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COMBUSTION DYNAMICS LABORATORY

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February 1, 1968 through April 30, 1968

"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"

Professor Harold C. Beachell

Principal Investigator

May, 1968

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i. FOREWORD

This research at the University of Delaware under Grant AF-AFOSR 922-67 for the period February 1, 1968 through April 30, 1968 was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

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ii. ABSTRACT

The combustion characteristics of crystalline oxidizers with methyl substitutions have been studied. Methyl, dimethyl and trimethyl A.P. have burning rates faster than A.P. itself. Preliminary studies have shown tetramethyl ammonium nitrate to be the slowest burning (ambient pressure) monopropellant yet found; only two-thirds to one-half as fast as A.P. A portion of the burning rate increase of the substituted oxidizers is due to the "molecular premixing" of fuel (methyl and ammonium) and oxidant (ClO_4^-) groups.

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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.

II. Properties of Substituted Ammonium Perchlorates

As described in Quarterly Report No. 2, we have prepared methyl, dimethyl and trimethyl A.P. for comparison with pure A.P.

Table 1 gives the measured crystal densities at 20°C, and also the high temperature density data of Stammler and co-workers[1]. As might be expected, the crystal densities drop as methyl groups are substituted for hydrogens in the ammonium cation. The change per methyl group added becomes less for each addition. Their paper gives an excellent evaluation of x-ray diffraction data, and a discussion of oxidizer phase transitions from theoretical and experimental points of view.

Table 1

Density of Substituted Ammonium Perchlorates

Compound	Density g/cc at 20°C	High Temp.* Density g/cc
Ammonium perchlorate	1.95	1.73 (250°C)
Methylammonium perchlorate	1.65	1.58 (200°C)
Dimethyl ammonium perchlorate	1.48	1.46 (45°C)
Trimethyl ammonium perchlorate	1.43	1.21 (245°C)
Tetramethyl ammonium perchlorate	1.35*(25°C)	---------

*Data of Stammler and co-workers[1].

NOS studies[2] on methylammonium perchlorate, A.P., HAP, and hydrazine perchlorate have shown by the cold matrix-isolation/infrared spectroscopic technique that these oxidizers vaporize by dissociation:

$$RNH_3\ ClO_4\ (\text{condensed}) \xrightarrow{(\text{proton transfer})} RNH_2\ (g) + HClO_4\ (g)$$

For hydrazine diperchlorate and guanidinium perchlorate the relative vaporization temperatures were correleted with the pK values of the bases in aqueous solution. Correlations were also made with relative thermal stabilities.

III. Combustion of Substituted Ammonium Perchlorates

The goal of these studies has been to prepare crystalline oxidizers releted to state-of-the-art materiels like A.P.; and then to meesure their monopropellant combustion rates. These rates are then to be correlated with characteristics like chemicel composition, energy release on combustion, crystal structure, DTA profile and impact sensitivity.

Quarterly report no. 2 described the tests with granular $CH_3NH_3ClO_4$ in sample tubes showing its burning rete to be about 2 1/2 times as fest as A.P. under the same ambient conditions. Tabla 2 gives the burning rates of three of these substituted oxidizers compared with A.P.

In conducting these powder burning tests, bulk density control is critical. It is estimated that the retio of bulk-to-crystel density should be kept to 0.5± 10% for useful comparisons of burning rate. In comparing the deta for trimethyl ammonium parchlorete in row 4 with that in row 5 (of much lower density), the effect of looser packing in providing a higher charecteristic burning surface and thus higher measured burning retes can be easily seen. Tests on the dimethyl and trimethyl materiels will be continued with gentle packing to increase the density retio. The quench diamete[illegible]or these materiels appeers to ba near 6.0 mm, as compared to 3.5 mm for A.P. Table 3 compares burning rete with seve[illegible]al thermochemical veriebles. We believe the best correlation will be with specific impulse for this homologous series. Further testing of the dimethyl material is most impor[illegible]ant. Proper density tests may place its burning rete somewhat below that of MMAP.

Table 2

Monopropellant Substitutad A.P. Compounds

Strand Physical Data vs. Combustion

Samples were combustible tubes loadad under dry (10-20% R.H.) conditions with -40 +50 mesh neat oxidizer except where noted.

