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**DEPARTMENT OF CHEMISTRY**

**COMBUSTION DYNAMICS LABORATORY**

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**"COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS"**

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**June, 1969**

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**Air Force Office of Scientific Research  
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1. FOREWORD

This research at the University of Delaware under Grant AF-AFOSR 922-67 for the period November 1, 1968 through April 30, 1969 was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force.

The overall goal of this research is to provide the Air Force with design criteria for obtaining a wider spectrum of solid propellant burning rates than is currently available.

ii. ABSTRACT

Single crystals have been prepared from A.P. solutions containing 20% by weight  $Ba(ClO_4)_2$ . Analyses for  $Ba^{++}$  content in the crystals are being made. Single crystals of methyl ammonium perchlorate were grown and submitted for combustion testing comparison with pure A.P. A number of new perchlorate and nitrate oxidizers were prepared and characterization was begun. To date, the fastest burning oxidizer has been methyl ammonium perchlorate (2 1/2 times as fast as A.P.); and the slowest has been tetramethyl ammonium nitrate (1/2 as fast as A.P.).

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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 the 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 the characteristic surface, 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. Preparation of New Monopropellants

As described in our previous report,<sup>(1)</sup> we have been preparing alkyl substituted derivatives of ammonium perchlorate and ammonium nitrate, the two chief oxidizers that have been used in solid propellants. The object is to learn more about oxidizer combustion



dynamics through studying the effects of anion and cation changes. During the current period, further compounds were prepared as shown in Table 1. The ammonium perchlorate series now includes the four methyl substitutes, the ethyl substitution for comparison with the combustion of the diethyl compound, and the isopropyl substitution for comparison with trimethyl ammonium perchlorate.

The analogous compounds have been prepared for the ammonium nitrate series. Some difficulty in obtaining crystal products was encountered. In addition, a few extra nitrates were made available. The combustion tests for the new compounds are still being run. However, it was found that neither tetraethyl AN nor ethyl tripropyl AN would burn at ambient pressure. Although we have not checked the specific impulse calculations for these two compounds, we suspect that these compounds are under-oxidized to the extent that they cannot support combustion as monopropellants. Recently, Pittman<sup>(2)</sup> has published a table showing the effects of a Ferrocene catalyst on: AP, ethylammonium perchlorate and tetramethyl ammonium perchlorate oxidized propellants among others. Extending studies by Flanigan, Pellet has shown that all of these propellants are catalyzed by Ferrocene materials, except tetramethyl ammonium perchlorate. The reason proposed is that tetramethyl ammonium perchlorate does not decompose to give perchlorate acid as a primary decomposition product. Iron compounds are known to be good catalysts for perchloric acid decomposition. We have found it interesting that the tetra-substituted materials have featureless DTA plots showing only the final endotherm and exotherm.

As far as possible, these crystalline oxidizers will be size classified to give -40+50 mesh material to check the powder burning rates. In a few instances, we are not able to obtain crystalline materials or the crystal habit was extremely plate-like or needle-like so that normal size classification is not too useful. These cases will be noted. The combustion tests for this series are now being completed.

TABLE 1

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## OXIDIZER COMBUSTION TESTS; SUBSTITUTED AMMONIUM PERCHLORATES AND NITRATES

(Samples -40+50 mesh (350 $\mu$ ) oxidizer loaded into 4mm diam. paper straws)

Oxidizer	Average Burn Rate (in/sec)	Press. (psia)	Average Bulk Density g/cc	No. of Samples	Burn Rate Range (in/sec)
AP UHP	0.033	14.7	1.05	10	0.003
UHP AP, NH <sub>4</sub> ClO <sub>4</sub>	5.52	500	1.17	4	2.62
UHP AP	9.34	1000	1.20	5	2.87
UHP AP	0.043	14.7		10	.004
MMAP	0.103	14.7	0.83	4	.009
DMAP	0.132	14.7	0.63	5	.006
TriMAP	0.065	14.7	0.65	9	.026
TetraMAP (No N-H- bonds present)					
n-propyl AP (To compare with Trimethyl)					
Ethyl AP (To compare with Dimethyl)					
AN, NH <sub>4</sub> NO <sub>3</sub>	4.45	1000 14.7	(ratio 0.55)	1 would not burn	--
Mono methyl AN					
Di " "					
Tri " " (above to compare with perchlorates)					
Tetra methyl AN	(would not burn) 0.022	500 14.7	0.53 0.53 0.55	- - 5	--- --- 0.008
Propyl AN (To compare with Trimethyl)					(could not obtain crystal product; oils were formed which then turned glassy)
Ethyl AN (To compare with dimethyl)		"	"	"	
Tetra ethyl AN		14.7		would not burn	
Ethyl Tripropyl AN		14.7		"	" "

### III. Combustion Modification Tests

As discussed in the previous report, an investigation was made of compounds which might possibly retard the combustion of ammonium perchlorate. It was felt that if extremely thermally resistant organic fuels were added to AP, there might be enough delay in the gas phase reaction to thicken the flame reaction zone and allow some surface cooling; and thereby, a lower burning rate.

As can be seen in Table II, we are thus far unable to slow a reduction in burning rate using two types of highly stable organic molecules. We tried tetraphenyl cyclopenta dienone (shown as "Dienone" in Table II) and tetraphenylthiophene (shown as "TPT"). The effect was checked at ambient pressure 500 psi and 1,000 psi. The only conclusion we have drawn is that although these compounds are highly resistant to thermal breakdown in the ammonium perchlorate flame, the breakdown must occur quite rapidly. Then the fuel value of the breakdown products, added to the oxidizer products, still produce a hotter flame soon enough to cause an increase in burning rate. It may be that these compounds could slow propellant combustion when incorporated in the binder. This will require a separate study.

