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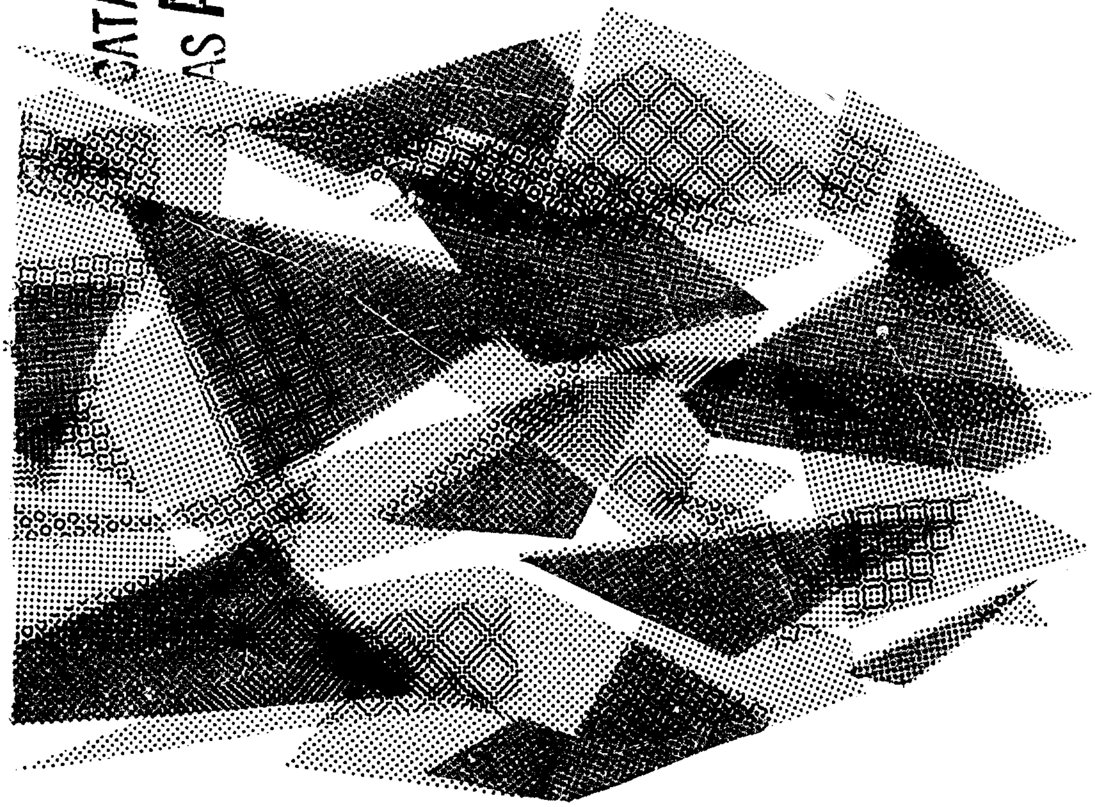
HUNTSVILLE, ALABAMA

SPECIAL REPORT NO. [redacted]

DEVELOPMENT OF A COMPOSITE PROPELLANT (U)



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ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

Report No. S-64

DEVELOPMENT OF A COMPOSITE PROPELLANT

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ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

DEVELOPMENT OF A COMPOSITE PROPELLANT

ABSTRACT

A program was undertaken by this Division to develop a composite propellant technology and capability based on plasticized carboxy-terminated polybutadiene polymer (CTPB). The effects of processing and compositional variables on cure time, curing rate and mechanical properties were studied with dummy propellant formulations. Highly plasticized compositions were shown to have adequate mechanical properties and to be easily castable.

Ballistic studies made on the CTPB propellants defined the effect of compositional changes on burning rate and specific impulse. Burning rates could be controlled through oxidizer particle size, aluminum size and concentration, and through catalysis. Plasticizers had no effect on burning rate or specific impulse. Specific impulse efficiencies were low in small motors except at low aluminum levels.

Impulse scaling studies showed that the use of ferrocene as a catalyst did not improve impulse efficiency in large motors. Its effect was to shorten the burning time and reduce heat losses, thus giving higher measured specific impulse values in small motors.

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DEVELOPMENT OF A COMPOSITE PROPELLANT (U)

1. Introduction

A program was undertaken by this Division to develop a composite propellant technology and capability based on plasticized carboxyl-terminated polybutadiene polymer (CTPB). The propellants were to have good mechanical properties, reliable and versatile ballistic characteristics, and reasonably high specific impulse. Emphasis was placed on developing formulations that were easy to mix and cast and that were adaptable to processing in the facilities of other organizations.

In the initial phase familiarization studies were carried out using sodium chloride in place of ammonium perchlorate oxidizer. Mixing, casting, and curing techniques were investigated with the dummy propellants to provide processing experience prior to initiation of live propellant work. Some formulations were developed that were useful in general mechanical properties studies.

Using these results, propellants were made to investigate the range of burning rate, specific impulse, and mechanical properties, and to determine combustion efficiency, scaling effects, and temperature coefficients. Much of the work was done with highly plasticized propellants in which the reduced viscosity improved processability and increased ballistic versatility.

This report provides basic information on the processing techniques, range of compositional variations, and ballistic characteristics of propellants based on CTPB binder.

2. Characteristics of the CTPB Propellant System

2.1 Curing Studies

2.1.1 Effect of Curing Agent Level

The cure mechanism of CTPB propellants is a relatively slow process that requires up to ten days to achieve reasonable physical properties.

The effect of curing agent level was investigated by making a series of dummy propellant batches using curing-agent-to-polymer equivalent weight ratios of 1.20, 1.35 and 1.50. The propellant binder was based on ZL 434 polymer[1] and dioctyl adipate (DOA) plasticizer; curing agents were MAPO[2], ERLA 0510[3], and iron linoleate. A $^{40}/_{60}$ bimodal blend of 55μ and unground sodium chloride was used as the filler, and duplicate batches were made for each curing agent level. The samples were cured at an oven temperature of 140° F and the progress of cure was followed by "Shore A" hardness measurements made each day on the cast samples.

The hardness level of a typical composition (CT-15) varied with the amount of curing agent but the curing rates were not strongly affected since each of the curves leveled off at about ten days (Fig. 1). Good agreement was obtained between duplicate batches. The formulation of the dummy propellant is given in Appendix A.

Other batches containing curing-agent-to-polymer equivalent weight ratios less than 1.0 (excess carboxyl groups) did not cure completely. It was concluded that rate and completeness of cure were not greatly affected by curing agent level as long as excess carboxyl groups were not present.

2.1.2 Effect of Moisture and Oxidizer Surface Area

Moisture was known to have an adverse effect on the cure of CTPB propellants primarily through its attack on the MAPO. No problems were encountered when reasonable care was taken to exclude moisture during mixing. This included mixing under a blanket of dry nitrogen but not pre-drying the raw materials. When batches were mixed on humid days without a nitrogen purge, cure was drastically affected and soft propellant resulted.

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[1] A carboxyl-terminated polybutadiene polymer, Thiokol Chemical Corp., Trenton, New Jersey.

[2] Tris[1-(2-methyl) oziridinyl] phosphine oxide, International Chemical Corp., Newark, New Jersey.

[3] Trifunctional epoxide, Bakelite Division of Union Carbide, New York, New York.

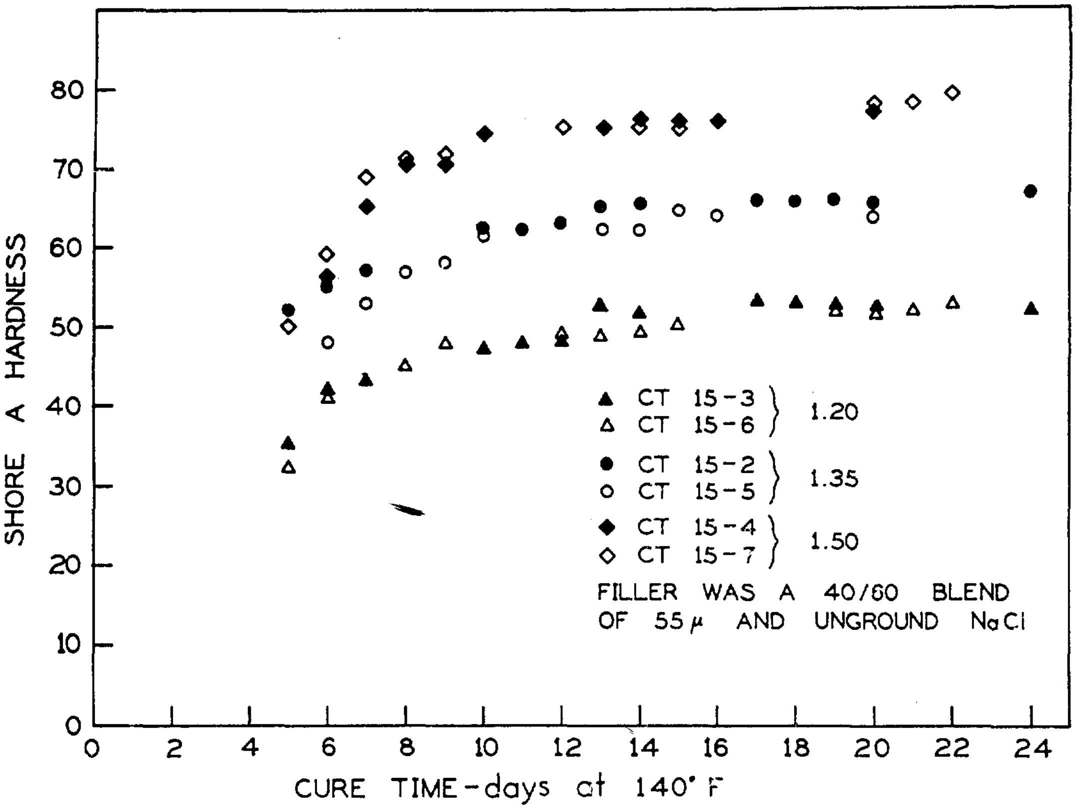

Fig. 1 Effect of curing agent concentration on cure time of CTPB dummy composition.

