4 high pressure aircraft hose, when subjected to 400° F, became brittle, and particles of degraded rubber spalled from the interior of the hose when it was flexed. Stainless steel tubing (14 in. long, 0.250 in. O.D., and 0.049 in. wall) was substituted for that portion of hose required to be in the oven for the hot firings. Since this substitution would result in lower peak pressures due to absorption of heat by metal tubing, a series of firings was held with production M73 cartridges to determine the length of rubber hose attached to the stainless steel tubing that would equal the ballistics obtained with the specified 15 feet of rubber hose only. From the data, a combination of 14 inches of stainless steel tubing and 10.5 feet of rubber hose was standardized for the hot firings.

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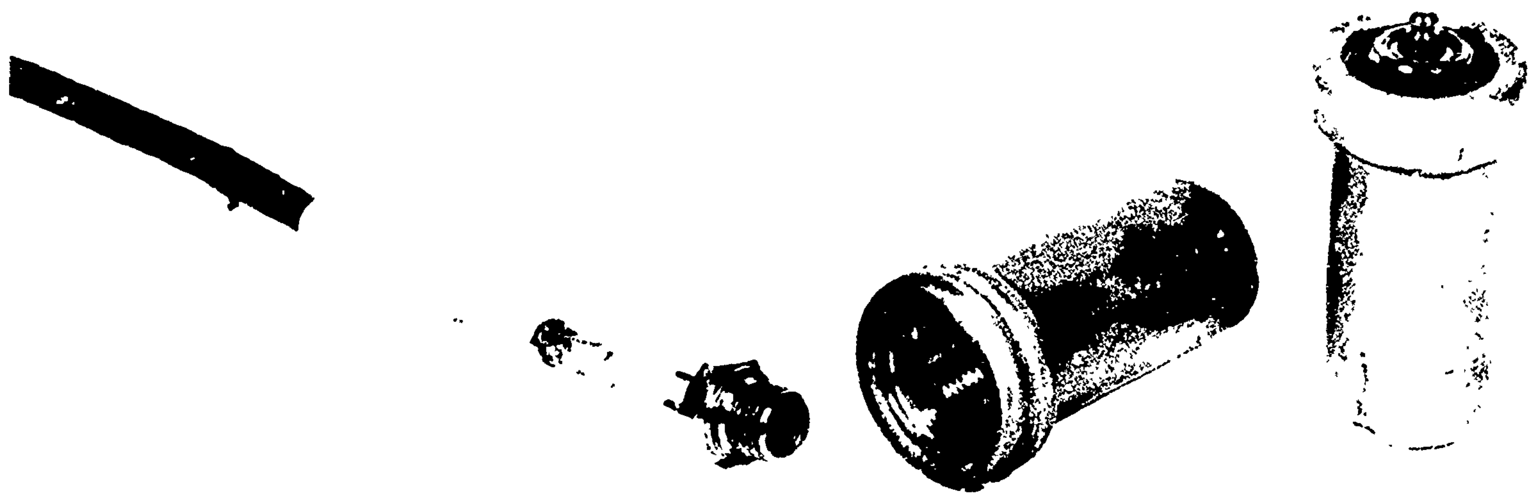

Figure 1. M73 PAD Cartridge, modified for 400° F Firings

During check-out tests of the hot firing system, it was found that repeated firings of the perchlorate-oxidized propellants through the same stainless steel tubing caused erosion of the tubing wall close to the initiator, with resultant failure of the tubing. This was attributed to the corrosive combustion products of the perchlorate propellants. Previous work by Geene[6] at the Ballistic Research Laboratories on the corrosion of metal rods by combustion products of perchlorate propellants had shown Hastelloy B and Inconel alloys to be among the most resistant.

Attempts to obtain small bore seamless tubing of Hastelloy B for this effort were abandoned when it was found that this could be fabricated only on an experimental basis, at prohibitive cost, and that there was doubt that it could be flared to 37° for AN fittings without cracking. Inconel tubing in the desired O.D. and wall thickness was available commercially. Therefore, the Inconel tubing was substituted for the stainless steel in the hot firing system. This tubing showed little erosion or pitting in the bore after 15 firings of perchlorate propellant with intermittent cleaning with detergent. The hot firing set-up with Inconel tubing is shown in Figure 2.

Low pressures in several hot firings were traced to leakage through the AN fittings which were subjected to the 400° F soak temperature. Of the several means investigated to maintain gas-tight fittings, the method adopted was the introduction of conical nickel seals which, when torqued properly, amounted to a malleable metal washer between the male and female parts (Figure 3). The conical seals were replaced after each firing at 400° F, and no evidence of gas leakage at the AN fittings employing these seals was ever detected. (As a by-product of this program, it is believed that the conical seals should be investigated further for use in all AN fittings employed in propellant actuated devices.)

Thermal Stability Study

Autoignition

Autoignition temperatures of the propellants under sealed cartridge conditions were obtained at linear heating rates from 5° to 30° F per minute. The apparatus and technique employed are described in a previous report.[1]

Examination of Propellant Decomposition Gases

The analysis of atmospheres from M73 cartridges containing nitrate ester propellants and heated at 225° F were reported earlier.[2] In the