Crystelline Oxidizer	Loaded Bulk Density, g/cc (sample range)	Crystal Density, g/cc	Density Ratio Bulk/ Crystal	Burning rate (in/sec) at 14.7 psia in air	Burning rate Range (no. of Samples)	Sample Tube Diam. (mm.)
NH_4ClO_4	0.99 (0.95) (1.05)	1.95	0.51	0.043	+0.002 -0.002 (10 samples)	6.5
$CH_3NH_3ClO_4$	0.83 (0.83) (0.84)	1.65	0.50	0.103	+ .005 - .004 (4 samples)	6.5
$(CH_3)_2NH_2ClO_4$	0.63 (.61) (.67)	1.48	0.43	0.132	+ .004 - .002 (5 samples)	6.0
$(CH_3)_3NHClO_4$	0.65 (.63) (.69)	1.43	0.45	0.065	+ .013 - .013 (9 samples)	6.0
$(CH_3)_3NHClO_4$	0.44 (.43) (.44)	1.43	0.31	0.111	+ .006 - .003 (5 samples)	6.0
$(CH_3)_3NHClO_4$ (-50+80)	0.44 (0.43) (0.44)	1.43	0.31	0.113	+ .003 - .004 (4 samples)	6.0

Tsble 3

Monopropellant Burning Rates of

Substituted Ammonium Perchlorates

Crystalline Oxidizer	Burning Rate (in/sec.) at 14.7 psia	Adiabatic Flame Temp. (°K)	Monopropellant Specific Impulse, 66/1 ATM (sec.)	Avarage Molecular Weight of Combustion Producta
NH_4ClO_4	0.043	1403	157.5	27.9
$CH_3NH_3ClO_4$	0.103	3020‡	252.5‡	26.0‡
$(CH_3)_2NH_2ClO_4$	0.132	2130‡	225.0‡	20.9‡
$(CH_3)_3NHClO_4$	0.065	1200‡	200.0‡	18.0‡

‡Data estimated using as basis calculations of Dobbins[4] for CH_2/A.P. mixtures.

Note that whereas flame temp. drops almost 2/3 in going from MMAP to TMAP, specific impulse only drops by 1/5. This is partly because the combustion products molecular weight has dropped by about 1/3, and $I_{sp} \propto \sqrt{T_f/M}$.

Although we have only predicted combustion changes through the use of substituted A.P.'s in standard propellant, our attention has been called to an earlier study by Schmidt and Stammler[3]. Their theories had a basis in very interesting crystallographic studies in combination with DTA examination of the substituted A.P.'s. Our theory of rate increase was based on thermochemical calculations showing greater energy release and the realization of a fundamental change in combustion reaction conditions (mass transfer) from a hetarogeneous mixture of fuel and oxidizer--to a "premixed" condition in which fuel and oxidizer are in each cryatal unit cell.

Schmidt and Stammler have pointed out that a critical point was reached--with all oxidizers they tested--when the temperature of the crystal provided sufficient energy to allow free rotation of the (ClO_4^-) ions. For methyl ammonium perchlorate (MMAP), this temperature is 180°C as compared with 240°C for A.P. (see Quarterly Report no. 2, Figures 1 and 2). This free rotation (and phase change) leads to a reactivity which is embodied in lower DTA exotherms. The lower exotherms mean final decomposition at lower temperatures, and should lead to higher burning rates. Most interesting was their propellant burning rate data showing the effects of methyl ammonium perchlorate and butyl ferrocene addition to a standard 71.5 wt.% A.P. oxidizer, 28.5% polybutadiene binder propellant (see Table 4). The good correlation they obtained between burning rates and DTA exotherms is of particular interest. This correlation possibly shows that in a given propellant system when only small formulation changes are made the relative position of the DTA exotherm can be an accurate indicator of burning rate level.

At first glance, one might expect little difference between the flame temperatures and specific impulse values of the various test propellants. However, for a -CH_2-(polybutadiene)/A.P. type of system, the maximum energy release is nearer 90% than 70% A.P. The 70% A.P. system is considerably underoxidized. In fact, the adiabatic flame temperature of a 90% A.P. system is 3020°K (the same as for pure MMAP), and the flame temperature of a 70% A.P. system is less than 1000°K. This means that almost any hydrocarbon

fuel addition (or its equivalent) will lead to even lower flame temperatures and energy release. Based on these considerations, it would seem that if flame temperatures had been held constant in the referenced experiments by increasing the A.P. fraction when the methyl A.P. was added, the burning rate increases would have been even greater than those shown in Table 4.