An interesting effect of filler surface area was illustrated by curing rate curves obtained for CT-15 made with 25μ sodium chloride. The "Shore A" hardness of these batches did not level off at ten days but continued to increase for twenty days or longer (Fig. 2). It is believed that the moisture absorbed on the surface of the filler caused this decrease in cure rate. No problem was encountered in live propellant containing only ammonium perchlorate as the filler.

2.1.3 Effect of Ammonium Perchlorate on Cure of Dummy Formulations

Cure times of the order of 17 days were necessary for the early dummy formulations such as CT-1 through CT-7 (Appendix A). Since small amounts of ammonium perchlorate were known to accelerate cure of CTPB gum stock, 3% of the sodium chloride was replaced by ammonium perchlorate. This had the effect of cutting the cure time almost in half, and the practice was continued in later formulations.

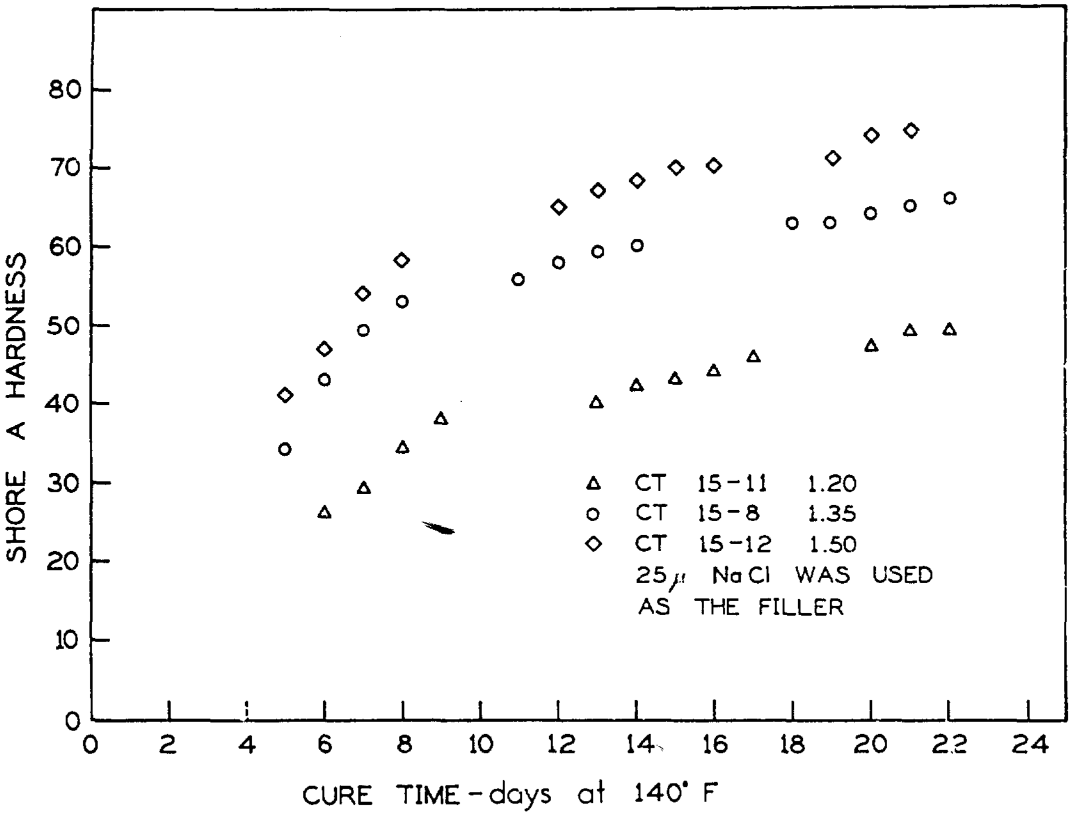

Fig. 2 Effect of curing agent concentration on cure of CTPB dummy composition.

2.1.4 Effect of Plasticizer Concentration on Cure Time

A series of compositions containing from 1% to 7% dioctyl adipate were made at an 82% solids level to determine the effect of plasticizer concentration on cure rate and physical properties. Time-to-complete-cure, as evidenced by the leveling off of "Shore A" hardness numbers, was essentially constant for the different plasticizer levels at about ten days (Fig. 3).

2.2 Processing Studies

2.2.1 Experimental Equipment and Procedures

The dummy propellants were processed at 140°F in a one-quart sigma-blade horizontal mixer.[1] Deaeration was accomplished by casting through a $^1/_4$-inch slit plate directly into a container held under a vacuum of at least

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[1] Baker Perkins Company, Saginaw, Michigan.

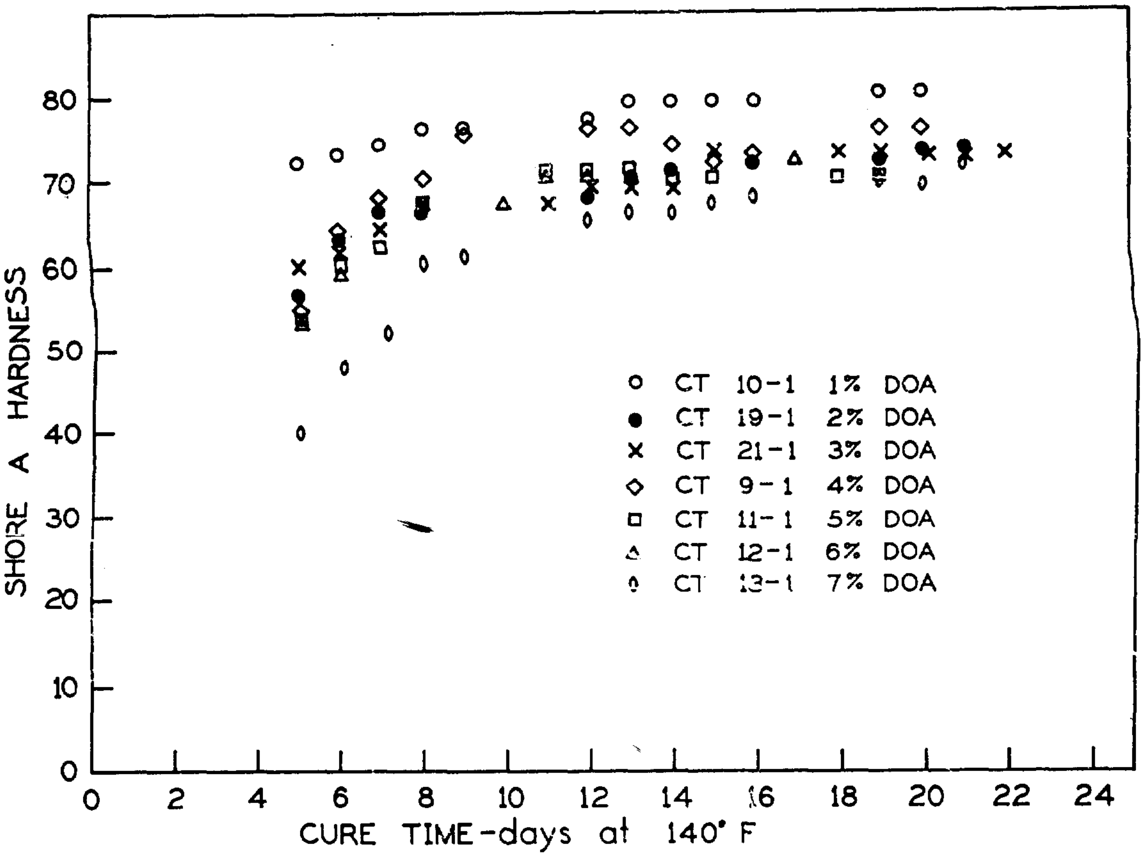

Fig. 3 Effect of plasticizer level on cure of CTPB dummy compositions.

28 inches of mercury. Live propellant was mixed remotely in a one-gallon planetary vertical mixer.[1] The processing temperature was 140°F and casting and deaeration methods were the same as those used with the dummy propellants.

Viscosity measurements were made on each propellant batch with a Brookfield Model RVT Viscometer.[2] Motor castings were made with compositions having viscosities up to 15 kilopoises using mandrel-insertion casting fixtures.

2.2.2 Effect of Particle Size on Viscosity

Since one object of this program was to develop easily castable composite propellants, low-viscosity propellants were needed. The four

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[1] Baker Perkins Company, Saginaw, Michigan.

[2] Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts.

primary factors affecting propellant viscosity are plasticizer level, particle size distribution, packing fraction, and solids loading. No extensive study of packing fraction or solids loading was undertaken in the formulation work, but the effects of plasticizer level and particle size distribution were investigated.

Initial studies on the CTPB system were made with reasonably low solids levels, e.g. CT-1 at 79.5%. Viscosities were usually in the 4 to 6 kilopoise range using bimodal salt such as 55µ/ unground or 25µ/ unground. (Unground salt had a particle diameter greater than 300µ). A minimum viscosity of 4 kilopoise was obtained with about 60% unground salt (Fig. 4). Slightly higher viscosities resulted from using 25µ salt in place of 55µ.

