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COMBUSTION DYNAMICS LABORATORY

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"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"

Professor Harold C. Beachell

Principal Investigator

February, 1968

Research Sponsored by:

**Air Force Office of Scientific Research
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FOREWORD

This research at the University of Delaware under Grant AF-AFOSR 922-67 for the period November 1, 1967, through January 31, 1968 was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

Air Force Director for this program is Dr. B. T. Wolfson, Propulsion Division, Directorate of Engineering Sciences, Air Force Office of Scientific Research.

ABSTRACT

The crystalline oxidizers methyl, dimethyl, and trimethyl ammonium perchlorate have been prepared as rhombic crystals. The methyl A.P. has an atmospheric pressure burning rate two and one half times as fast as ammonium perchlorate. The thermal stability is comparable to that of A.P., although the methyl derivative is perfectly balanced chemically for a CH₂/A.P. type system. The flame temperature is twice that of A.P.

This system of A. P. derivatives should prove useful in determining the value of bringing high temperature flames closer to propellant surfaces in the overall study of combustion dynamics.

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I Introduction

A fundamental understanding of the combustion characteristics of a range of physical conditions of crystalline oxidizers is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involves theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. A strandburner, window bomb and high-speed motion picture photography will be used to obtain burning rates versus pressure, and to record stability of combustion for a variety of particle sizes and pressure (density) packings of selected crystalline oxidizers (i.e., ammonium perchlorate) and analogous compounds. The study of large single crystal burning will remove particle size, shape and packing factors as complications. Data from low bulk density powder combustion studies, when compared with single crystal data, provides vital information about combustion zone thickness, ignition and conductivity contributions to the overall combustion phenomena. In addition, it is believed that simple combustion tests of powder oxidizer samples can serve as an efficient screening technique for determining whether chemical modifications have increased or decreased the intrinsic burning rate. Crystalline decomposition mechanisms observed during burning will be related to the oxidizer intrinsic burning rate and the basic properties of the oxidizer such as chemical nature, crystal type, and ion sizes. The validity of the models will be determined by correlation with the experimental data obtained.

Prior work in these laboratories, and also at Thiokol Chemical Corp., Atlantic Research Corp., Naval Weapons Center, China Lake and University of California have shown that anion or cation changes to the standard crystalline oxidizers can produce profound changes in combustion characteristics.

At University of Delaware, it was determined that simple alkyl substitutions for the hydrogens in the NH_4^+ cation would provide materials useful in combustion evaluations. It was decided that mono-, di-, and trimethyl ammonium perchlorate should be the starting compounds. DTA data and oxidizer powder burning rates for each compound would be measured, and compared with A.P. as the control. There was little information available in the literature on these compounds. During the early 1900's, there were two studies (1, 2) of a series of alkyl ammonium perchlorates; one concentrating on solubilities - and one on explosion temperatures. Subsequently, there was a U.S. patent issued for methyl ammonium perchlorate as an explosive (3). Our interest was in combustion characteristics of these materials . . . and no information was uncovered in that area.

II. Preparation of Substituted Ammonium Perchlorates

The most straightforward and safest method of preparing pure substituted A.P.'s was felt to be the neutralization reaction of amine with perchloric acid in water solution. The amines solutions (methyl, dimethyl and trimethyl) ranged from 40% to 25% by weight in water. The perchloric acid used was 24% by weight in water.

In the preparation of one gram mole of methyl ammonium perchlorate, the dropwise addition of dilute HClO_4 produced a maximum temperature rise of 20°C , even with ice bath cooling of the $1/2$ liter reaction flask.

When reaction was completed, a rotary vacuum evaporator was applied to draw off excess amine and water. The sample was then recrystallized and dried in a vacuum desiccator. The crystals were rhombic and resembled ammonium perchlorate. The crystal density, based on an average of four determinations in methyl polysiloxane, was 1.6484g/cc at 20.20°C . A rough estimate of sensitivity was obtained by subjecting samples of the methyl compound to hammer blows against a steel block, and qualitatively comparing results with pure A.P. Although the methyl ammonium perchlorate was harder to initiate than A.P.; when it did explode, it gave a louder report.

The dimethyl and trimethyl substituted compounds were prepared in essentially the same fashion.

The purified crystals were carefully removed from the final drying watchglasses, and ground in small quantities. The resulting powders were screened to obtain the -40 +50 mesh (350 micron) fraction and stored in sealed bottles. Based on solubilities, it is believed that methyl A.P. is more hygroscopic than A.P.; and dimethyl A.P. and trimethyl A.P. are less hygroscopic.

Further density, purity and stability determinations are needed.