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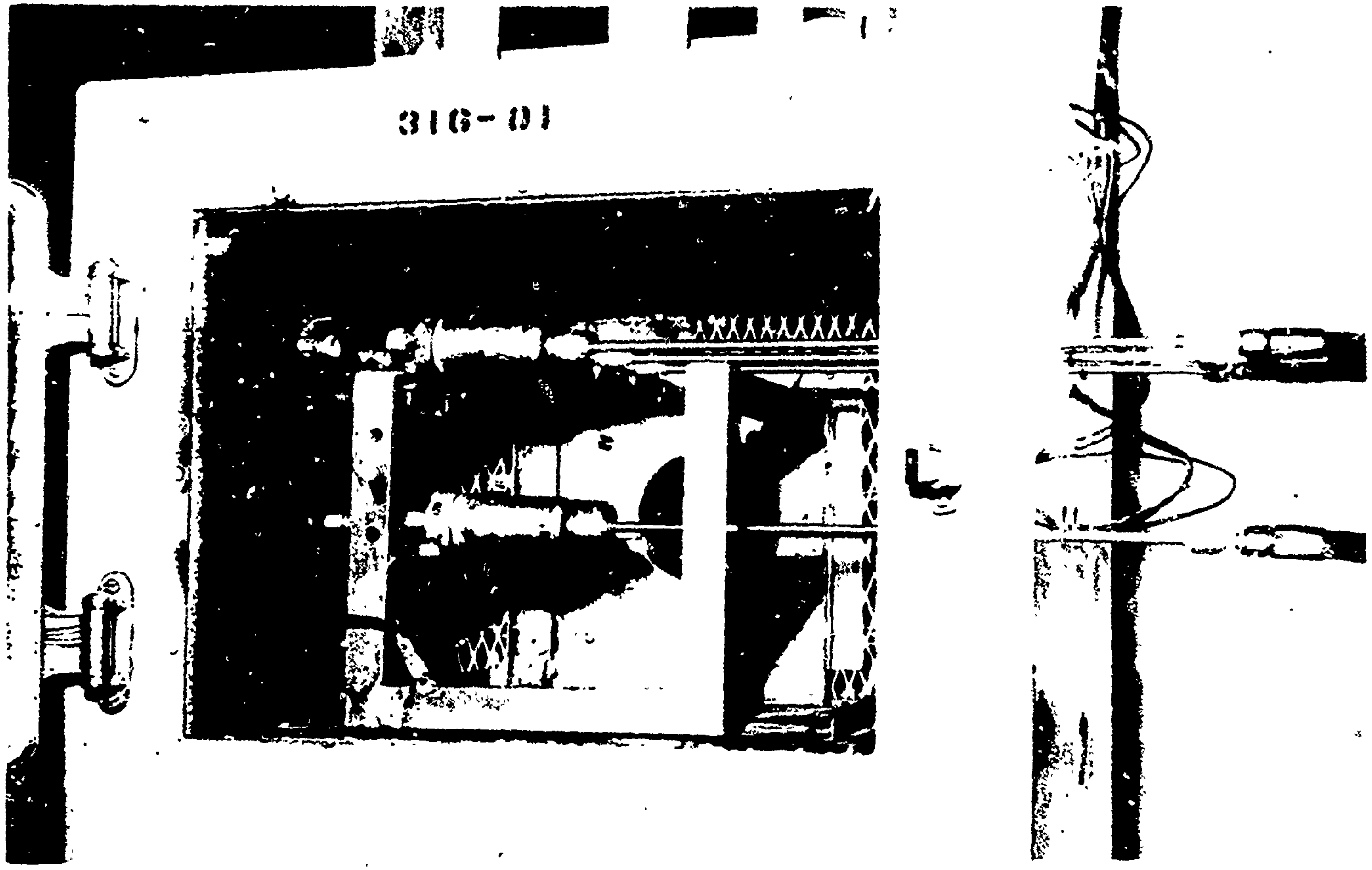

Figure 2. Hot Firing System

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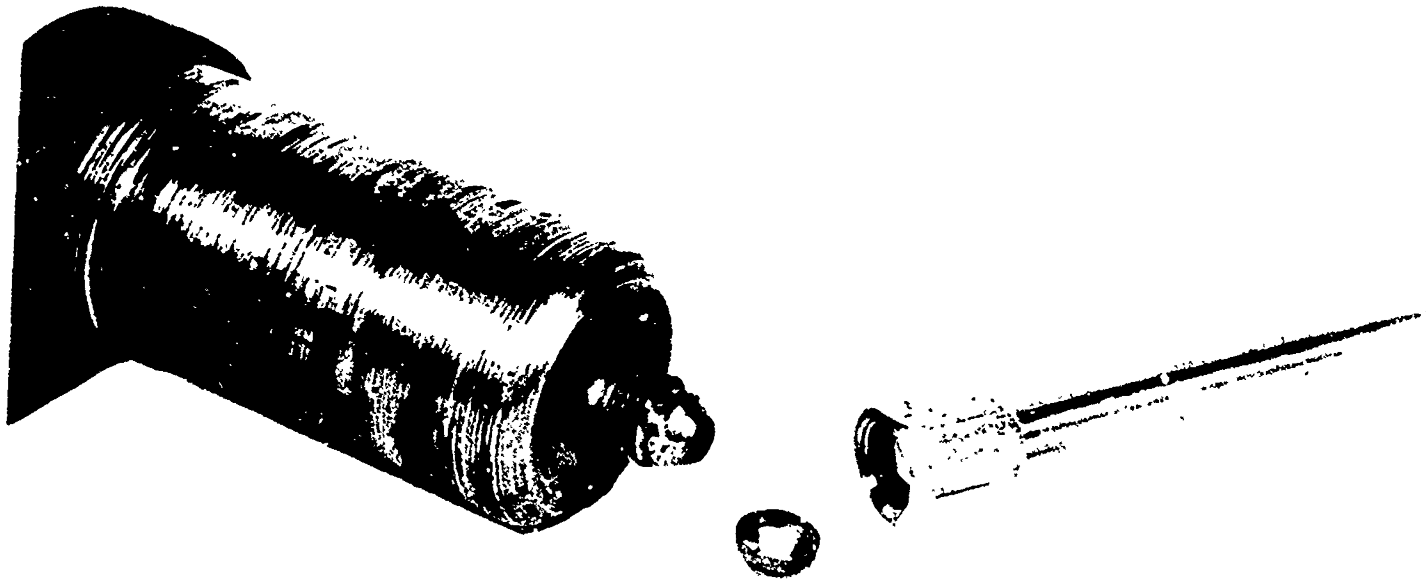

Figure 3. M5 PAD Initiator with Conical Seal and Inconel Tubing

present work, exposures were made at 400° F. It was found that, at this temperature, the M73 cartridge atmospheric contents would diffuse through the O-ring seal. An improved propellant sealing method was devised.