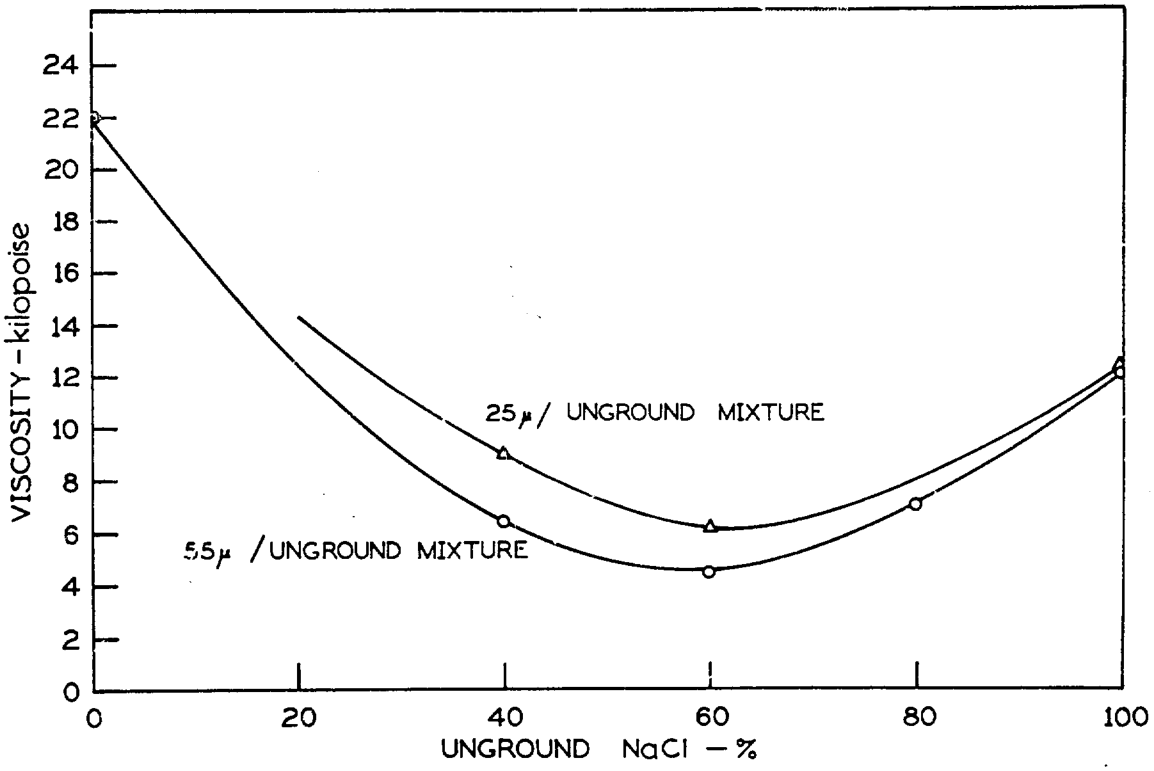

Fig. 4 Effect of NaCl particle size on batch viscosity. (CT - 1)

2.2.3 Effect of Plasticizer Level on Viscosity and Motor Casting

A series of batches containing 0%, 1%, 2%, and 3% plasticizer level showed the effect of this variable on batch viscosity of an 82% solids composition. The addition of 3% dioctyl adipate reduced the viscosity by 50% (Table I).

Table I

Effect of Plasticizer on Propellant Viscosity

Composition	Plasticizer Level %	Viscosity (kilopoise)
CT 7-1[a]	0	18
CT 6-1	1	14
CT 5-1	2	13
CT 3-1	3	9

[a] CT 7-1 is Composition CT 7, Batch 1.

A batch of CT-1 was mixed, deaerated, and cast into a 2-inch motor case with a $\frac{1}{2}$-inch web to determine if a 4 kilopoise viscosity would permit use of conventional slurry casting techniques. Some vibration was used to insure flow into the motor but this was probably not necessary. The dummy propellant bonded to the clean metal wall and the grain appeared to be well consolidated. The maximum viscosity which can be used for this type of casting was not determined, but this test demonstrated the feasibility of pour-casting low viscosity composite propellants.

Studies with propellant made with ammonium perchlorate have shown that viscosity data from the dummy compositions cannot be extrapolated to live compositions. Much lower viscosities are obtained in live propellants; however, relative effects of plasticizer level and particle size within each system should be the same.

2.2.4 Pot-Life of CTPB Propellants

Pot-life was not a problem in the mixing of CTPB propellants. The normal mixing time after addition of all ingredients was increased from 20 minutes to 90 minutes on batches of CT-1. There were no changes in mix appearance or viscosity.

2.2.5 Processing of Live Propellants

The results of processing studies with inert propellant permitted evaluation of live propellant to proceed with a minimum of additional work. It was found that the mix viscosity of propellants with ammonium perchlorate filler was much lower than equivalent dummy compositions and, as expected, the cure times for live propellant were much shorter. Most of the work on the live propellant was concerned with ballistic evaluation of the CTPB system. A complete list of CTPB propellant compositions is given in Appendix B.

2.3 Mechanical Properties

2.3.1 Effect of Curing Agent Level

Previous work in the Division had shown that curing agent concentration was the primary variable affecting the mechanical properties of polybutadiene-acrylic acid compositions. A series of CT-15 dummy propellant batches were made containing three levels of MAPO/ERLA curing agent to determine the effect on mechanical properties. Curing agent levels above and below the normal 1.35 equivalent weight ratio of curing agent-to-polymer were used.

Tensile strength was a strong function of curing agent level, but elongation was only slightly affected (Table II). These data indicated that regulation of curing agent level can be used to control mechanical properties of CTPB propellants; at the same time, good control of this variable must be maintained to get reproducible properties. Another series of batches using smaller size filler gave similar results.

Table II

Mechanical Properties of CTPB Dummy Propellants at Different Curing Agent Levels

Filler consisted of 58% unground NaCl, 39% 55μ NaCl, and 3% 15μ NH_4ClO_4

Batch No.	Curing Agent/Polymer	Tensile Strength at 77° F (psi)	Elongation at 77°F (%)
CT 15-3	1.2	79	31
CT 15-6	1.2	79	32
CT 15-2	1.35	138	29
CT 15-5	1.35	142	29
CT 15-4	1.5	178	24
CT 15-7	1.5	160	20

2.3.2 Effect of Plasticizer Level

As expected, the tensile strength decreased with the increase in plasticizer level; however, there was no accompanying increase in elongation (Table III).

Table III

Mechanical Properties of Plasticized CTPB Compositions at +77° F

Composition No.	Plasticizer Level		Tensile Strength (psi)	Elongation (%)
	% of Propellant	% of Binder		
CT-10[a]	1	5.6	260	29
CT-19	2	11.1	180	23
CT-21	3	16.7	160	26
CT-9	4	22.2	140	31
CT-11	5	27.8	125	27
CT-12	6	33.3	77	23
CT-13	7	38.9	52	26

[a] Formulations are given in Appendix A.

2.3.3 Typical Values for Live Propellants

The only mechanical property data obtained on live propellant were from routine samples from the ballistic evaluation. Typical properties for a plasticized CTPB propellant are shown in Table IV. As with the dummy propellants, high plasticizer levels reduced the tensile strength markedly. Mechanical properties were controlled by adjusting the curing agent-to-polymer ratio.

Table IV

Mechanical Properties of RH-C-2[a] at +77°F

Tensile Strength, psi	75-100
Elongation at Max. Stress, %	20-30
Density, lbm/in^3	0.064

[a] Formulation is given in Appendix B.

3. Ballistic Evaluation of CTPB Propellants

3.1 Characterization of Burning Rate

3.1.1 Effect of Oxidizer Particle Size

As with most other propellant systems, the burning rates of CTPB propellants were highly dependent on the particle size of the oxidizer. A series of propellants were fired in 2C1.5-4[1] motors containing RH-C-2 with different size ammonium perchlorate. The burning rates varied from 0.31 in/sec to 0.50 in/sec at 1000 psia (Fig. 5). The higher rate was obtained with a 70/30 ratio of $15\mu/200\mu$ oxidizer. The pressure exponent was about 0.25. The range of burning rates available for uncatalyzed propellant and a plot for a typical composition is shown in Fig. 6.

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[1] The 2C1.5-4 motor has a case I. D. of 2.0 in., a cylindrical grain design, a grain I. D. of 1.5 in., and a motor case length of 4.0 in.