III. Differential Thermal Analysis

The most meaningful single analytical test for oxidizer powders was felt to be D.T.A. DuPont Model 900 apparatus was used with a micro sample tube, at a heating rate of 20°C/min. , and with glass beads as the thermal reference.

Figure 1 shows the standard D.T.A. thermogram for pure A.P. The single sharp endotherm showing orthorhombic to cubic transition appears at about 240°C . The single exotherm begins gradually at about 300°C . and peaks at about 405°C . (Impure

Figure 1

DTA ULTRA HIGH
PURITY AMMONIUM
PERCHLORATE

SIZE: Micro (2 mm depth)

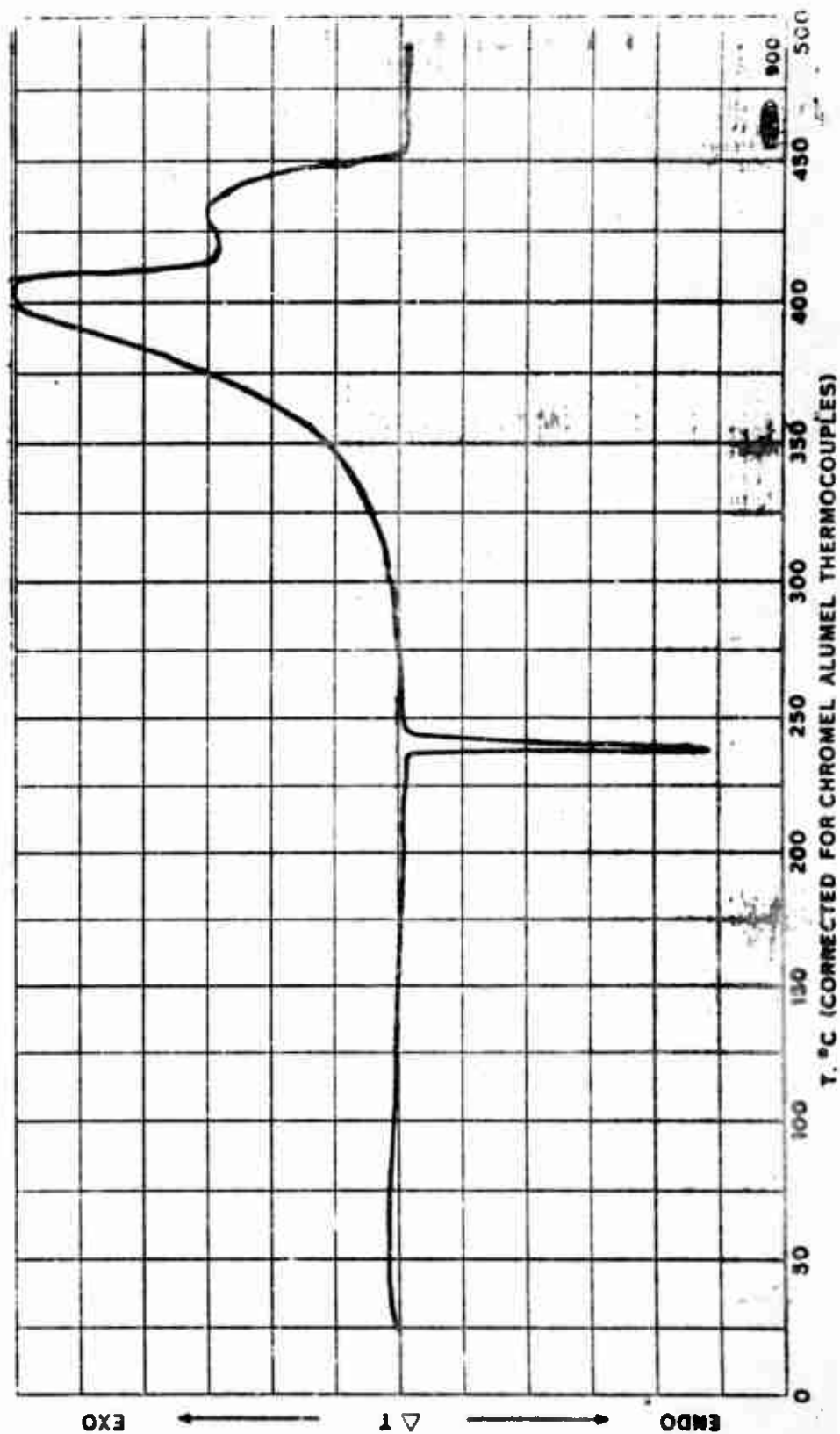
SCALF: 50°C/in.