The propellants were hermetically sealed in small 0.5 inch diameter aluminum capsules, using a novel technique. The method employs the Koldweld* process of joing metal surfaces by cold flow without the application of heat as in standard welding methods. In this technique, the aluminum container of propellant and matched sealing cap are welded by a shaped punch and die. The resultant hermetically sealed container is able to contain the build-up of decomposition gases under heat without leakage.

The Koldweld-sealed capsules of propellant were heated for the specified time at 400° F, then tapped for atmospheric content in an evacuated system. The procedure and the handling of the mass spectrometer data are described in the previous report.[2]

Ballistic Evaluation at 400° F

The propellants were evaluated ballistically in the M73 cartridge-M3 initiator device, using the specification test fixture. In this system, the initiator i. fired through 15 feet of M28741-4 high pressure aircraft hose, terminating in a one cubic inch volume pressure chamber. This specification test rig is used routinely for all firings conducted from -65° to 200° F. Modification of this sytem for 400° F firings is described under "Development of Test Equipment."

RESULTS

Thermal Stability Study

Autoignition

Autoignition temperature data were obtained on HES 6468.1, HES 6484.1, and HES 6573.1 propellants in sealed M73 cartridges at linear heating rates of 5°, 10°, 20°, and 30° F per minute. Individual run data and standard deviations for five runs at each heating rate are shown in Table 2. The temperatures reported are those measured by the control thermocouple in contact with the cartridge case wall at the moment of propellant autoignition.

*Trademark and patent of Koldweld Division, Kelsey-Hayes Company.

TABLE 2
Individual Run Data, Autoignition Temperatures
at Linear Heating Rates (Sealed M73 Cartridges)

Propellant		Autoignition Temperatures (°F) at Linear Heating Rates of 5° F/min	10° F/min	20° F/min	30° F/min
HES 6468.1		622	644-	694+	721-
		628+	651+	688	726
		622-	649	693	728
		623	650	693	725
		626	648	684-	730+
	Avg	624	648	690	726
	Std dev	2	3	4	3
HES 6484.1		620	637	670	700
		622+	636	670	700
		619-	633-	671	702
		620	635	674+	700-
		622	638+	668-	707+
	Avg	621	636	671	702
	Std dev	1	2	2	3
HES 6573.1		618-	639-	679+	705-
		619	648+	678	705
		620+	645	677	705
		620	647	675-	711+
		620	644	678	711
	Avg	619	645	677	707
	Std dev	1	4	2	3

+ = maximum value; - = minimum value.

The data show the usual trend of higher autoignition temperature as heating rate is increased; however, this is largely due to increased thermal lag through the case wall at the faster heating rates. Autoignition temperatures for all three propellants are in the same general range.

Examination of Propellant Decomposition Gases

Hermetically sealed capsules of 3 grams of HES 6468, HES 6484, and HES 6573 propellants were conditioned at 400° F for four and eight hour periods. Capsule atmospheres were analyzed by mass spectrometer. Gases were also analyzed from similarly heated 0.5 gram samples of inert binders of these propellants in order to detect differences in thermal decomposition which could be attributed to the presence of potassium perchlorate oxidizer in the propellants. Comparisons were made with capsule atmospheres from unheated control samples. Mass spectrometer data are shown in Tables 3, 4, and 5. Gas sample bulb volumes were corrected for additional volume of the evacuated system and corrected gas volumes calculated to standard temperature and pressure (0°C and 760 mm Hg, respectively).

Evaluation of the data shows that there was little or no difference in the amount of gas between the unheated controls and the heated samples, although the composition of the atmospheres changed. Both the heated propellants and their respective binders absorbed atmospheric oxygen. In all cases, the addition of potassium perchlorate to the binder (i.e., complete propellant) resulted in increased evolution of CO_2 and CO at high temperature.

Small quantities of chlorine-containing organic compounds were detected from both heated propellants and their binders. Their appearance in heated binder gases is evidence that they may be attributed to the thermal decomposition of one of the binder ingredients. (Information from the contractor is that the Hycar 4021 polymer contains about five percent of a compound tentatively identified as chloro-ethyl vinyl ether.) Acetone is added by the manufacturer during propellant mixing.

Although most of the solvent is driven off during propellant cure, remaining traces account for its detection by the mass spectrometer. Small quantities of 2-methoxyethanol (methyl cellosolve) appear only in gases from heated HES 6468 propellant and its binder, and ethanol, similarly, from heated HES 6573 propellant and its binder. Since all three propellants employ the same Hycar 4021 polymer, this may be due either to the difference in curing agents or these solvents may have been incorporated as mixing aids in the individual propellant batches.

The deviation of atmospheres from unheated control samples to that of typical air is due mostly to differences in ambient humidity at the time the capsules were sealed.

Visual Examination

Sealed cartridges were opened from all high temperature exposures and the propellants were examined. The grains were hardened and discolored, generally in proportion to the severity of the heat exposure, but all appeared to retain their original configuration, with no evidence of perforation closure. Sectioned grains of HES 6573 propellant are shown in Figure 4.