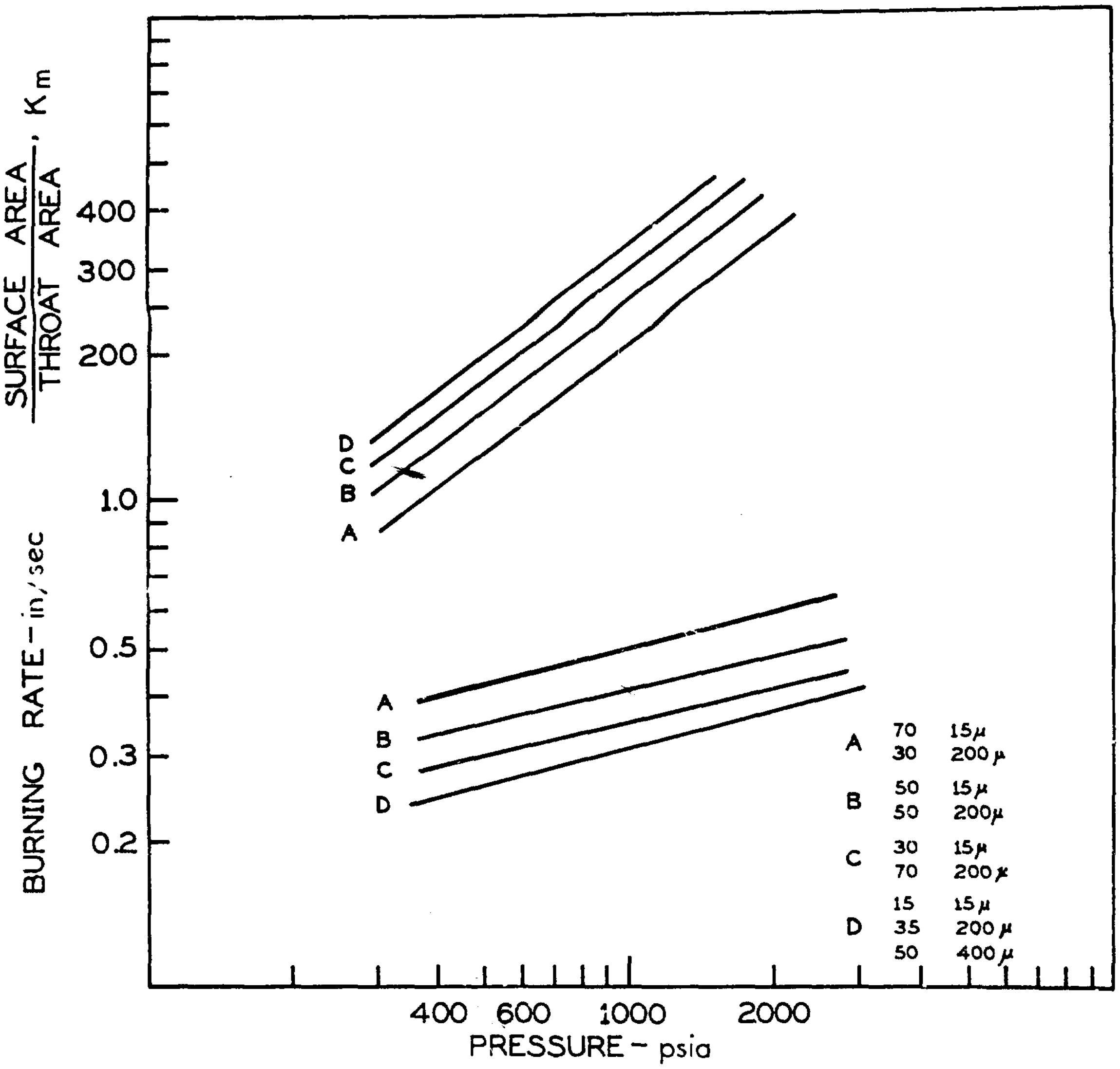

Fig 5 Effect of ammonium perchlorate particle size on K_m and burning rate of RH-C-2.

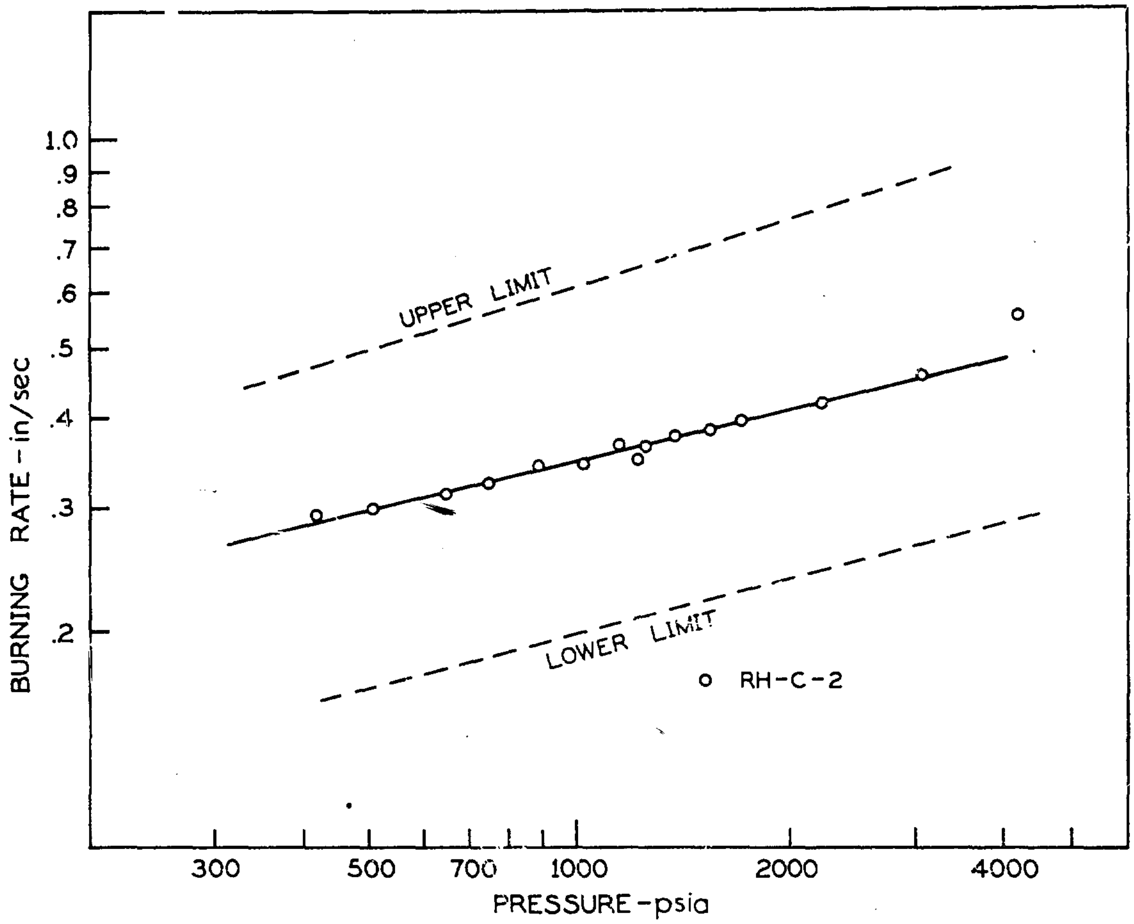

Fig. 6 Burning rate limits of uncatalyzed CTPB propellants and burning rate curve of a typical composition.

3.1.2 Effect of Aluminum Particle Size

The effect of aluminum particle size was investigated by firing 2C1.5-4 motors containing propellants with three sizes of aluminum at 10% and 20% aluminum levels. The rate decreased with increasing particle size (Table V). The large effect of aluminum particle size on burning rate was not expected. The burning rate of plastisol nitrocellulose composite propellant is insensitive to both size and amount of aluminum. The dependence of burning rate on aluminum could be useful in tailoring burning rates of CTPB propellants. The burning rate of a composition could be varied, for instance, by a change in aluminum size instead of oxidizer size without significantly affecting processibility. A change in ammonium perchlorate particle size can greatly alter the viscosity of the propellant mix.

Table V

Effect of Aluminum Particle Size on Burning Rate

(Oxidizer was 50/50 of $15\mu/200\mu$)

Aluminum Particle Size (microns)	Aluminum Level (%)	Burning Rate at 1000 psia (in/sec)
3[a]	10	0.45
10[b]	10	0.40
30[c]	10	0.37
3[a]	20	0.40
10[b]	20	0.32
30[c]	20	0.30

[a] Alcoa 140, Aluminum Company of America, Pittsburg 19, Pennsylvania.

[b] Valley H-10, Valley Metallurgical Processing Company, Rt. 9, Essex, Connecticut.

[c] Valley H-30, ibid.

3.1.3 Compositional Effects

The effect of plasticizer type and level, oxidizer-to-metal ratio, and catalysts on burning rate were investigated.

Dioctyl adipate plasticizer was shown to produce no significant effect on burning rate of the CTPB compositions when substituted for polymer at concentrations up to 33% of the binder. Limited studies with TP-90B,[1] a plasticizer giving good low temperature properties, also gave the same rates. Thus the plasticizer can be adjusted to meet mechanical property requirements without regard for burning rate changes.

The effect of ammonium perchlorate-to-aluminum ratio was studied by firing 2C1.5-4 motors with compositions containing from 1% to 25% aluminum at a total solids level of 85% (RH-C-27 thru RH-C-32). A significant reduction in burning rate occurred at ammonium perchlorate-to-aluminum ratios less than 70/15 (Fig. 7). Table V also shows this effect.

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[1] Butyl carbitol formal, Thiokol Chemical Corporation, Trenton, New Jersey.