IV. Impact Sensitivity Test Results

Impact sensitivity was considered the next most important safety test to differential thermal analysis. With DTA, we look for exothermic reactions, and in particular, the final exotherm which usually leads to ignition.

In the impact test, a weighed steel ball of several pounds is allowed to fall from an adjustable measured height and impact on a hardened steel sample holder. This fixture has a movable upper steel plate with protruding striker which compresses the test sample into a well in a fixed lower plate. The original potential energy of the ball before dropping is converted to kinetic energy on dropping and then to thermal energy, shock waves and strain in the sample and the confining block. The impact sensitivity values are usually reported in energy units, always with a well-known compound as a control. The positive ("fire") test varies from flashing and smoking, to a loud report. Table 5 shows results for the alkyl substituted perchlorates. The third column data is taken from Stammler[4]. It can be seen that there are several ways of recording sensitivity. A conservative value is the highest energy input that will not cause a single positive ("fire") test in ten trials.

Some investigators prefer the higher value, which is where the first "fire" occurs. Stammler's data uses the energy input that results in 50% of the sample firing. The trends in the data and relative values are more important than the absolute energy values. The agreement between the second and third columns is considered very good. It can be seen that the particle size of the material can affect sensitivity considerably (compare ground vs. unground A.P.). Starting with

Table 4

Propellant Burning Rate Modification‡

with MMAP and Butyl Ferrocene

Oxidizer System	Butyl Ferrocene Conc.(wt.%)	Burning Rate at 2000 psi (in/sec.)	DTA Exotherm (°C)
AP (Control)	0	0.47	460
AP	4.5%	1.45	230
85% AP + 15% MMAP	4.5%	2.40	190
78% AP + 22% MMAP	4.5%	2.95	180

‡ Data taken from Schmidt and Stammler[3].

Control propellant is 71.5 wt.% A.P., 28.5 wt.% polybutadiene binder. Butyl ferrocene additions were apparently made with proportionate reductions in oxidizer and binder.

Table 5

Alkyl Substituted Ammonium Perchlorates

Compound	Impact Sensitivity in inch-pounds		
	No Fires in 10 Trials	First Fire Point	50% Fira Point Stammler's Data[1]
$CH_3NH_3ClO_4$	18	22	35
$(CH_3)_2NH_2ClO_4$	28	32	38
$(CH_3)_3NHClO_4$	32	36	43
$(CH_3)_4NClO_4$	--	--	61
NH_4ClO_4 (ground)	--	60	--
NH_4ClO_4 (unground)	--	80	173
AP Propellants	10-20	15-25	--

Note: The first two columns give data from Thiokol-Elkton using a modified JPL impact apparatus. Column 3 (Stammler) givas data from a Bureau of Mines Apparatus.

$CH_3NH_3ClO_4$, there is a regular decrease in sensitivity with methyl substitution. However, all of the alkyl substituted compounds are more sensitive than pure A.P.

Table 6 shows good correlation (inverse relationship) between impact sensitivity and specific impulse in the homologous series of ammonium perchlorates. Flame temperature and Isp estimates were taken from Dobbins[4], except in the case of tetramethyl A.P. where it was felt that the extrapolation would be too great. Neither DTA exotherm nor adiabatic flame temperatures correlated well with the other variables.

V. DTA Comparison: Ammonium Nitrate vs. Tetramethyl Ammonium Nitrate

It is well known that ammonium nitrate (AN) is difficult to burn, even under pressures of 50-70 atmospheres. Also, ammonium nitrate propellants are difficult to ignite, and a number of additives, notably ammonium dichromate, have been used to promote smooth burning. In the section following, it is shown that although AN will not burn at ambient in the powder burning test, tetramethyl AN burns smoothly. In comparing the DTA curves of these two compounds, it is seen that there are both qualitative and quantitative differences.