Table 3
Major Gas Components of Capsule Atmospheres from Heated HES 6468 Propellant and Binder

Gas Components	Typical Air	HES 6468			HES 6468 Binder		
		Unheated	400°F/4 hr	400°F/8 hr	Unheated	400°F/4 hr	400°F/8 hr
	Values (mole percent)[a]						
O_2	20.9	20.0	1.6	0.3	19.4	1.2	0.8
N_2	78.1	76.3	24.5	15.5	74.1	85.9	70.2
CO_2	0.0	0.2	37.2	45.8	0.2	3.9	2.2
CO	-	0.3	12.3	10.6	0.9	1.0	1.1
H_2O	-	2.4	8.4	5.7	3.9	6.6	21.6
H_2	-	trace	12.3	18.0	trace	0.3	0.2
Acetone	-	trace	-	-	-	-	-
3-chloropropene	-	trace	-	-	-	-	-
CH_4	-	-	0.2	0.3	trace	trace	trace
CH_3Cl	-	-	0.5	0.4	-	trace	0.1
C_2H_5Cl	-	-	1.6	2.1	-	0.3	0.4
2-methoxyethanol	-	-	0.5	0.3	-	0.3	0.3
ml gas at STP	-	0.09	0.10	0.06	0.10	0.08	0.06

[a]Argon omitted.

TABLE 4
Major Gas Components of Capsule Atmospheres from Heated 6484 Propellant and Binder

Gas Components	Values (mole percent)[a]						
	Typical Air	HES 6484			HES 6484 Binder		
		Unheated	400°F/4 hr	400°F/8 hr	Unheated	400°F/4 hr	400°F/8 hr
O_2	20.9	18.7	0.6	0.6	16.6	1.3	0.5
N_2	78.1	73.4	23.4	15.3	70.7	46.3	51.1
CO_2	0.0	0.6	52.7	62.3	0.5	34.9	38.3
CO	-	0.6	12.2	10.4	trace	2.5	3.0
H_2O	-	5.5	9.9	10.2	11.2	13.1	4.4
H_2	-	0.3	0.3	0.2	0.3	0.8	0.3
Acetone	-	trace	-	-	trace	-	-
3-chloropropene	-	trace	-	-	trace	0.3	0.4
CH_4	-	trace	0.03	0.3	trace	-	0.2
CH_3Cl	-	-	-	-	-	trace	trace
C_2H_5Cl	-	-	-	-	-	trace	trace
$CH_2{:}CH_2$	-	-	0.5	0.4	-	trace	0.5
ml gas at STP	-	0.10	b	0.07	0.10	0.09	0.06

[a]Argon omitted.
[b]No quantitative measurement obtained.

TABLE 5
Major Gas Components of Capsule Atmospheres from Heated HES 6573 Propellant and Binder

Gas Components	Typical Air	HES 6573 Unheated	HES 6573 400°F/4 hr	HES 6573 400°F/8 hr	HES 6573 Binder Unheated	HES 6573 Binder 400°F/4 hr	HES 6573 Binder 400°F/8 hr
	Values (mole percent)[a]						
O_2	20.9	19.9	0.2	0.4	20.3	0.2	0.3
N_2	78.1	70.2	13.4	18.1	76.0	72.9	75.5
CO_2	0.0	0.4	71.1	66.7	0.3	14.5	16.4
CO	-	-	8.5	8.8	-	2.9	1.3
H_2O	-	8.6	1.3	1.0	2.5	1.0	1.3
H_2	-	-	4.8	4.3	-	0.5	0.6
C_2H_5Cl	-	trace	0.1	0.5	-	5.3	2.6
Ethanol	-	-	0.3	0.4	-	1.6	0.9
ml gas at STP	-	0.18	0.18	0.22	0.19	0.20	0.21

[a]Argon omitted.

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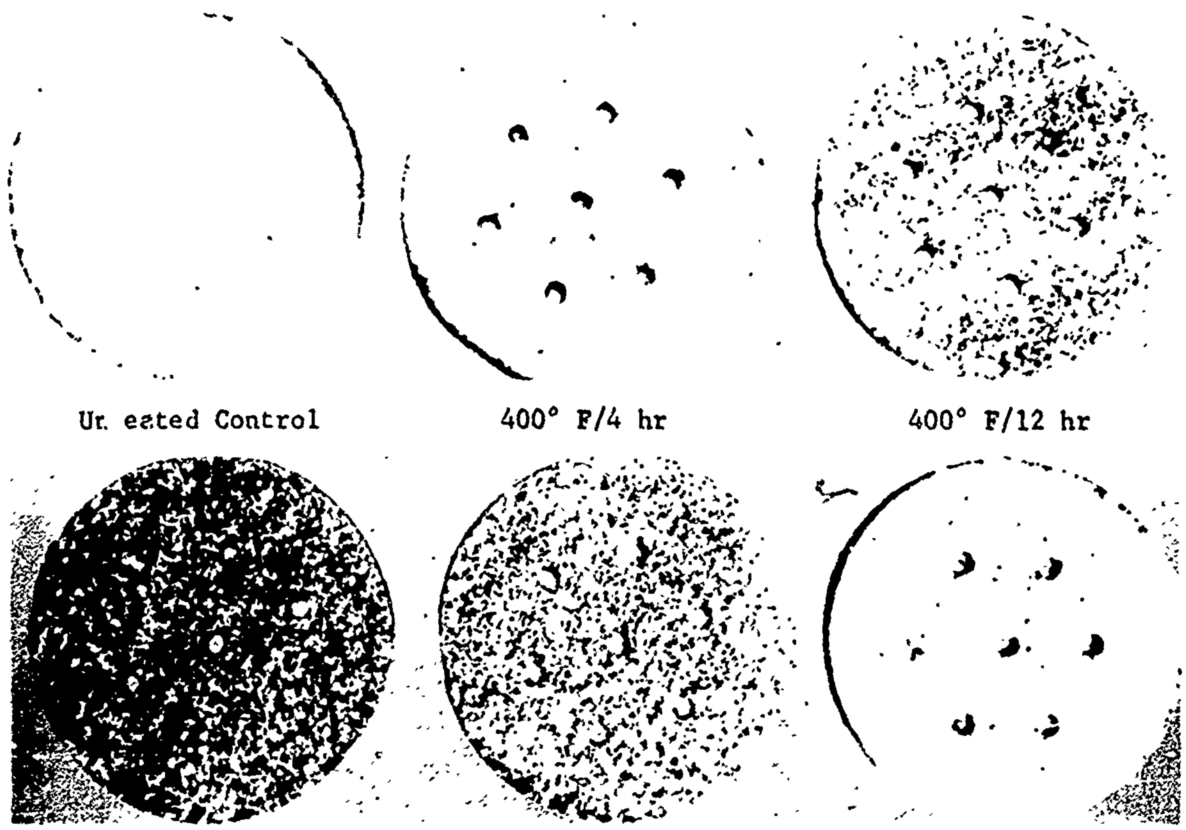