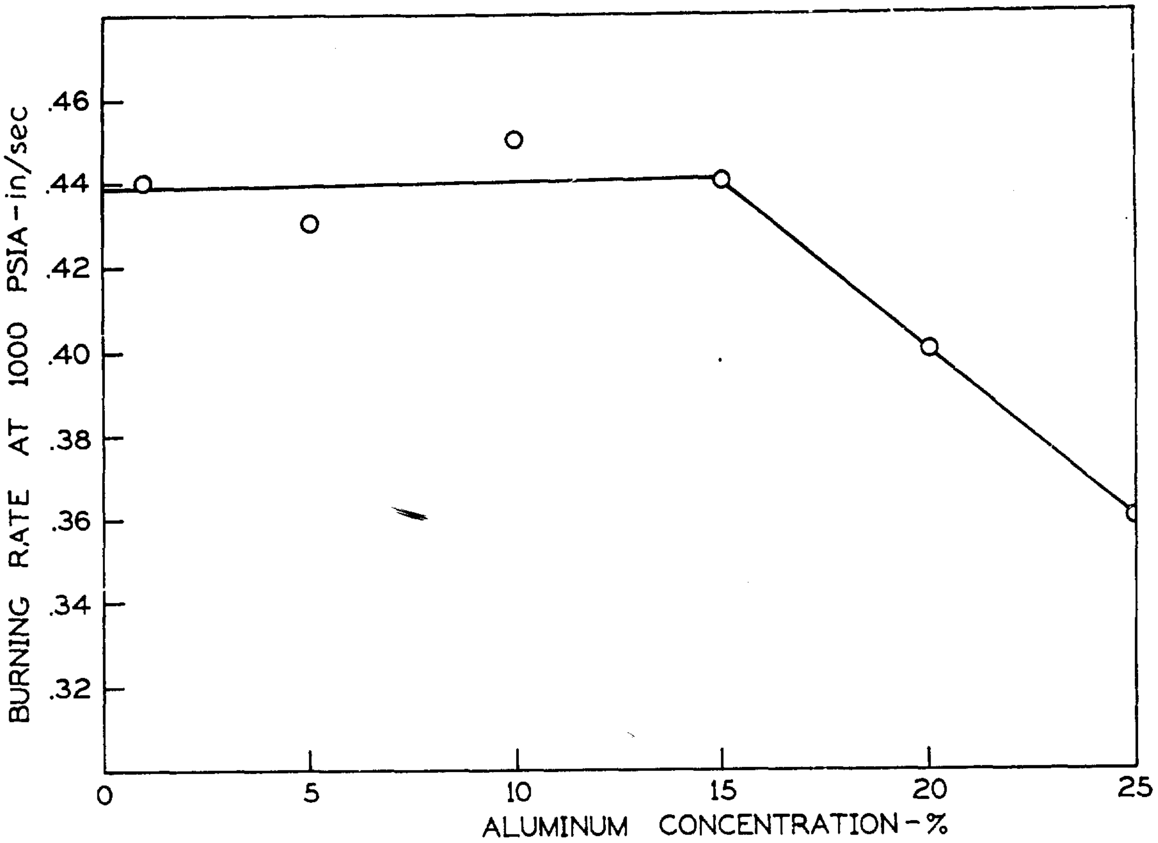

Fig. 7 Effect of aluminum level on the burning rate of a propellant with 85% solids.

It has been shown that ferrocene is an effective burning rate catalyst for CTPB propellants.[1] When ferrocene was added to CTPB compositions at the 1% level, a 50% increase in burning rate was obtained. Burning rates as high as 0.90 in/sec at 1000 psi were obtained with 1% ferrocene (Fig. 8). No attempt was made to obtain higher rates in this program.

3.2 Specific Impulse of CTPB Propellants

3.2.1 Theoretical Calculations

Thermochemical calculations on CTPB propellant compositions have shown optimum specific impulse values in the 260 to 265 lbf-sec/lbm

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[1] "Sprint Composite Development Program," Monthly Status Letter No. 1, July 11, 1963, Thiokol Chemical Corporation, Huntsville, Alabama.

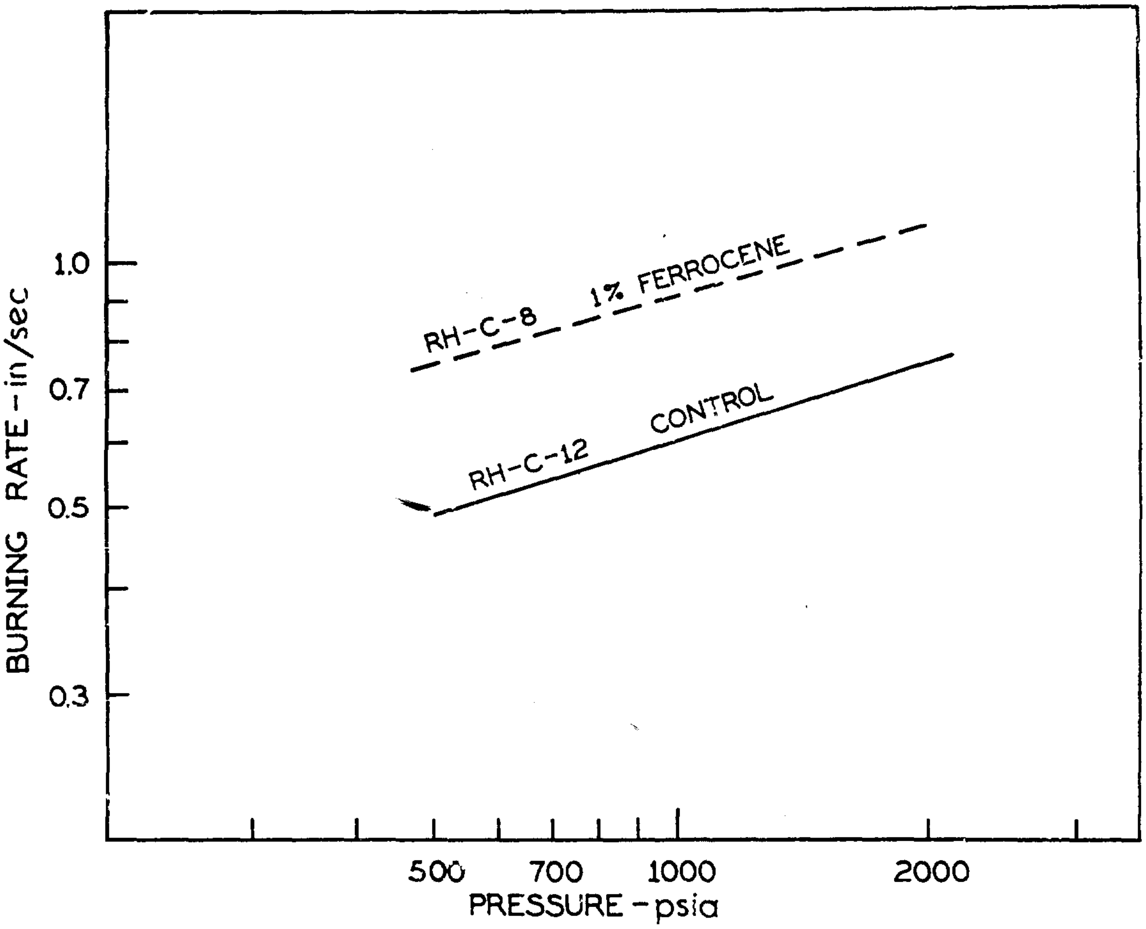

Fig. 8 Burning rate of CTPB propellants with and without ferrocene catalyst.

range at an 85% solids level. The effect of aluminum level is appreciable but plasticizer level has essentially no effect on specific impulse (Fig. 9). Slightly higher impulse can be obtained at higher solids levels at a sacrifice in processibility.

3.2.2 Specific Impulse Measurements

The specific impulse of CTPB propellants at various aluminum levels was determined from firings in 2C1.5-4 motors which contained about 0.3 lbm of propellant (Fig. 10). Compositions containing from 1% to 25% aluminum (RH-C-27 to RH-C-32) were investigated. The oxidizer was a 50/50 bimodal blend of 15μ/200μ ammonium perchlorate and the aluminum was 3μ Alcoa 140. Five motors were fired from each batch.

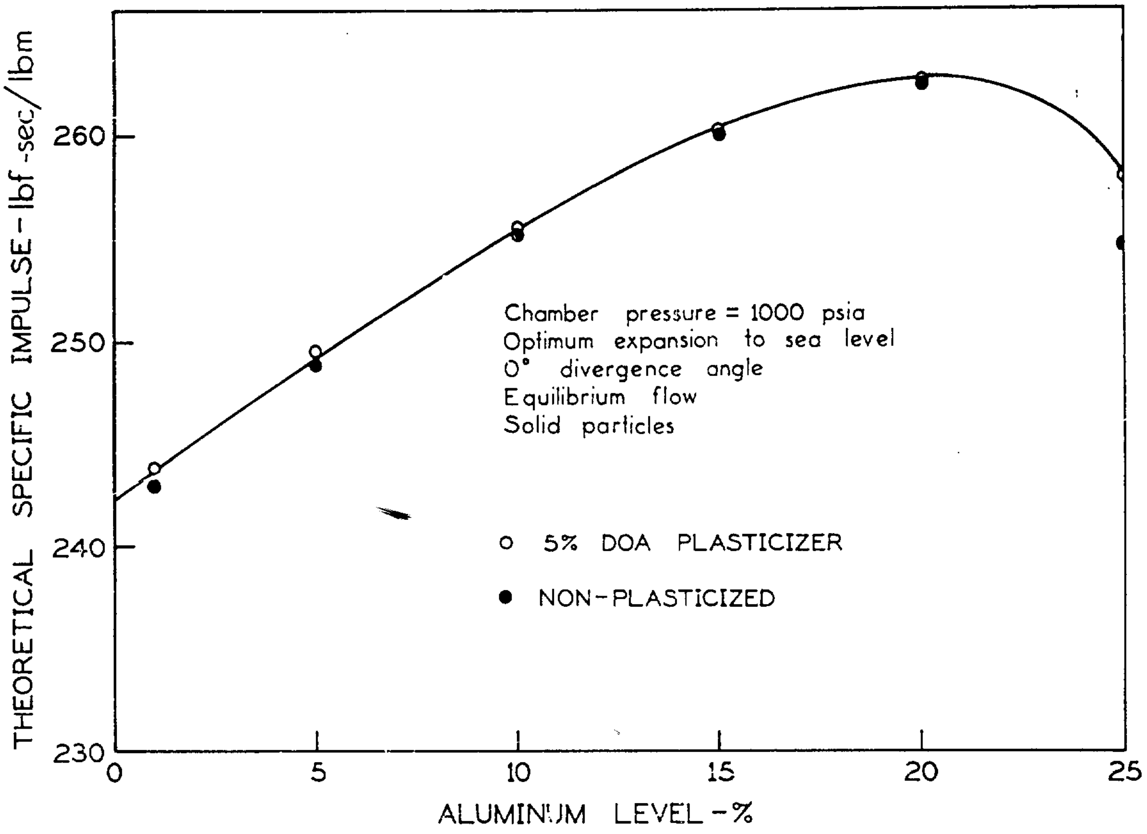

Fig. 9 Theoretical specific impulse vs. aluminum level for CTPB propellants at 85% total solids.