Figure I is the DTA plot from 25°C to beyond decomposition for AN. Figure II is the plot for tetramethyl AN (TMAN). Most interesting is the lack of any real endotherm for TMAN. AN shows four distinct phase change endotherms between 40°C and 175°C. It may well be that the combustion difficulties of AN are strongly influenced by the several forms of energy absorption available to the compound before it reaches exothermic temperatures. The AN exotherm is at about 290°C, whereas the TMAN exotherm occurs at about 360°C. With this difference in exotherms, other things being equal, we would expect AN to burn faster and more readily than TMAN. However, referring to our analysis of alkyl substituted A.P.

Table 6

Alkyl Substituted Ammonium Perchlorates

Performance Potential vs. Sensitivity

Crystalline Oxidizer	Impact Sensitivity (inch-pounds)	DTA Exotherm (°C)	Adiebatic Flame Temp. (°K)	Specific Impulse (sec.) 68ATM/1ATM
NH_4ClO_4	80	405	1403	157
$CH_3NH_3ClO_4$	22	350	3020	252
$(CH_3)_2NH_2ClO_4$	32	330	2130	225
$(CH_3)_3NHClO_4$	36	310	1200	200
$(CH_3)_4NClO_4$	55	425	*	*

*Too great an extrapolation of Dobbins' data would be required.

compounds in Quarterly Report no. 2, it may be reesonable to consider TMAN as a molecular scale mixing of $(CH_2)_n$ end NH_4NO_3. Such mixtures whether on a perticulate or moleculer scale generate high flame temperaturee (as compared with the unsubstituted oxidizer) end thus, even though thair exotherms may be higher, their monopropellant combustion (ignition and rete) will be enhanced. An excellent reference on the correlation between DTA plots end crystal cell transformations is that of Stammler and co-workers[1]. Stammler shows e DTA plot for tetramethyl ammonium perchlorete and the resemblance to onr DTA plot of TMAN is striking.

VI. Combustion of Substituted Ammonium Nitrate

It was decided to compare pure ammonium nitrate versus a substituted compound in the combustible tube type of test used es e screening test in this leboratory. The substituted compound used was tetramethyl ammonium nitrate (TMAN). Both powders were -40+50 mesh, at their pour density (about half of theoretical crystal density), end were loeded into 4 mm i.d. paper straws.

The samples were 6 to 7 cm in length; they were burned in ambient air; the AN bulk density wes 0.825 g/cc ± 0.025, and the TMAN bulk density 0.545 g/cc ± 0.105. A minimum of five samples eech were burned.

Table 7

Substituted AN Combustion

Oxidizer	Burning Rate in/sec at 14.7 psia	Rate Range
A.P. Control	0.033	+ 0.0015 - 0.0018
Ammonium nitrete	Would not burn	-----
Tetramethyl ammonium nitrate	0.022	+ 0.005 - 0.003

SAMPLE: Ammonium Nitrate
ORIGIN: Recrystallized

SIZE: Micro
REF: Glass bead
RATE: 20°C/min.
START: 37.95°C.

ATM. N_2
SCALE SETTING: 50°C/in.
1/2°C/in.