ATTN NO. AP-1

REF: Glass bead

RATE: 20°C/min.

START: 35.2°C.



A.P. also shows a sharp exotherm at 300-320°C).

Figure 2 is a thermogram for methyl ammonium perchlorate showing two sharp endotherms; one at 175°C., and one at 257°C. The exotherm begins at 300°C. and peaks at 350°C.; or about 55°C. lower than A.P.

Figure 3, the dimethyl ammonium perchlorate thermogram, shows a single endotherm at about 172°C. At about 275°C., the exotherm begins and peaks at about 330°C.; or about 75°C. lower than A.P.

Figures 4 and 5 are thermograms for trimethyl ammonium perchlorate. The material in Figure 4 was not purified and shows an extra low temperature endotherm and a slight general shifting of the other peaks.

Figure 5 (trimethyl ammonium perchlorate - purified), shows the three sharp endotherms at 115°C., 200°C. and 280°C. The exotherm seems partially influenced by the last endotherm, but at any rate, peaks at about 310°C, or about 95°C. below that of pure A.P.

Table 1 summarizes this data. With increasing alkyl substitution, there is a decrease in both initial endotherm, and in the exotherm. The thermograms show a decrease in thermal stability with increasing alkyl content. However, the most sensitive compound (trimethyl) is not considered hazardous from this point of view. More sophisticated impact sensitivity

TABLE 1

Thermal Response of Alkyl Substituted
Ammonium Perchlorates

<u>Compound</u>	<u>Endotherm(s) (°C.)</u>	<u>Exotherm (°C.)</u>
Ultra high purity ammonium perchlorate	240	405
Methyl ammonium perchlorate	175, 257	350
Dimethyl ammonium perchlorate	172	330
Trimethyl ammonium perchlorate	115, 200, 280	310

tests are needed next - and possibly friction tests. The simple tests with a hammer against a steel block show that these materials are not extremely sensitive to shock.

FIGURE 2

DTA MONOMETHYL
AMMONIUM PERCHLORATE

SIZE: Micro 3 mm depth. SCALE SETTING: 50°C/in.
1°C/in.