6C5-11.4 motors containing about 6 lbm of propellant were fired at 10% and 20% aluminum levels. Maximum specific impulse values were obtained between 5% and 20% aluminum (Table VI). The specific impulse efficiency decreased almost linearly over the entire range (Fig. 11). Slightly higher efficiencies were obtained in the six-inch motors due to better combustion efficiency and lower two-phase-flow losses. More detailed impulse scaling studies are discussed later in the report.

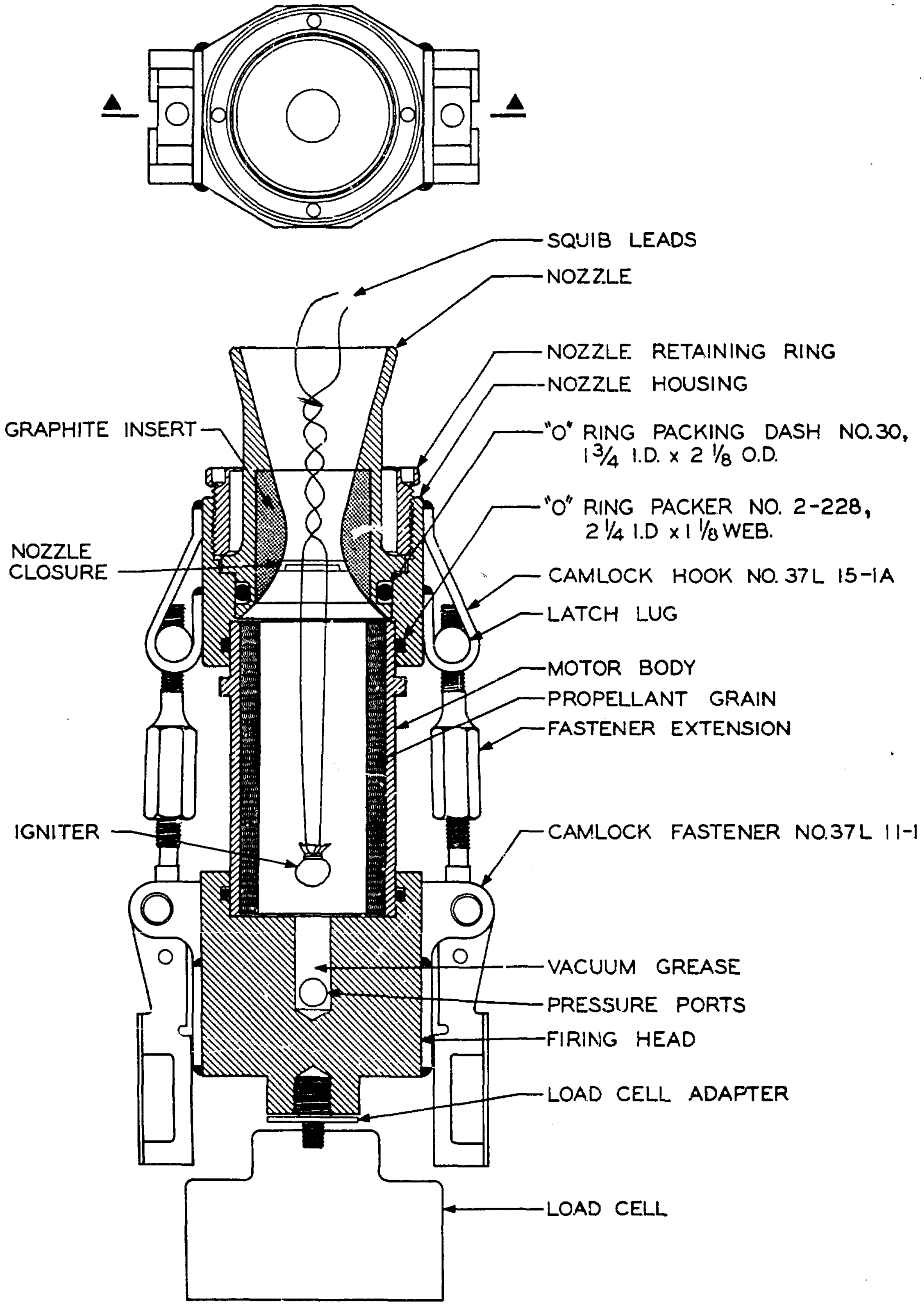

Fig. 10 Clamp-type 2C1.5-4 motor firing assembly.

Table VI

Specific Impulse of CTPB Propellants at Various Aluminum Levels

(85% total solids; oxidizer was a 50/50 blend of 15μ/200μ)

Composition No.	Aluminum Level[a] (%)	$I^{0\,b}_{sp}$ (lbf-sec/lbm)	F^{0}_{1000} (2C1.5-4) (lbf-sec/lbm)	F^{0}_{1000} (6C5-11.4) (lbf-sec/lbm)
RH-C-27	1	243.8	234.9	----
RH-C-28	5	249.5	236.4	----
RH-C-29	10	255.5	237.3	240.6
RH-C-30	15	260.1	236.4	----
RH-C-31	20	262.6	235.3	240.4
RH-C-32	25	257.9	229.3	----

[a] Alcoa 140

[b] Chamber pressure = 1000 psia, optimum expansion to sea level, zero divergence angle, equilibrium flow with solid particles

To determine the effect of aluminum particle size on impulse efficiency, propellants containing 10% and 20% of 20μ and 30μ aluminum were fired in 2C1.5-4 motors and compared with the compositions fired with 3μ aluminum. The oxidizer blend was also the same. The specific impulse did not decrease with larger size aluminum but remains nearly constant (Table VII). Good ignition, traces and reproducibility were obtained.

For certain applications, propellant burning rates around 0.20 in/sec at 1000 psia are required. Several compositions were made containing predominantly large size ammonium perchlorate (82% 400μ, 12% 55μ, 6% 15μ) to study impulse and combustion efficiency in this region. Three aluminum types and two aluminum levels were investigated. In 2C1.5-4 firings, there was no difference in specific impulse at 10% aluminum when compared with compositions containing smaller size oxidizer (Table VIII). However, at 20% aluminum, the specific impulse decreased about 10 units. No slag build-up in the nozzle was noticed even at the largest aluminum size and level and there was very little effect of aluminum particle size on specific impulse. Composition RH-C-31 burned at 0.2 in/sec at 1000 psia. Ignition of these compositions was more difficult due to the larger size oxidizer.

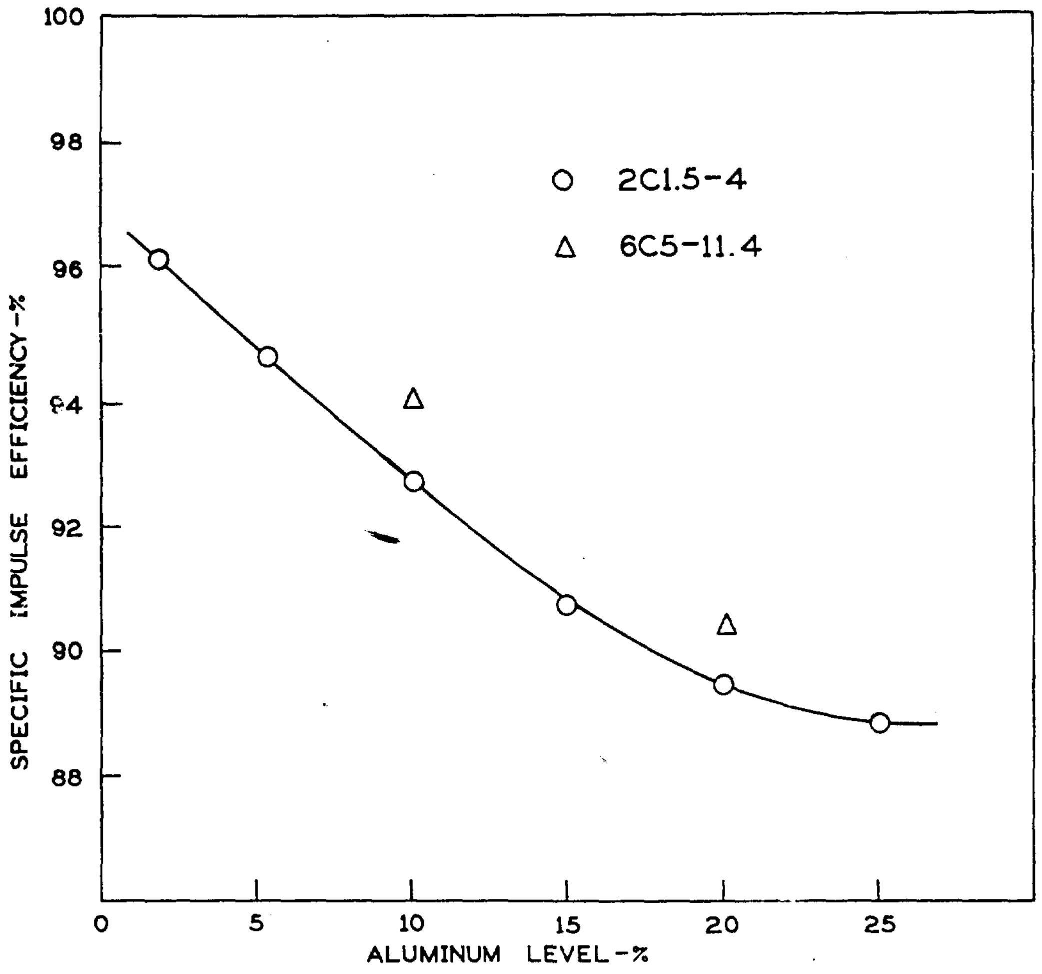

Fig. 11 Impulse efficency vs. aluminum level for CTPB propellants at 85% total solids.