RUN NO AN-1
DATE: Jan. 11, '65
OPERATOR: Y.C. Kim

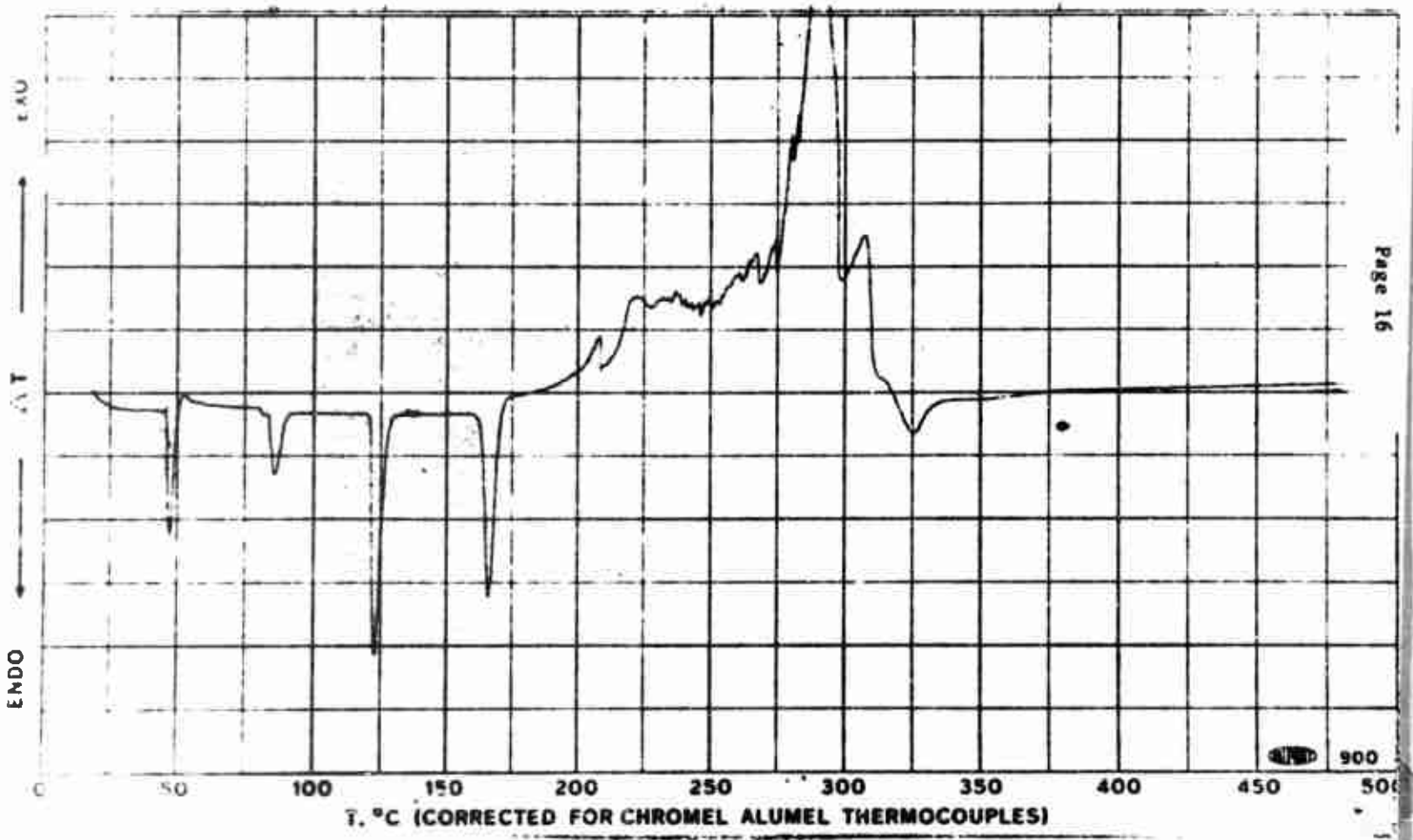


FIGURE II

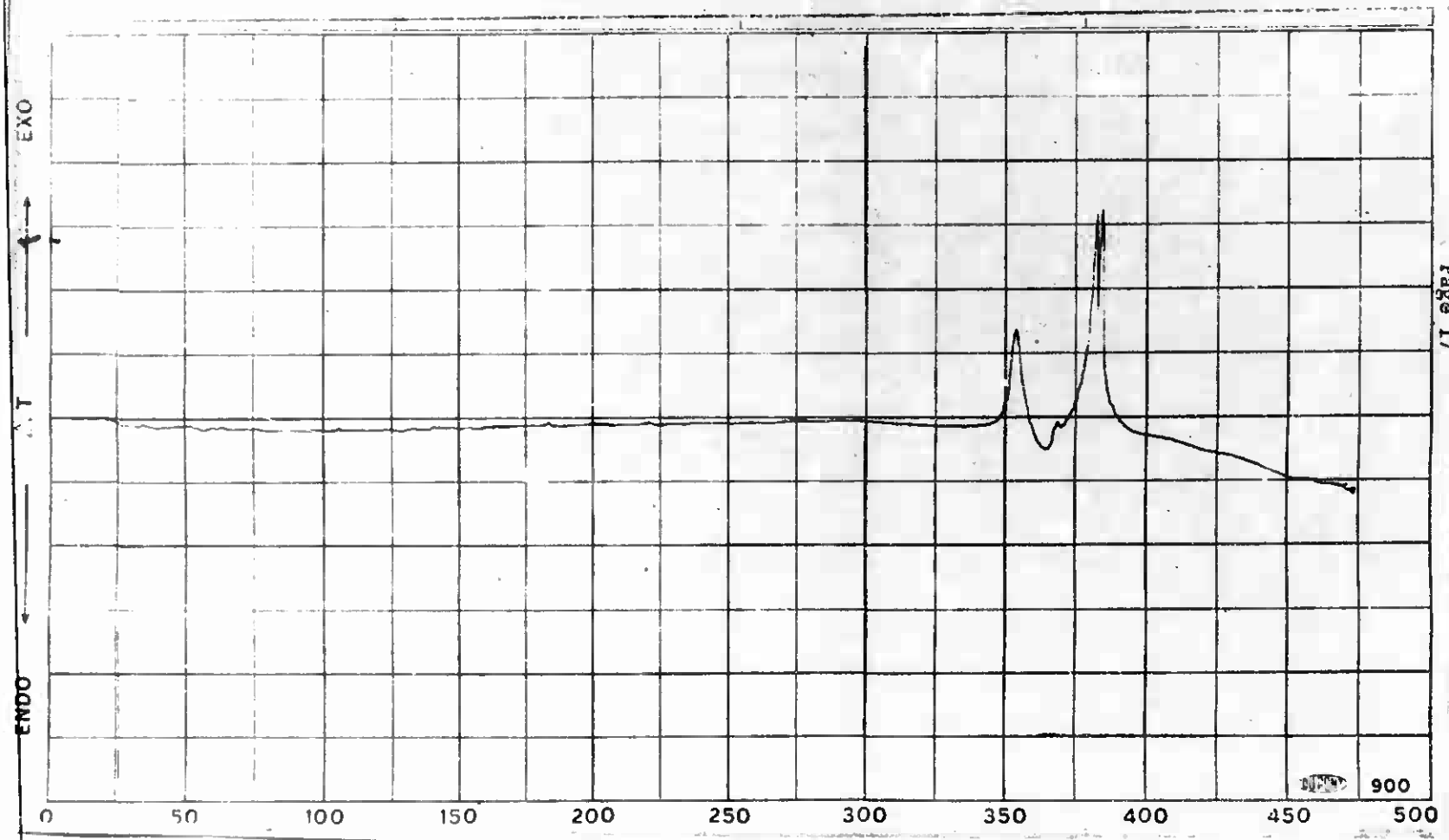
SAMPLE: Tetramethyl AN
$(CH_3)_4$ NNO_3

ORICIN: Eastman Org.Chem.

SIZE: Micro
REF: Class bead
RATE: 20°C/min.
START: 39°C

ATN. N_2
SCALE
SETTINC: 50°C/in.
1°C/in.

RUN NO: TMAN
DATE: Mar. 29, '68
OPERATOR: KYC



As shown in Table 7, the AN samples would not burn, and the TMAN burned one-third slower than the A.P. control. TMAN burned with a smooth steady flame and is the slowest burning monopropellant we have found thus far. The alkyl substitution converts AN to a monopropellant.

VII. Conclusions

1. Methyl subetitutad ammonium oxidizers burn faster than the unsubstituted compounds.

2. In pure substituted perchlorate and nitrate oxidizer combustion, the faster burning appears to be partly due to the greater energy release provide by a better balance of oxidizing and reducing species.

3. Impact sensitivity is directly correlatad with specific impulse in a homologous seriee.

4. The faster burning attributable to a "molecular premixing" of reducing and oxidizing species is demonstrated when propellants having lower energy, but containing a portion of methyl substituted oxidizer, show a significant burning increase over reference propellants.

5. When compering eimilar propellants, DTA exotherms correleted well with burning rate. This ie not true for the pure oxidizer burning rates.

VIII. Future Work

1. The dimethyl A.P. granuler oxidizer burning rate will be determined at higher bulk density.

2. Further attention will be given to quench diameters and the phenomenon of unstable (pulsating) combustion.

3. Attempts to produce large eingle crystals of divelent cetion doped A.P. will be continued.

IX. References

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Dimethyl Ammonium Perchlorate						
Trimethyl Ammonium Perchlorate						
Tetramethyl Ammonium Nitrate						
Burning Rate						
Quenching Diameters						
Combustion Stoichiometry						