Figure 4. Grain sections of HES 6573.1B Propellant

Ballistic Evaluation

A complete ballistic evaluation of the potassium perchlorate propellants was carried out in the M73 cartridge-M3 (or M5) initiator system. The program follows.

1. Firings to compare black powder vs boron-potassium nitrate ignition of these propellants.

2. Firings, at ambient temperature and -65° F, of propellants exposed from -65° to 400° F.

3. Firings at 400° F after 400°F-4 hr exposure.

4. Firings at 400° F with experimental heat-resistant percussion primers (when these became available at the end of the program.)

The ballistic evaluation began with HES 6468 propellant. Early in the program it was found that tightly packed HES 6468 grains adhered to one another at points of grain contact after 400° F exposure. The grains themselves retained their geometrical configuration. Although the grain adhesion did not appear to affect performance in 400° F exposed cartridges undesirably, improved curing agents were sought.

The ballistic evaluation was continued with HES 6484 propellant, a polyacrylic rubber-triallyl cyanurate binder formulation. Solvent solubility studies with this composition later showed that cross-linking was not attained. Grain adhesion at 400° F was also noted with the HES 6484. The ballistic tests were completed with HES 6573, a modification of HES 6468 propellant in that trimene base was substituted for sulfur and DMP-30 as curing agent. Adhesion of HES 6573 grains at 400° F was considerably reduced.

Since HES 6468.1, HES 6484.1, and HES 6573.1 propellant lots were essentially similar as regards contractor closed bomb data, and identical in grain configuration, little difference among them was expected in their performance in the M73 cartridge. The most severe exposures and firings of the previous propellant were repeated with the succeeding formulation before the ballistic test program was continued.

<u>Firings with Boron-Potassium Nitrate Igniter</u>

HES 6468 propellant was fired with 1.2 grams of A4 grade black powder igniter and with 0.8 and 1.2 gram weights of U.S. Flare No. 2A boron-potassium nitrate igniter composition in a 14/35 Tyler mesh granulation. Individual round data are shown in Table 6. All cartridges gave performance within specifications.

Peak pressures were higher with the boron-potassium nitrate igniter than with an equivalent weight of black powder. This fact was considered significant since black powder is a gaseous igniter which contributes to the pressure peak in this system, while the boron-potassium nitrate is a relatively gasless metal oxidant "hot particle" igniter. This increased igniter efficiency of boron-potassium nitrate was demonstrated repeatedly with a variety of other composite propellants in this system.

Based on these data and the thermal stability of the $BKNO_3$ at 400° F, all further ballistic evaluation of the potassium perchlorate/Hycar propellants was carried out using $BKNO_3$ igniter. The igniter weight for the M73 cartridge was maintained at 1.0 gram, regardless of the ballistics obtained, in order to compare the effect of the various temperature exposures on the same propellant/igniter charge.

TABLE 6
Ballistic Data, HES 6468.1 Propellant Firings
in M73 Cartridge-M3 Initiator System
(Black Powder vs $BKNO_3$ Igniter)

Igniter	Igniter Weight (gm)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
A4BP	1.2	1100	13	17
		1180	15	17
		1030	14	18
		1040	14	22
		1080	19	18
	Avg	1086		
$BKNO_3$	0.8	1140	16	21
		1080	16	23
		940	16	24
		1240	18	15
		1100	18	19
	Avg	1100		
$BKNO_3$	1.2	1370	11	16
		1310	12	20
		1460	12	16
		1430	13	12
		1430	10	17
	Avg	1400		

Firings at Ambient and Low Temperature

The temperature conditioning and firing schedule for the firings at ambient and low temperatures follows.

Cartridge Exposure	Firing Temperature
Unconditioned (control)	Ambient (70° F)
Unconditioned	-65° F
400° F-4 to 24 hours	Ambient
400° F-4 to 24 hours	-65° F
Unconditioned	-65° F, locked shut
350° F-8 to 168 hours	Ambient
350° F-24 to 168 hours	-65° F
350° F-168 hours	-65° F, locked shut
300° F-2 to 4 weeks	Ambient
300° F-2 to 4 weeks	-65° F
300° F-2 to 4 weeks	-65° F, locked shut

The firings began with HES 6468.1 propellant, and continued with HES 6484.1 and HES 6573.1 propellants, as described. All cartridges exposed to high temperature were unprimed. Following exposure the cooled cartridges were primed with the 72M styphnate percussion primer. Lengthened high temperature exposures were arbitrarily stopped at 400° F-24 hours, 350° F-168 hours, 300° F-4 weeks. Firing data are shown in Tables 7, 8, and 9.

It is seen that there was little difference between the performance of the unconditioned control cartridges and all exposures of HES 6468.1 and HES 6484.1 propellants. In the case of HES 6573.1 propellant, one set of unconditioned control cartridges ("repeat" extended 400° and 350° F exposures) had a higher average peak pressure than the other control cartridges. It will also be noted that, in addition to this set, individual cartridges throughout Tables 7, 8, and 9 gave peak pressures exceeding 1500 psi, the desired maximum. This spread in the peak pressures of these propellants is attributed partially to variations in propellant weight due to random grain lengths. (In Table 9, note the sample designation HES 6573.1B. Lot HES 6573.1A was discarded because of excessive variability in grain length, which was visible to the naked eye.)