REF: Glass leads

RATE: 20°C/min.
START: 39.1°C

RUN NO. MV 2

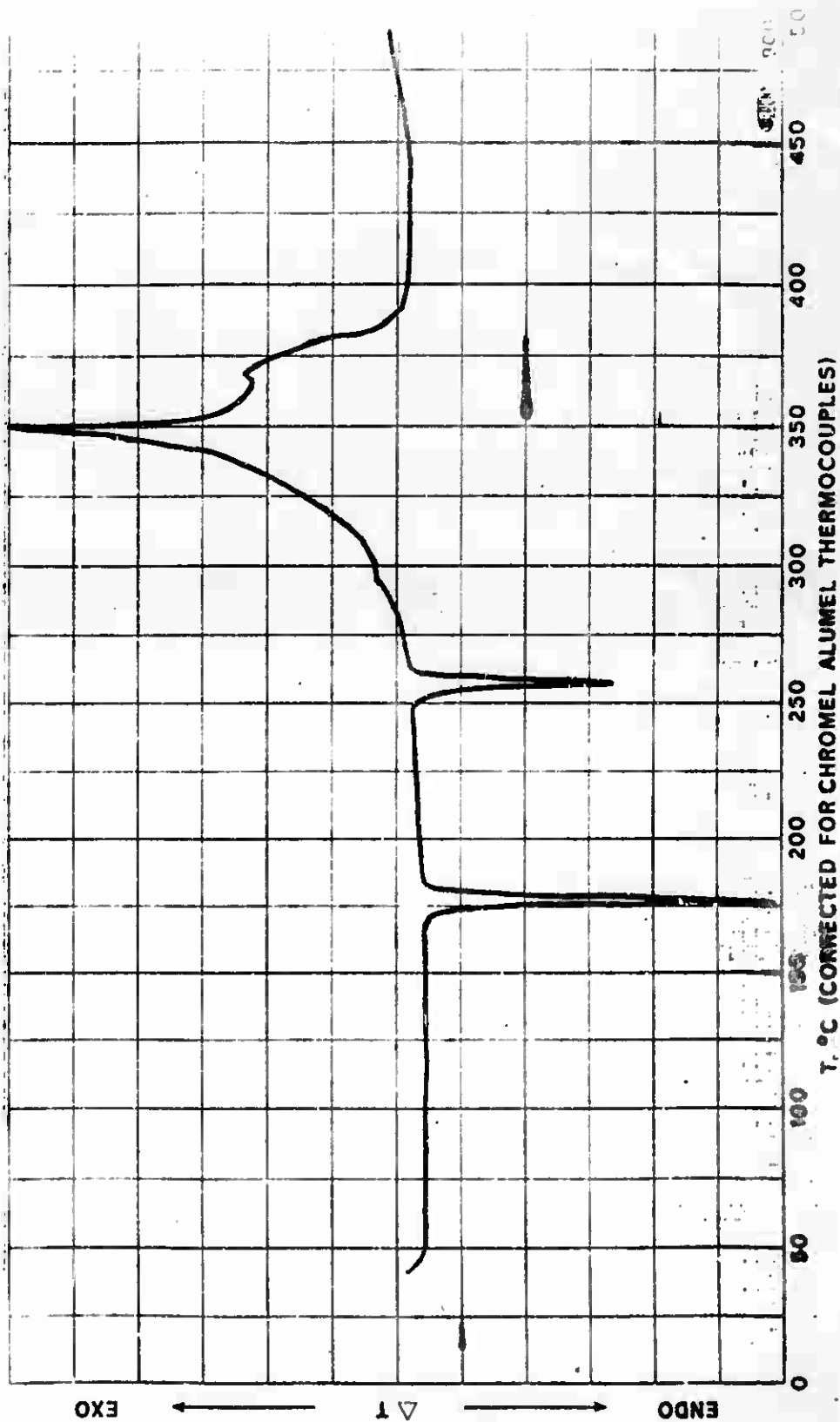


FIGURE 3

DTA DIMETHYL AMMONIUM
PERCHLORATE

SIZE: 3 mm Depth in Micro Tube

SCALE SETTING: 50°C/in.
1°C/in.

REF: Glass beads

RATE: 20°C/min.

START: 39°C.