Table VII

Effect of Aluminum Particle Size on Specific Impulse

(85% total solids ; Oxidizer was a 50/50 blend of 15μ/200μ)

Aluminum Particle Size (microns)	Aluminum Level (%)	F^0_{1000} (lbf-sec/lbm)
3[a]	10	237.3
10[b]	10	236.2
30[c]	10	238.5
3[a]	20	235.3
10[b]	20	236.5
30[c]	20	236.3

[a] Alcoa 140
[b] Valley H-10
[c] Valley H-30

Table VIII

Specific Impulse of Low Burning Rate CTPB Propellants in 2C1.5-4 Motors

(85% total solids ; Oxidizer was a 82/12/6 blend of $400\mu/55\mu/15\mu$)

Propellant Composition	Aluminum Level (%)	F^0_{1000} (lbf-sec/lbm)		
		(3μ)[a]	(10μ)[b]	(30μ)[c]
RH-C-27	1	238.1	----	----
RH-C-29	10	239.5	239.1	240.0
RH-C-31	20	226.4	227.8	228.1

[a] Alcoa 140
[b] Valley H-10
[c] Valley H-30

3.2.3 Specific Impulse in Large Motors

Impulse scaling factors,[1] which can be used for the prediction of specific impulse in large motors, were determined for two CTPB propellant compositions. A basic composition (RH-C-2) and a similar composition containing 1% ferrocene (RH-C-14) were fired in 6C5-11.4 motors and three lengths of two-inch motors. The 8- and 16-inch lengths were stacked 2C1.5-4 cases. At least five motors of each size were fired. A summary of ballistic data for these compositions is given in Table IX. As with previous scaling studies on other propellant systems, burning rate was not a function of motor size whereas K_m and F^0_{1000} were dependent on heat loss and two phase flow.

Scaling factors, which were determined on a digital computer, were in close agreement for the two compositions (Table X).

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[1] "Ballistic Evaluation of Propellants in Micro-Motors," Rohm & Haas Company, Report S-49, October 1964.

Table IX

Summary of Ballistic Data from Various Size Motors[a]

	K_m	$\bar{P}_b$ (psia)	$\bar{r}_b$ (in/sec)	F^0_{1000} (lbf-sec/lbm)	Impulse Efficiency (%)
		2C1.5-4			
RH-C-2	266.7	1041	0.412	231.3	88.7
RH-C-14	184.4	1110	0.629	238.7	91.6
		2C1.5-8			
RH-C-2	261.4	1044	0.411	236.7	90.8
RH-C-14	175.9	1050	0.617	241.7	92.7
		2C1.5-16			
RH-C-2	258.2	1041	0.411	238.9	91.6
RH-C-14	169.6	1018	0.615	244.4	93.7
		6C5-11.4			
RH-C-2	252.0	995	0.428	235.4	90.3
RH-C-14	174.8	997	0.606	243.3	93.3

[a] Five motors fired each configuration for each composition.

Table X

Comparison of Scaling Factors for RH-C-2 and RH-C-14

	N, effective particle diameter (microns)	q, effective heat flux, (Btu/ft^2-sec)
RH-C-2	1.0	1200
RH-C-14	1.0	1300

The specific impulse efficiency in the small test motors was 2 to 3% higher with the ferrocene-catalyzed propellant. However, when the specific impulse was scaled to a low-heat-loss motor containing about 100 lbm of propellant[1], the values were 247.5 and 248.3 lbf-sec/lbm for RH-C-2 and RH-C-14 respectively. A comparison of the specific impulse efficiencies shows that the burning-rate-catalyst ferrocene does not actually improve

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[1] 5KS4500, Unit 96, Rocket Motor Manual, SPIA/MI, Vol. I, Chemical Propulsion Information Agency, Silver Spring Maryland, September 1964.

combustion efficiency per se, but that the higher burning rate reduces heat losses and leads to higher measured impulse values in small motors (Table XI). The measured performance in large motors will be about the same.

Table XI

Effect of Ferrocene Catalyst on Specific Impulse Efficiencies in Several Motors

	RH-C-2	RH-C-14
ZL 434 Polymer	10.1	10.1
Ammonium Perchlorate, {50/50 blend of 15μ/200μ}	68.9	67.9
Dioctyl Adipate	5.0	5.0
Aluminum	16.0	16.0
Ferrocene	----	1.0
r_b at 1000 psia, in/sec	0.40	0.61
K_{1000} (6C5-11.4)	252	178
Theoretical Specific Impulse, lbf-sec/lbm	260.7	260.7
Specific Impulse Efficiency (2C1.5-4)	88.7	91.6
Specific Impulse Efficiency (2C1.5-8)	90.8	92.7
Specific Impulse Efficiency (2C1.5-16)	91.6	93.7
Specific Impulse Efficiency (6C5-11.4)	90.3	93.3
Specific Impulse Efficiency (5KS4500)	94.9	95.2

3.3 Temperature Coefficient of CTPB Propellants

Temperature coefficient measurements were made on composition RH-C-2 by firing 2C1.5-4 motors at a constant K_m but at three different temperatures. The motors were enclosed in styrofoam containers and conditioned at the firing temperature for at least twenty-four hours. A photograph of an assembled motor ready for conditioning is shown in Fig. 12. Thermocouple measurements made on this assembly showed that the temperature of the propellant grain changed less than 1°F during the time interval between conditioning and firing. Excellent reproducibility in average pressure at each temperature was obtained owing to the precise control of temperature and careful control of K_m (Table XII). Four motors each were fired at -13°F, 62°F, and 130°F.

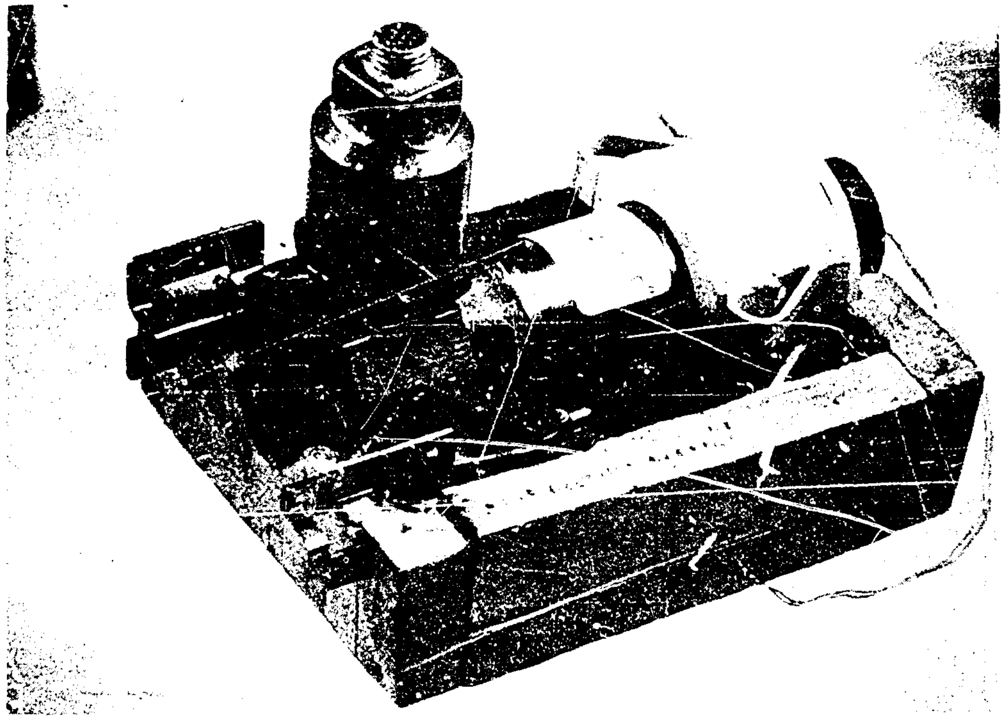

Fig. 12a Cut-away of insulated box for 2-inch motor.

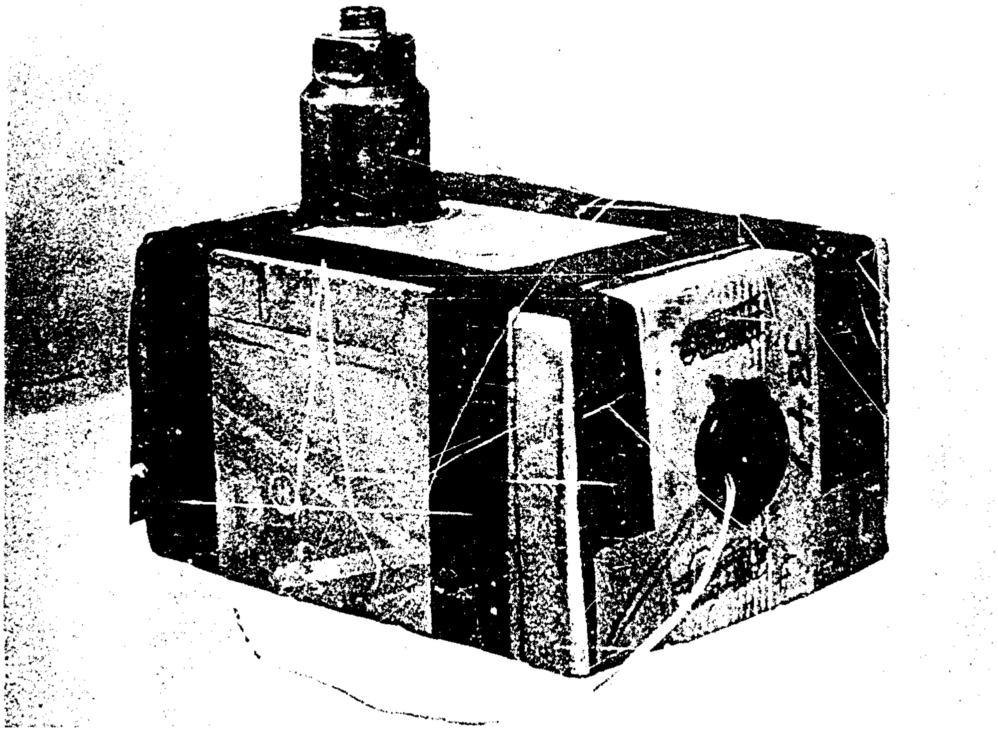

Fig. 12b Insulated 2-inch motor ready for firing.