In all the firings, no general trend is shown of decrease (or increase) in peak pressure, ignition delay, or rise-to-peak, with exposure time at high temperature.

Firings at 400° F after Four-hour Exposure

Cartridges were fired through the system as follows.

Cartridge	Exposure	Firing Temperature
Standard production M73	70° F	70° F
Modified M73 (HES 6573)	70° F	70° F
	400° F-4 hr	400° F

Since the production M73 cartridges contained percussion primers, they were fired by a different method than the glow plug cartridges. The percussion primers were gas-initiated by a T14 electric primer outside the oven, firing through stainless steel tubing and actuating the M5 initiator firing pin inside the oven. Glow plugs were fired with a 375-microfarad capacitor charged to 300 volts.

Firing data are shown in Table 10. Average peak pressures of the HES 6573 propellant cartridges were higher than the production cartridges at both 70° and 400° F, but were within specification limits. Peak

TABLE 7
Ballistic Data, HES 6468.1 Propellant Firings
in M73 Cartridge/M3 Initiator System

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
Unconditioned	70	1070	23	14
		1190	17	21
		1240	18	19
		1160	16	18
		1130	16	23
	Avg	1158		
Unconditioned	-65	1340	14	12
		1280	18	14
		1330	17	10
		1210	15	13
		1440	13	18
	Avg	1320		
400° F-4 hr	70	1220	16	21
		1220	18	23
		990	19	26
		1010	18	21
		1080	21	32
	Avg	1104		
400° F-4 hr	-65	1130	20	19
		1340	15	17
		1210	15	16
		1260	13	20
		1220	14	18
	Avg	1232		
Unconditioned	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		Repeat Firings		
Unconditioned	70	1170	18	17
		1320	13	33
		1410	13	15
		1280	15	25
		1270	15	20
	Avg	1290		
Unconditioned	-65	1190	15	26
		1240	12	22
		1200	15	23
		1220	13	23
		1270	16	24
	Avg	1224		
400° F-4 hr	70	1130	12	32
		1160	15	29
		1340	12	24
		980	16	24
		1100	15	39
	Avg	1142		
400° F-4 hr	-65	1210	12	28
		1160	18	21
		1320	12	20
		1140	14	18
		1080	15	20
	Avg	1182		
Unconditioned	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	

[a]Locked shut

TABLE 8
Ballistic Data, HES 6484.1 Propellant Firings in M73 Cartridge/M3 Initiator System

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
		400° F Exposure		
Unconditioned	70	1220	21	20
		1290	21	22
		1190	16	23
		1270	15	14
		1210	19	19
	Avg	1236		
Unconditioned	-65	1240	20	20
		1220	16	16
		1170	18	22
		1120	19	20
		1240	18	17
	Avg	1198		
400° F-4 hr	70	1220	21	23
		1080	25	18
		1170	22	21
		1040	22	18
		860	23	14
	Avg	1074		
400° F-4 hr	-65	1030	19	25
		1120	18	21
		1240	29	12
		1050	16	20
		1230	25	13
	Avg	1134		
Unconditioned	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
400° F-6 hr	70	1180	8	21
		1100	11	24
		1180	11	18
		1100	12	24
		1190	9	21
	Avg	1150		
400° F-8 hr	70	1290	10	21
		1230	11	26
		1230	10	20
		1140	12	22
		1280	10	18
	Avg	1234		
400° F-10 hr	70	1170	9	20
		1090	12	22
		1190	11	19
		1200	12	23
		1130	12	17
	Avg	1156		
400° F-12 hr	70	1080	11	22
		1000	10	21
		980	10	21
		1080	11	20
		1030	12	18
	Avg	1034		

[a]Locked shut.

TABLE 8 (Cont'd)

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
		350° F Exposure		
Unconditioned	70	1520	15	19
		1470	12	20
		1400	12	22
		1330	11	21
		1130	12	22
	Avg	1364		
350° F-8 hr	70	1230	10	23
		1130	13	22
		1300	11	29
		1340	10	18
		1290	10	27
	Avg	1258		
350° F-16 hr	70	1440	12	20
		1390	12	24
		1330	13	24
		1280	12	23
		1190	11	22
	Avg	1326		
350° F-24 hr	70	1230	12	23
		1210	13	25
		1210	11	22
		1030	12	25
		1130	12	22
	Avg	1160		
350° F-24 hr	-65	1140	11	18
		980	12	25
		1280	11	21
		1150	12	25
		1130	12	20
	Avg	1136		
350° F-24 hr	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
350° F-48 hr	70	1530	10	20
		1380	12	22
		1390	10	24
		1300	10	20
		1290	10	22
	Avg	1378		
350° F-72 hr	70	1290	11	22
		1230	11	23
		1180	10	23
		1140	8	23
		1300	10	23
	Avg	1228		
350° F-96 hr	70	1490	11	21
		1230	11	20
		1290	9	22
		1300	10	23
		1370	10	26
	Avg	1336		

[a]Locked shut.