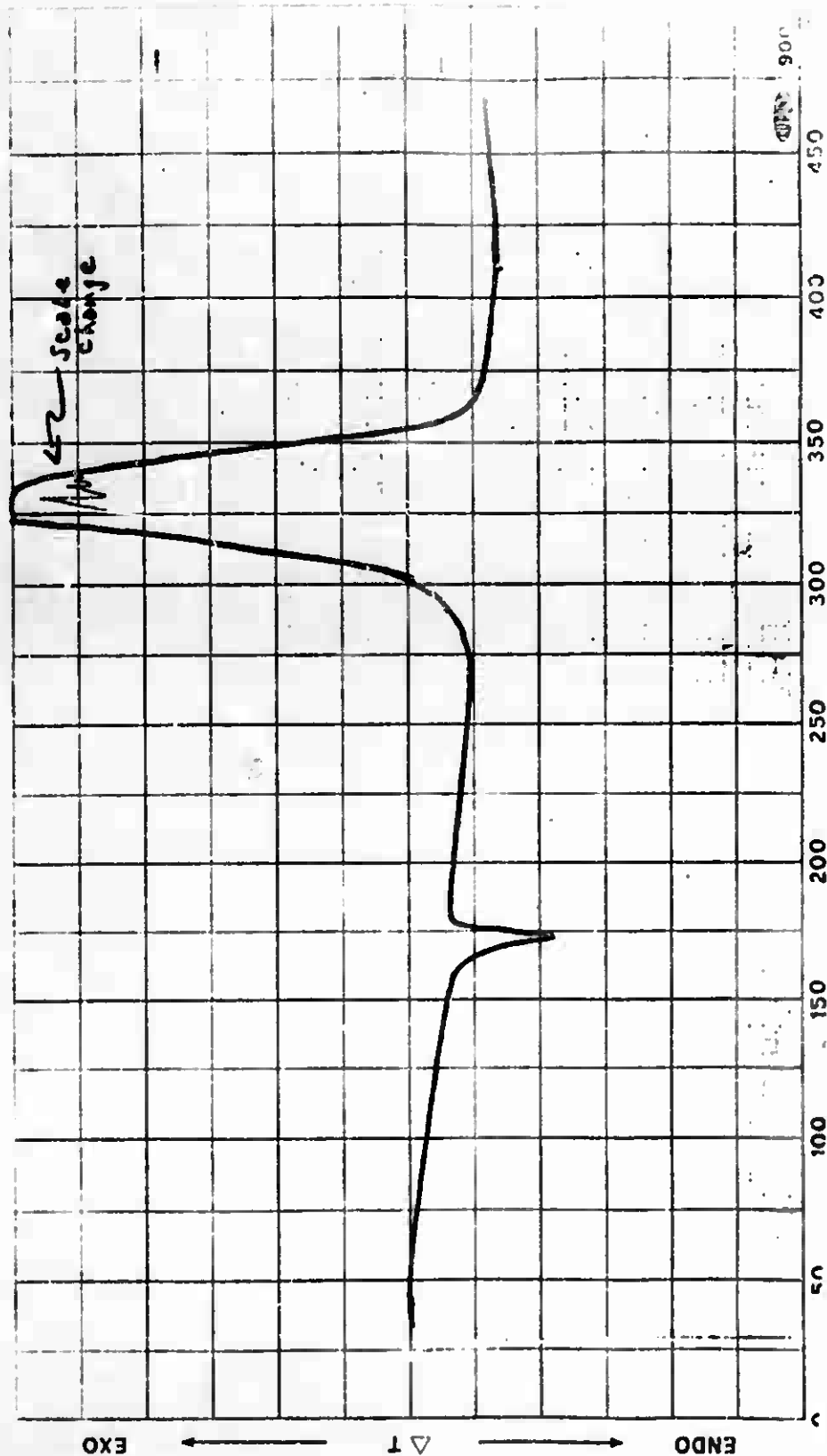


FIGURE 4

DTA
TRIMETHYL AMMONIUM
PERCHLORATE
(T.M.P.R.E.)

SIZE: Micro 3 mm depth

REP: Glass beads

RATE: 20°C/min.

START: 29.1°C.

SCALE SETTING: 50°C/in.
1 mil 2°C/in.

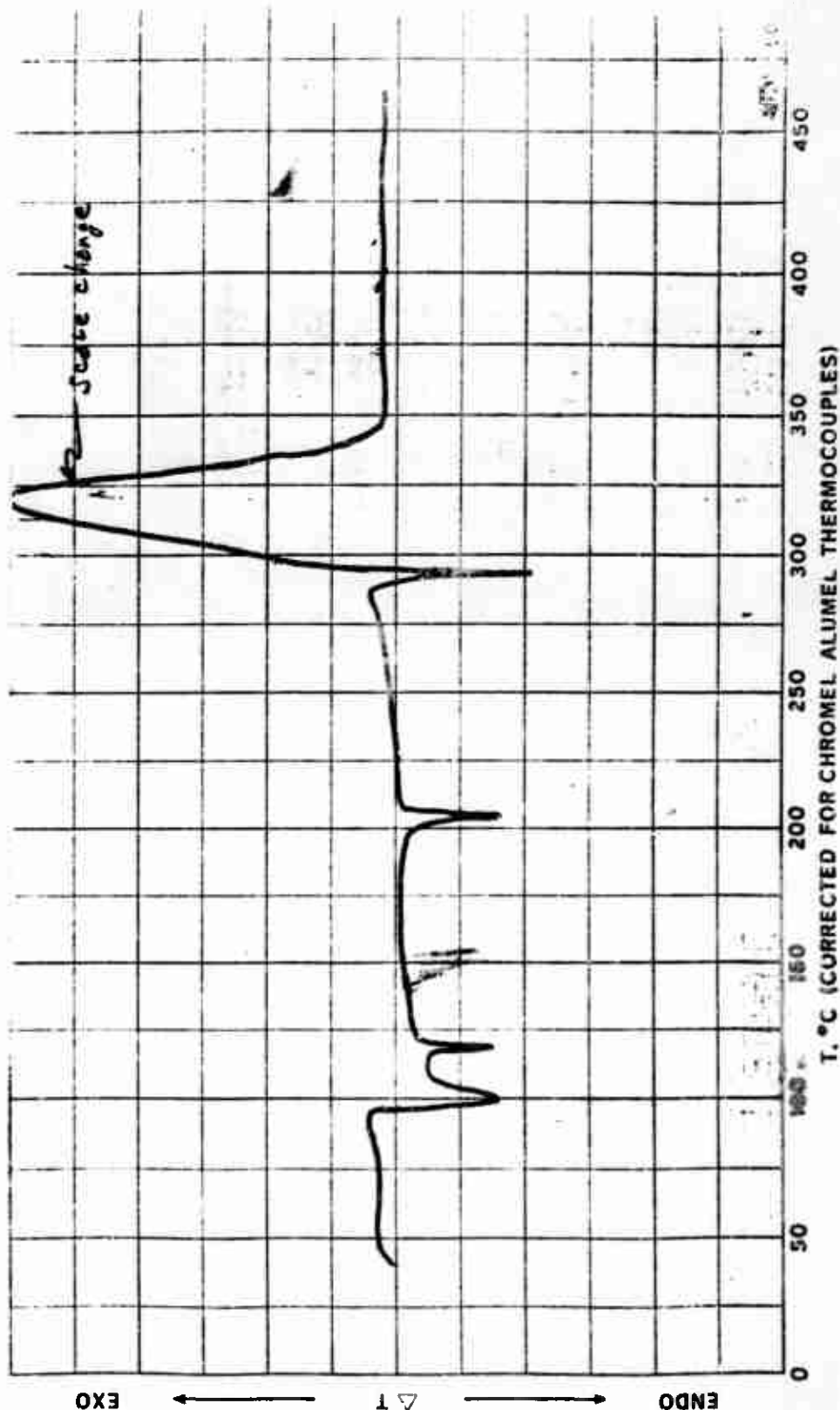


FIGURE 5

DTA THERMITY:
AMMONIUM PERCHLORATE
(POPE)