Table XII

Temperature Coefficient Data for RH-C-2

	K_m	$\overline{P}_b$ (psia)	$\overline{r}_b$ (in/sec)	$\int P_b dt / \int P_{total} dt$	Nozzle dia. (in.)
			-13°F		
	250.4	930	.399	.96	.322
	254.6	940	.401	.96	.319
	250.8	932	.397	.97	.320
	248.2	934	.391	.98	.321
Avg.	251.0	932	.397	.97	.321
			62°F		
	252.1	1041	.427	.95	.321
	254.2	1043	.440	.97	.319
	253.5	1026	.425	.98	.319
	251.1	1023	.431	.96	.320
Avg.	252.7	1033	.431	.96	.320
			130°F		
	250.8	1102	.459	.98	.318
	247.6	1066	.449	.97	.320
	249.3	1083	.449	.97	.321
	249.7	1017	.459	.96	.322
Avg.	249.4	1082	.454	.97	.320

The calculated temperature coefficients were

π_K (cold) -13°F to 62°F = 0.13%/°F

π_K (hot) 62°F to 130°F = 0.07%/°F

π_K (overall -13°F to 130°F = 0.10%/°F

These data substantiate the excellent temperature coefficient of about 0.10%/°F, reported by other agencies.

4. Summary

Composite propellants based on carboxyl-terminated polybutadiene binder are quite versatile in both processibility and ballistic properties. The use of a plasticizer to reduce viscosity improves processibility without affecting ballistic properties. Burning rates can be varied quite extensively by control of oxidizer particle size, aluminum particle size and level, and catalysis.

Specific impulse efficiencies were low in small test motors owing to two-phase-flow losses (except at low aluminum levels). Ferrocene increases burning rate significantly but does not increase impulse in large motors. Temperature coefficients were low.

Appendix A

CTPB DUMMY FORMULATIONS

Composition No.	Ingredients—Wt. %					
	ZL434,[a] MAPO,[b] ERLA,[c] Iron Linoleate	Aluminum	Sodium Chloride	Ammonium Perchlorate	Dioctyl Adipate	TP90B[d]
CT-1	17.68	9.30	70.23	---	2.79	---
CT-3	15.00	10.00	72.00	---	3.00	---
CT-4	13.00	10.00	74.00	---	3.00	---
CT-5	16.00	10.00	72.00	---	2.00	---
CT-6	17.00	10.00	72.00	---	1.00	---
CT-7	18.00	10.00	72.00	---	---	---
CT-8	17.68	9.30	67.23	3.00	2.79	---
CT-9	14.00	10.00	69.00	3.00	4.00	---
CT-10	17.00	10.00	69.00	3.00	1.00	---
CT-11	13.00	10.00	69.00	3.00	5.00	---
CT-12	12.00	10.00	69.00	3.00	6.00	---
CT-13	11.00	10.00	69.00	3.00	7.00	---
CT-14	8.00	10.00	73.00	3.00	6.00	---
CT-15	14.00	15.00	64.00	3.00	4.00	---
CT-16	14.00	20.00	59.00	3.00	4.00	---
CT-17	10.00	16.00	66.00	3.00	5.00	---
CT-18	14.00	15.00	62.00	5.00	4.00	---
CT-19	16.00	10.00	69.00	3.00	2.00	---
CT-20	14.00	15.00	64.00	3.00	---	4.0
CT-21	15.00	10.00	69.00	3.00	3.00	---

[a] Carboxyl-terminated polybutadiene polymer, Thiokol Chemical Corporation, Trenton, New Jersey.

[b] Tris[1-(2-methyl)oziridinyl]phosphine oxide, International Chemical Company, Newark, New Jersey.

[c] Trifunction epoxide, Bakelite Division of Union Carbide Chemical Company, New York, New York.

[d] Plasticizer, Thiokol Chemical Corporation, Trenton, New Jersey.

Appendix B

CTPB PROPELLANT FORMULATIONS

Composition No: RH-C	1	2	3	4	5[a]	6[a]
ZL 434-MAPO-ERLA	10.0	10.0	12.0	12.9	69.0	74.0
Ammonium Perchlorate	68.9	68.9	68.9	68.0	30.0	25.0
Aluminum	16.0	16.0	16.0	16.0	----	----
Dioctyl Adipate	----	5.0	3.0	----	----	----
Butyl Carbitol Formal (TP-90B)	5.0	----	----	2.0	----	----
Ferrocene	----	----	----	1.0	----	----
Iron Linoleate	0.1	0.1	0.1	0.1	1.0	1.0

Composition No: RH-C	7[a]	8	9	10[a]	11[a]	12
ZL 434-MAPO-ERLA	79.0	9.0	12.9	84.0	89.0	9.0
Ammonium Perchlorate	20.0	69.0	68.0	15.0	10.0	70.0
Aluminum	----	16.0	16.0	----	----	16.0
Dioctyl Adipate	----	4.9	2.0	----	----	4.9
Ferrocene	----	1.0	1.0	----	----	----
Iron Linoleate	1.0	0.1	0.1	1.0	1.0	0.1

Composition No: RH-C-	13	14	15[a]	16[a]	17[a]	18[a]
ZL 434-MAPO-ERLA	9.9	10.0	64.0	64.0	64.0	99
Ammonium Perchlorate	68.0	67.9	15.0	15.0	15.0	----
Plasticat IV[c](n-butyl ferrocene)	8.0	----	----	----	----	----
Aluminum	14.0	16.0	----	----	----	----
Dioctyl Adipate	----	5.0	----	----	----	----
Ferrocene	----	1.0	1.0	----	----	----
Copper Chromite	----	----	----	1.0	----	----
Acryloid®[b] K-120	----	----	19.0	19.0	20.0	----
Iron Linoleate	0.1	0.1	1.0	1.0	1.0	1.0

Composition No: RH-C-	19	20	21	22[a]	23[a]	24[a]	25[a]	26[a]
ZL 434-MAPO-ERLA	15.75	15.65	15.50	64	64	64	64	15.9
Ammonium Perchlorate	68.00	68.00	68.00	20	25	30	35	66.0
Aluminum	16.0	16.0	16.0	---	---	---	---	18.0
Ferrocene	0.15	0.25	0.40	---	---	---	---	---
Acryloid® [b] K-120	---	---	---	15.0	10.0	5.0	---	---
Iron Linoleate	0.10	0.10	0.10	1.0	1.0	1.0	1.0	0.1

Composition No: RH-C-	27	28	29	30	31	32	33
ZL 434-MAPO-ERLA	9.9	9.9	9.9	9.9	9.9	9.9	18.4
Ammonium Perchlorate	84.0	80.0	75.0	70.0	65.0	60.0	40.0
Aluminum	1.0	5.0	10.0	15.0	20.0	25.0	8.5
Dioctyl Adipate	5.0	5.0	5.0	5.0	5.0	5.0	3.0
RDX	----	----	----	----	----	----	30.0
Iron Linoleate	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Composition No: RH-C-	34[a]	35[a]	36[a]	37[a]	38[a]	39	40
ZL 434-MAPO-ERLA	49	44	39	54	64	9.9	17.9
Ammonium Perchlorate	40	45	50	35	20	85.0	75.0
Acryloid® [b] K-120	10	10	10	10	14	----	----
Ferrocene	----	----	----	----	1	----	----
Dioctyl Adipate	----	----	----	----	----	5.0	7.0
Iron Linoleate	1.0	1.0	1.0	1.0	1.0	0.1	0.1

[a] Hybrid Propellant
[b] Rohm & Haas Company, Philadelphia, Pennsylvania
[c] Thiokol Chemical Corporation, Huntsville, Alabama

Appendix C

TABLE OF NOMENCLATURE

F^0_{1000} = specific impulse corrected to 1000 psia chamber pressure, optimum expansion ratio at sea level atmospheric pressure (14.7 psia), and 0° nozzle exit divergence angle.

K_m = $S_m / \overline{A}_t$, where S_m is an integral average surface area and $\overline{A}_t$ is the arithmetic average of throat area before and after firing.

μ = micron

$\overline{P}_b$ = average pressure over burning time

π_K = temperature coefficient based on pressure, $\frac{\partial(\ell nP)}{\partial T}$

$\overline{r}_b$ = average burning rate over the burning time

I^0_{sp} = theoretical specific impulse

Initial distribution of this report was made in accordance with the Joint Army-Navy-Air Force mailing lists for Solid Propellant and Liquid Propellant technical information plus approved supplements

SUPPLEMENTARY

INFORMATION

AD-361714

ERRATA

In Rohm & Haas Co., Redstone Division, Report S-64 the publication date was inadvertantly left off the title page. Please write-in the date, June 22, 1965.