TABLE 9
Ballistic Data, HES 6573.1B Propellant Firings
in M73 Cartridge/M3 Initiator System

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
		400° F Exposure		
Unconditioned	70	1220	12	24
		1330	11	25
		1230	10	29
		1230	13	26
		1670	12	23
	Avg	1336		
400° F-4 hr	70	1290	13	28
		1300	11	24
		1280	12	22
		1500	11	24
		1400	12	24
	Avg	1354		
400° F-6 hr	70	1240	11	31
		1430	13	20
		1300	12	22
		1270	12	23
		1270	13	24
	Avg	1302		
400° F-8 hr	70	1580	10	25
		1540	12	22
		1430	12	22
		1420	9	21
		1400	10	26
	Avg	1474		
400° F-10 hr	70	1300	11	27
		1300	11	24
		1320	9	20
		1230	10	25
		1290	10	23
	Avg	1288		
400° F-12 hr	70	1340	9	20
		1340	10	20
		1390	10	25
		1480	9	22
		1460	10	21
	Avg	1402		
		350° F Exposure		
350° F-24 hr	70	1340	13	26
		1390	13	27
		1300	12	24
		1240	13	3[illegible]
		1190	12	27
	Avg	1292		
350° F-48 hr	70	1300	11	22
		1180	10	25
		1300	12	25
		1230	11	24
		1290	10	29
	Avg	1260		
350° F-72 hr	70	1140	10	23
		1280	12	25
		1470	10	21
		1530	10	23
		1330	10	26
	Avg	1350		
350° F-96 hr	70	1190	14	24
		1300	13	22
		1330	11	22
		1230	12	24
		1140	13	25
	Avg	1238		

TABLE 9 (Cont'd)

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
		Extended 400° and 350° F Exposures		
Unconditioned	70	1440	16	25
		1440	14	20
		1320	16	22
		1480	17	24
		1270	16	21
	Avg	1390		
400° F-24 hr	70	1230	17	27
		1230	17	26
		1240	18	20
		1200	19	25
		1200	18	22
	Avg	1220		
350° F-168 hr	70	1340	21	18
		1340	24	21
		1320	25	26
		1180	20	24
		1320	19	25
	Avg	1300		
		Repeat Extended 400° and 350° F Exposures		
Unconditioned	70	1600	11	21
		1540	13	18
		1470	16	17
		1540	11	15
		1390	11	25
	Avg	1508		
400° F-24 hr	70	1380	14	16
		1280	13	25
		1240	12	21
		1180	12	18
		1230	14	21
	Avg	1262		
400° F-24 hr	-65	1180	15	21
		1230	12	27
		1380	12	20
		1100	15	24
		1030	24	26
	Avg	1184		
400° F-24 hr	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
350° F-168 hr	70	1500	10	24
		1330	13	21
		1390	14	22
		1330	14	23
		1300	13	20
	Avg	1370		
350° F/168 hr	-65	1200	11	26
		1140	13	27
		1290	11	23
		1180	12	25
		1040	16	30
	Avg	1170		
350° F-168 hr	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	

[a]Locked shut.

TABLE 9 (Cont'd)

Cartridge Exposure	Firing Temperature (°F)	Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
		300° F Exposure		
Unconditioned	70	1280	8	24
		1330	11	24
		1280	8	26
		1280	11	27
		1340	11	28
	Avg	1302		
300° F-2 weeks	70	1330	10	29
		1340	9	27
		1270	11	24
		1500	9	23
		1180	9	27
	Avg	1324		
300° F-2 weeks	-65	1340	9	19
		1230	10	26
		940	11	25
		1230	8	23
		1090	10	28
	Avg	1166		
300° F-2 weeks	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	
300° F-4 weeks	70	1340	10	28
		1140	11	25
		1270	9	24
		1120	10	25
		1050	9	28
	Avg	[illegible]		
300° F-4 weeks	65	1300	12	19
		1340	10	20
		1270	9	23
		1200	9	23
		1240	9	23
	Avg	1270		
300° F-4 weeks	-65, LS[a]	-	Function O.K.	
		-	Ditto	
		-	Ditto	
		-	Ditto	
		-	Ditto	

[a]Locked shut.

TABLE 10
Ballistic Data, HES 6573.1B Propellant Firings
in M73 Cartridge/M5 Initiator System

Cartridge	Exposure	Firing Temperature (°F)		Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
Standard M73, Lot FA 10-1	Unconditioned	70		1020	15	17
				1040	13	22
				1050	10	18
				1000	10	20
				1000	8	20
			Avg	1022		
Modified M73, HES 6573.1B	Unconditioned	70		1400	61	18
				1060[a]	58	25
				1140[a]	56	26
				1330	58	25
				1300	51	21
			Avg	1246		
Modified M73, HES 6573.1B	400° F-4 hr	400		1450	53	11
				1350	54	17
				1230[a]	53	15
				1520	51	15
				1550	53	14
			Avg	1420		
		Repeat Firings				
Standard M73, Lot FA 10-1	Unconditioned	70		1100	9	18
				1060	9	21
				1080	9	23
				1100	11	21
				1140	9	18
			Avg	1096		
Modified M73, HES 6573.1B	Unconditioned	70		1340	58	19
				1190	58	24
				1270	56	18
				1380	56	23
				1390	50	19
			Avg	1314		
Modified M73, HES 6573.1B	400° F-4 hr	400		1330	63	18
				1490	45	18
				1570	50	15
				1460	46	18
				1440	58	15
			Avg	1458		

[a]Gas leak through glow plug.

pressures of the 400° F heated and fired cartridges were higher than those of the unheated cartridges. It will be noted that ignition delay for the HES 6573 propellant cartridges is unusually long for both ambient and 400° F firings. This is due to long "heat-up time" for the heavy bridge wire in the glow plugs and, consequently, is of little importance in the ballistic evaluation of the propellant.

Firings with Heat-resistant Percussion Primers

In an effort to evaluate a completely 400° F-resistant PAD cartridge, the ballistic tests were conducted in M73 cartridges loaded with HES 6573 propellant, boron-potassium nitrate igniter, and experimental heat-resistant percussion primers currently under development on another program.[5] Two primer compositions, G-11 and G-16, were selected as having the best characteristics of sensitivity and thermal stability for this application. Both compositions were employed in the tests.

The cartridges were fired in M5 initiators, employing the hot firing system. The percussion primers were initiated by M52A3 electric primers functioning outside the oven through stainless steel tubing and actuating the initiator. Comparison was made with standard production M73 cartridges and with 72M styphnate primers as follows.