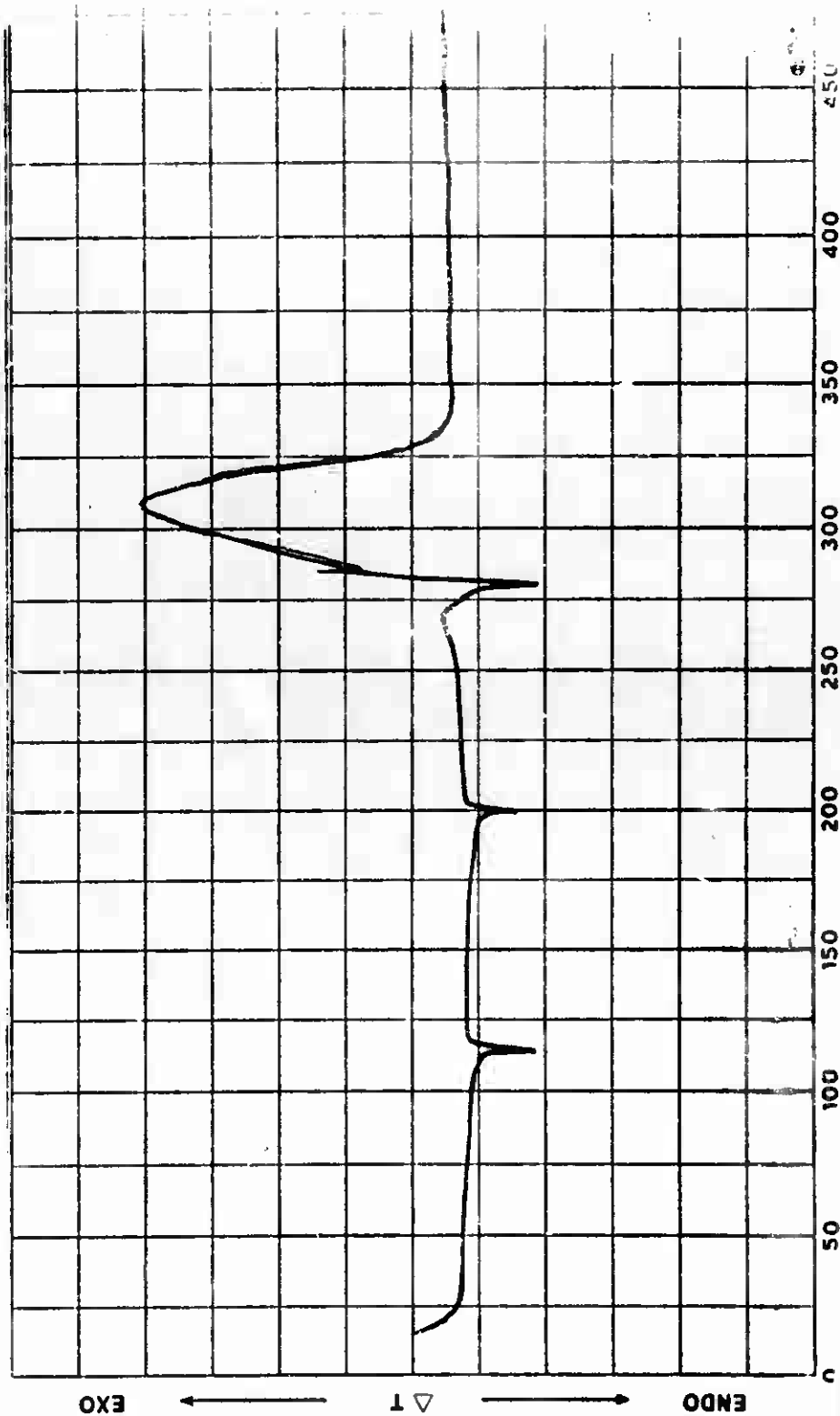
SIZE: Micro (3 mm depth)

REF: glass beads

RATE: 20°C/min.