It appears that a fundamental slowing of the ammonium perchlorate monopropellant combustion reaction is going to have to come from significantly stabilizing the perchloric acid molecule in the gas phase. There is still the possibility of stabilizing the crystal by slowing electron transfer in the solid phase which could also lower burning rate. Maycock has described this effect with perchlorates<sup>(3,4)</sup>. To that end, we have attempted to place divalent cations in the A.P. crystal lattice.

### IV. Single Crystal Growth

During this period, many attempts were made to grow AP doped with barium ( $Ba^{++}$ ). In most cases, needle- and plate-like modifications were obtained. However, recently, we have obtained

TABLE II

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## COMBUSTION TESTS; AP PLUS HIGH THERMAL STABILITY ORGANIC ADDITIVES

(Samples -40+50 mesh (350 $\mu$ ) oxidizer plus  
cststlyst loaded into 4 mm diam. paper straws)

<u>Oxidizer</u>	<u>Average Burn Rate (in/sec)</u>	<u>Pressure (psis)</u>	<u>Average Bulk Density g/cc</u>	<u>No. of Samples</u>	<u>Burn Rate Range (in/sec)</u>
AP UHP	0.033	14.7	1.05	10	.003
UHP AP	5.52	500	1.17	4	2.62
UHP AP	9.34	1000	1.20	5	2.87
A.P. + 7% Dienone	0.042	14.7	1.15	5	.003
A.P. + 11% Dienone	0.048	14.7	1.13	5	.005
A.P. + 2% Dienone	6.05	500	1.18	3	0.44
A.P. + 2% Dienone	11.07	1000	1.18	3	1.83
A.P. + 10% Dienone	4.74	500	1.10	3	1.33
A.P. + 10% Dienone	10.86	1000	1.10	3	2.55
A.P. + 2% TPT	12.61	1000	1.13	4	6.46
A.P. + 5% TPT	18.32	1000	1.12	4	2.50

good single crystals that have been cut to remove all impurities. They will be analyzed for barium content. These crystals were finally prepared from water solution containing 20% by weight of solids as barium perchlorate and 80% ammonium perchlorate.

Also during this period, two single crystals of methylammonium perchlorate were grown. Since they appeared suitable for combustion tests, they were sent to Mr. E. W. Price at China Lake. Methylammonium perchlorate, tested as a powder, has been the fastest burning monopropellant identified thus far.

#### V. Conclusions

1. A variety of substituted ammonium cations, and the perchlorate and nitrate anions, can be used to prepare crystalline oxidizers.
2. Many of these are monopropellants and some can be made as single crystals.
3. Simple combustion tests of the unpressed granular materials show interesting burning rate changes with ion changes.
4. Correlation of burning rate with monopropellant oxidizer chemical and physical properties has not been accomplished yet - but specific impulse, adiabatic flame temperature and crystal response to thermal input as shown by DTA, seem to be key factors.
5. Highly stable organic compounds (500°C-900°C decomposition) as powder additives have not shown the ability to reduce burning rate of A.P. powder. Apparently, an even higher decomposition point, possibly nearer the A.P. adiabatic flame temperature of 1077°C, is required.

6. DTA's of the methyl tetra-substituted ammonium perchlorate and ammonium nitrate are relatively featureless with high temperature endo and exotherms. Neither of these compounds would tend to form the free acids as primary decomposition products. Flanigan has shown that where  $\text{HClO}_4$  is not formed iron catalysts are not effective. Schmidt(5) has shown that the temperature of the first endotherm, indicating force rotation of  $\text{ClO}_4^-$  ions, is the lowest temperature to which decomposition can be shifted by catalysis. Thus, by either of these criteria, tetramethyl AP and tetramethyl AN should have high solid phase stability, having first endotherms at about  $350^\circ\text{C}$ , as compared with AP and AN having endotherms  $100^\circ\text{C}$  and  $200^\circ\text{C}$  lower, respectively.

#### VI. Future Work

1. Continued growth of doped single crystals to obtain both high and low burning rates.
2. Growth of single crystals of new oxidizers for comparison with A.P. combustion.
3. Powder combustion tests of substituted AP's and AN's.
4. Study of effects of catalysts on varying oxidizer structures.
5. Continued study of the effect of stability of organic compounds on combustion dynamics in the presence of perchlorate oxidizers.

#### VII. References

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13. ABSTRACT

Single crystals have been prepared from A. P. solutions containing 20% by weight Ba(ClO<sub>4</sub>)<sub>2</sub>. Analyses for Ba<sup>++</sup> content in the crystals are being made. Single crystals of methyl ammonium perchlorate were grown and submitted for combustion testing comparison with pure A. P. A number of new perchlorate and nitrate oxidizers were prepared and characterization was begun. To date, the fastest burning oxidizer has been methyl ammonium perchlorate (2 1/2 times as fast as A. P.; and the slowest has been tetramethyl ammonium nitrate (1/2 as fast as A. P.).

ammonium perchlorate (A.P.)



KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Combustion						
Burning Rate						
Solid Oxidizers						
Monopropellants						
Substituted Ammonium Perchlorates						
Substituted Ammonium Nitrates						
Differential Thermal Analysis						