Cartridge Load	Primer	Exposure	Firing Temperature
Standard M73	72M	70° F	70° F
HES 6573.1B/$BKNO_3$	72M	70° F	70° F
HES 6573.1B/$BKNO_3$	G-11	70° F	70° F
HES 6573.1B/$BKNO_3$	G-11	400° F-4 hr	400° F
HES 6573.1B/$BKNO_3$	G-16	70° F	70° F
HES 6573.1B/$BKNO_3$	G-16	400° F-4 hr	400° F

Firing data are shown in Table 11. All cartridges primed with the G-11 and G-16 compositions functioned satisfactorily at 70° and at 400° F. Peak pressures for all HES 6573.1B-loaded cartridges were higher than those of production cartridges. (It is believed that this can be easily corrected by adjustment of propellant and igniter weight.) At ambient temperature, comparable pressures were obtained between G-16 and 72M primed cartridges. Comparison of G-11 and G-16 primers showed somewhat higher peak pressures for G-11 primers. This is believed due to the presence of 10 percent TACOT* heat-resistant high explosive in the G-11 composition.

*Trademark of E. I. dupont de Nemours & Co., Inc.

TABLE 11
Ballistic Data, HES 6573.1B Propellant Firings
in M73 Cartridge/M5 Initiator System
(G-11 and G-16 Experimental Primers)

Cartridge Load	Primer	Exposure	Firing Temperature (°F)		Peak Pressure (psi)	Ignition Delay (ms)	Rise Time (ms)
Standard M73 Lot FA 10-1	72M	70° F	70		1030	13	18
					1020	13	15
					1080	11	18
					1080	11	18
					1100	13	20
				Avg	1062		
HES 6573.1B	72M	70° F	70		a	a	a
					1370	19	15
					1240	18	20
					1320	15	21
					1320	13	20
				Avg	1312		
HES 6573.1B	G-11	70° F	70		1330	15	23
					1610	13	15
					1460	13	20
					1340	13	22
					1510	9	22
				Avg	1450		
HES 6573.1B	G-11	400° F-4 hr	400		1590	9	15
					1590	9	13
					1540	9	19
					1760	9	14
					1540	9	14
				Avg	1604		
HES 6573.1B	G-16	70° F	70		1320	16	21
					1410	15	18
					1150	18	20
					1200	19	19
					1390	14	23
				Avg	1294		
HES 6573.1B	G-16	400° F-4 hr	400		1560	11	16
					1410	10	14
					1270	18	16
					1610	10	13
					1440	11	15
				Avg	1458		

[a]No reading; instrument malfunction.

In summary, these firings were considered to have demonstrated a complete primer-igniter-propellant train for PAD cartridges to meet 400° F-4 hour operation. These firings concluded the ballistic evaluation of the small grain potassium perchlorate/Hycar propellants.

DISCUSSION

Thermal Stability Study

The autoignition data on the HES 6468, HES 6484, and HES 6573 propellants show the same high level of autoignition temperatures for these propellants as were obtained with potassium perchlorate propellant during previous screening of propellant types.[1] The gas evolution data and visual examination show that their resistance to deterioration at 400° F for up to eight hours is of a high order. Gassing of the propellants at these temperatures is virtually negligible. The discussion of what gases are evolved (see RESULTS) points to a small amount of binder deterioration which, apparently, can be tolerated within the temperature-time objective of this program.

Ballistic Evaluation

The firings of the potassium perchlorate/Hycar acrylic binder propellants in a typical propellant actuated cartridge demonstrated their ability to survive and perform under extremely wide temperature conditions. As far as is known, the 400° F conditioning, -65° F firing temperature span is the widest to which any specification propellant device has ever been subjected and fired satisfactorily.

Deviations from specified M73 cartridge-M3 initiator performance did not take the form of a lowering in peak pressures or overly long rise-to-peak time, as would be expected from a deteriorated propellant, but, rather, an increase in peak pressure above the desired 1500 psi maximum occurred. This is attributed to a combination of several causes.

First, an extensive charge establishment program for optimum propellant and igniter weight for this cartridge was not undertaken, but an arbitrary charge of eight pieces of propellant and 1.0 gram of $BKNO_3$ was adhered to for the entire firing program. It is possible that an igniter weight of 0.8 or 0.9 gram may be preferable.

Second, the propellant lots furnished by the contractor were experimental, and not subject to the rigid grain dimension specifications under which gun propellants are procured. Considerable variation in grain length was experienced, particularly with HES 6573 propellant.

Third, higher peak pressures were obtained, mostly in firings at 400° F, which was to be expected. A minimum temperature coefficient of performance over a temperature spread of approximately 465° F remains an area still to be explored.

The adoption of Inconel tubing for the 400° F firing of perchlorate propellant is described (see EXPERIMENTAL). Although this was successful here, it is not suggested that this solves the problem of the effect of corrosive combustion products of perchlorate propellant on metal in propellant actuated devices. Heat-resistant propellants employing nonhalogen oxidizers and binders would be preferable.

CONCLUSIONS

1. Based on autoignition temperature, amount and nature of gas evolution, and retention of grain configuration, the extrudable potassium perchlorate/Hycar acrylic binder propellants showed thermal stability sufficient to meet the 400° F-4 hr high temperature objective of this program.

2. When evaluated ballistically in the M73 cartridge/M3 (or M5) initiator system, these propellants demonstrated their ability to survive and function, as designed, after exposures from -65° to 400° F.

RECOMMENDATIONS

1. The potassium perchlorate/Hycar polyacrylic binder propellants should be considered for propellant actuated cartridge applications with -65° to 400° F exposure requirements.

2. Further work should be done with these propellants, with the objective of attaining a minimum temperature coefficient of ballistics over a temperature span of -65° to 400° F.

3. High temperature-resistant, halogen-free propellants should be explored for the added advantage of noncorrosive combustion products.

4. Conical seals should be investigated further for use in all AN fittings employed in propellant actuated devices.

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