START: 58.1°C.

SCALE SETTING: 50°C/in.
200 in.



IV. Combustion Testing

The first type of combustion test run in these laboratories, when investigating a new monopropellant, is the straw burning test of the powdered material. The important control features when running these tests to assure accuracy and reproducibility have been described. (4)

During this quarter, the atmospheric pressure burning rate for methyl ammonium perchlorate was determined. Pure A.P. was used as the control. The samples were -40 +50 mesh dry powders loaded to the pour density (1/2 of crystal density) in 6.5 mm diameter tubes. The burning rates obtained, in air, at ambient pressure, averaged from at least four tests, were:

NH_4ClO_4 - 0.043 inches/sec.

$\text{CH}_3\text{NH}_3\text{ClO}_4$ - 0.103 inches/sec.

Thus the methyl derivative had a burning rate of about 2-1/2 times that of pure A.P. Visual observation of M.A.P. burning showed a flame height of ten to fifteen times higher than that of A.P. - and also a bright orange color as compared with A.P.'s faint blue color.

Whereas A.P. powder is relatively insensitive to tube diameter, the M.A.P. would not burn reproducibly in 4 mm i.d. or smaller tubes. When it did burn, there were burning pulsations with a frequency of about one every two seconds. The quiescent portion of the pulse indicates an incipient quenching condition. In the 6.5 mm tube, there were no pulsations. Thus under these test conditions the quench diameter was 4 mm. A good discussion of other aspects of quench diameters has been given by Von Elbe and McHale (5).

Preliminary tests with the di- and tri- substituted compounds indicates burning rates midway between A.P. and M.A.P. Further work will be conducted in the next quarter.

V. Calculated Combustion Properties of Alkyl Substituted Ammonium Perchlorates

Although the heat of formation of methyl ammonium perchlorate (MAP) has not yet been determined, we estimate it to be in the range of -60 to -80 Kcal/Mole.

Related perchlorates have values in this range. Ammonium perchlorate, for example, has a standard heat of formation (ΔH_f°) of about -70.7 Kcal/Mole. When one hydrogen is replaced with hydroxyl, to give hydroxylammonium perchlorate, the value is -66.5 Kcal per Mole (Reference 5). Considerably further afield, the value for

hydrazine diperchlorate is -72 Kcal/Mole.

A rough estimate of the heat of formation of MAP can be derived from the observed reaction conditions during synthesis, if we neglect solution effects. When a one mole quantity of MAP was prepared in a total aqueous reaction mixture of about a kilogram; an estimate of the temperature rise of the uncooled mixture was about 20°C. Taking the specific heat of the reaction mix as an average of 1 cal/gram °C, this would give a heat of reaction of -20 Kcal/Mole. The following estimate can then be made:

ΔH_f° aqueous methylamine	=	<u>Kcal/Mole</u>
		-17.0
ΔH_f° aqueous perchloric acid	=	-30.0
ΔH_r of amine and acid	=	<u>-20.0</u>
ΔH_f° methyl ammonium perchlorate	=	-67.0

Another estimate can be made if we treat MAP, $\text{CH}_3\text{NH}_3\text{ClO}_4$, as NH_4ClO_4 plus $(-\text{CH}_2-)$ (as polyethylene).

There is little net energy change due to breaking and forming bonds as follows, to make the conversion from A.P. and polyethylene to MAP.

		<u>Kcal/Mole</u>
1)	Breaking an NH bond in NH_4^+	= +95
2)	Breaking a (CH_2) unit from polyethylene	= +70
3)	Forming a C-N bond, $-\text{CH}_2\text{NH}_3^+$	= -79
4)	Forming a C-H bond, CH_3NH_3^+	= <u>-87</u>
	Net energy change	= - 1

Lattice energy changes have not been estimated, but the above transition only gives -1 Kcal/Mole. Thus it would seem that for thermochemical approximations, a heat of formation for MAP based on using the equivalent ΔH_f° contributions would be reasonable. Bond energies were taken and extrapolated from data by J.A. Kerr and K.S. Pitzer.

	<u>Mole %</u>	<u>ΔH_f°</u>	<u>Contribution to MAP ΔH_f°</u>
- CH ₂ - (solid)	10.6	-6.5	-0.75
NH ₄ ClO ₄ (solid)	89.4	-70.7	-63.30
Bonding Contribution	-	-	-1.00
Estimate for MAP			-65.05 Kcal/Mole

This latter estimate (-65.05) compared with the former (-67) gives us some confidence in being able to treat MAP as 10.6% - CH₂ - and 89.4% NH₄ClO₄ for the purpose of calculating monopropellant enthalpy balances during combustion. The values of interest like: adiabatic flame temperature, and the propulsion parameters of C*, Isp, and exhaust temperature when subjected to combustion at 68 atmospheres, with exhaust to sea level; may be obtained from the data of Dobbins (6). These values are shown in Table 2 compared with similar data for pure A.P. Table 3 shows more complete data for A.P.

Table 2

Combustion Properties Comparison for
Monopropellants

	<u>NH₄ClO₄</u>	<u>CH₃NH₃ClO₄</u>
	<u>A. P.</u>	<u>M.A.P.</u>
Adiabatic flame temp.(68 ATM)(°K)	1403	3020
Adiabatic flame temp.(1 ATM)(°K)	1375	—
C*, ft/sec.	3213	4960
Chamber M.W.	27.9	26.0
Exhaust Temp., 68 ATM/1 ATM, (°K)	620	1600
Specific Impulse, 68 ATM/1 ATM	156.7 sec.	252.0 sec.

Table 3

Ammonium Perchlorate Monopropellant
Combustion Equilibrium Data

Heat of Formation (Enthalpy) -70.69 Kcal/mole
Initial Temperature 298.15°K
Density 1.95 g/cc

Pressure

<u>Parameters</u>	<u>1 atm</u>	<u>34 atm</u>	<u>68 atm</u>
Temp., °K	1375	1397	1403
Temp., °F	2015	2054	2066
Enthalpy, cal/g	-601.6	-601.6	-601.6
Entropy, cal/g - °K	2.212	1.960	1.911
Average Molecular Wt.	27.691	27.871	27.930
Heat Capacity cal/g - °K	0.352	0.364	0.367
Ratio of Specific Heats cp/cv	1.264	1.259	1.258

Combustion Species
Moles/100 grams

Cl	0.0054	0.0022	0.0019
HCl	0.8168	0.7301	0.7005
ClO	0.0001	0.0002	0.0002
Cl ₂	0.0144	0.0593	0.0742
OH	0.0002	0.0001	0.0001
H ₂ O	1.2937	1.3371	1.3519
NO	0.0011	0.0013	0.0013
N ₂	0.4250	0.4249	0.4249
O ₂	1.0546	1.0329	1.0254

Additional products which were considered but whose mole fractions were less than 0.000005 for all assigned conditions: H, NH, H₂, NH₃, N and O.

Methyl ammonium perchlorate is seen to burn with a flame twice as hot as that of A.P. Actually, it is found to be at the peak of the flame temperature, C* and Isp curves for the CH₂/AP system. Probably this perfect stoichiometric balancing to give maximum theoretical heat release, combined with complete flame premixing on the molecular level, explains the fast burning rate that was measured.

M.A.P. is a near perfect monopropellant from an energy viewpoint, however, it may well catalyze the combustion of other propellant ingredients by bringing highly exothermic reactions much closer to the solid propellant surface.

VI. Conclusions

1. Alkyl substituted ammonium perchlorates are monopropellants, like A.P.
2. The methyl substituted perchlorates have a rhombic crystal form, and are not strongly hygroscopic.
3. The DTA exotherm for these substituted perchlorates is 50°C. to 100°C lower than for A.P., with the lowering proportional to the alkyl content.
4. As a monopropellant, methyl ammonium perchlorate burns about two and a half times as fast as A.P., and with a much hotter and higher flame. (MAP = 0.103 in/sec.; AP = 0.043 in/sec.; both at atmospheric press.)
5. Di and tri methyl A.P. burn at rates between A.P. and M.A.P., apparently M.A.P. gives the best balanced products for maximum heat release.
6. Whereas the A.P. powder burning quenching diameter is about 3 mm, the methyl substituted quench diameter is about 4 mm.
7. For most oxidizer powders studied, a 6.5 mm i.d. tube gives stable burning (although a 4 mm tube is satisfactory for A.P.)
8. As tube diam. is reduced, an unstable burning condition (pulsating burning) develops, with the period of pulsation inversely proportional to tube diameter. A 4 mm tube gives 30 pulses in about 60 sec., or one every 2 sec.

VII. Future Work

1. Further density, purity and stability determinations will be made on the substituted compounds.
2. Burning rates for dimethyl and trimethyl A.P. will be determined.
3. Correlations will be made between combustion products, flame temperatures, rates and reactant premixing conditions.
4. Reasons for combustion instability and quenching will be sought.

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Methyl Ammonium Perchlorate						
Dimethyl Ammonium Perchlorate						
Trimethyl Ammonium Perchlorate						
Burning Rate						
Quenching Diameters						
Combustion Stoichiometry						