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COMBUSTION CHARACTERISTICS OF CRYSTALLINE OXIDIZERS

by

Elmer Ellsworth Hackman, III

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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Original signed

Approved: _____
Professor in charge of thesis on behalf
of the Advisory Committee

Approved: _____
Chairman of the Department of Chemistry

Approved: _____
Dean of the School of Graduate Studies

DEDICATION

This dissertation is dedicated to

my wife, Edna,

our children, Matthew and Christian;

and

to our parents;

Mr. and Mrs. L. B. Oaks, and

Mr. and Mrs. E. E. Hackman

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ABSTRACT

A fundamental understanding of the combustion characteristics of crystalline oxidizers like ammonium perchlorate is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involved theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. Single crystals, visually perfect throughout most of their mass, were grown from saturated water solution by a temperature lowering technique using a bath-control system-data acquisition combination that maintained temperatures to $\pm$ 0.001°C. Electrical conductivities and UV absorption measurements showed them to be of high purity. A strand-burner, window-bomb and high-speed cinematography were used to obtain burning rate versus pressure. The study of large single crystal burning removed particle size, shape and bulk density factors as complications. The intrinsic burning rate, r_i, of a single crystal is defined and postulated as a fundamental combustion variable. Low bulk density powder combustion was shown to be feasible. The characteristic burning surface, A*, for powder combustion was defined and shown to relate powder burning to single crystal burning.

The explanation proposed for the large difference found between physical surface area available in the burning zone and the actual burning surface area, is the necessity for a minimum flame zone height, Z_f, above a stable burning surface.

I. INTRODUCTION

This research was conducted during the period May 1, 1965 through April 30, 1967.

The overall aim was to gain a better understanding of the combustion of the major ingredient in solid propellants, the oxidizer. The crystalline oxidizer chosen for study was ammonium perchlorate (A.P.) because it is a monopropellant (combustion is self-sustaining) and also because it is the chief crystalline oxidizer now in use in solid propellants.

A. Scope of Research — The goals of this study were:

1. To prepare single, optically clear, oxidizer crystals of a size and shape suitable for combustion measurements.

2. To use the above crystals to determine linear burning (combustion reaction) rates versus pressure, and to observe other combustion characteristics.

3. To compare results from (2) above with the linear burning of oxidizer powders of varying densities

loaded into suitable simple tubes.

4. To investigate reaction rate modification through crystal changes, both physical and chemical.

5. To propose mechanisms to account for the several effects observed in the study.

Throughout the decade 1955-1965 there had been increasing interest in mechanisms of oxidizer combustion, both alone and with added fuel. Questions had arisen as to the importance of density variation on burning of pressed powders, and the importance of cracks and crack formation on burning rate. Since a considerable amount of valuable data had already been collected on pressed sticks of oxidizer, pressed to a density of about 1.90 g/cc, this study was to investigate the combustion at the lower limit of bulk density, the "pour" density of about 1.00 g/cc of powders; and perfect ammonium perchlorate crystals at 1.95 g/cc.

B. Accomplishments of this Study

The unique contribution of this study to the oxidizer combustion field has been the measurement of combustion rates and analysis of the burning mechanism of varying density oxidizer samples. The density study ranged from the theoretical crystal density, (using perfect single crystals)

down to powders with a bulk density of only half the theoretical crystal density. Oxidizers that were chemically modified by alteration of the anion or cation showed reaction rate changes in the predicted direction.

1. Crystal Growth

Excellent quality (visually perfect) single crystals were grown in apparatus specifically designed for oxidizers, modelled after earlier designs for ammonium dihydrogen phosphate crystals by the National Bureau of Standards. A unique small scale apparatus was designed and constructed. It also produced excellent crystals. UV analysis of sample crystals and electrical conductivities showed them to be of high purity. High-quality single crystal samples were cut to dimensions suitable for window bomb burning and photography.

2. Combustion Tests

The differences between single crystal combustion and combustion of fine crystal powders loaded into cylindrical tubes were investigated. It was found that powder samples like those normally used in propellant compounding, will burn s ly and reproducibly, by themselves, at bulk densities ranging down to about one-half the crystal density. Prior to this time, most combustion investigators thought such samples would either detonate, burn very erratically, or not burn at all. The rates are of course

many times faster than normal propellant burning rates. For example, a -40 +50 mesh A.P. sample at a bulk density of about half the crystal density, has a burning rate of 9.30 in./sec at 1000 psia. On the other hand, a single crystal was found to burn at 0.33 in./sec. The vast difference in the reaction rates that were measured illustrates the importance of effective surface area, that is, the contribution of non-planar surfaces (due to voids and cracks) in materials being burned. It was found that burning rate increased with increasing void volume (decreasing bulk density) and with decreasing particle size. Both of these factors increase effective surface area. To our knowledge these are by far the fastest controlled burning rates that have been measured for solids or propellants at pressures of 30 to 100 atmospheres; and with a rate versus pressure slope of less than one. All other studies of rates beyond several inches per second have led to detonations; whereas the burning reported herein seems quite stable.

3. Data Interpretation

The "characteristic burning surface" has been designated A*. This is defined as the ratio of the effective burning surface area for a powder to that of a single crystal (which is taken as the nominal geometrical cross sectional area). The single crystal burning rate is designated r_i, that is, the intrinsic combustion rate for that oxidizer. These tests have shown that A* (dimensionless) for both ammonium perchlorate

and ammonium nitrate 360 micron powders, burning at 1000 psia, and at a bulk density of about one-half the crystal density, is about 20. This means that although for a powder of this type that BET specific surface measurements indicate has about 100 times the area of a single crystal available in the burning zone, only a small portion of this surface is available for reaction. What this is showing is a relationship between a minumum reaction zone thickness designated Z_f, and voids within powders during combustion.

4. Oxidizer Modification

It was found that "doping" ions (foreign ions placed in the crystal lattice, or interstitially) with significantly different properties from those of the host ions can be added to ammonium perchlorate crystals so that the burning rate is affected. An example of a doping ion similar to the host ion is that of rubidium. Insertion of .2% rubidium ion in the ammonium perchlorate crystal lattice caused only negligible changes in the burning rate at sea level or at rocket combustion pressures (1000 psia). The rubidium ion was chosen for initial studies because its size is closest to that of the ammonium ion, while maintaining chemical similarity. However, by insertion of only 0.01% NO_2^+ (nitronium) ion in the A.P. lattice, and keeping particle size and pressure constant, a burning rate of 15.0 inches per second was measured; about a 50% increase over the comparable

"undoped" A.P. powder rate. The nitronium ion is known for its reactivity, and in addition undoubtedly strains the A.P. lattice.

Tests of the effect of the complete change of anion to the less reactive nitrate were made by holding all other factors constant and burning ammonium nitrate powder. The rate was 1/2 that of A.P. confirming the general expectations.

5. Tests of Validity

For further interpretation, it was of prime importance to be able to relate the combustion observations to a model type of burning. This was done by comparing the measured data with the analyses of Penner, Johnson and Nachbar, and Barrere and Williams. An interesting parallelism was found in log burning rate versus log pressure response between theoretical predictions for single crystals, actual burning of single crystals, and powder burning in the range 300 to 1500 psia. This similarity in response (equal slope of the burning rate versus pressure curves) tended to support the conclusion that the essential difference between powder and crystal burning was one of effective surface area change which can be characterized by the value A*, and is controlled by Z_f.

C. The Role of Oxidizer Combustion Studies in Solid Propellant Research

This section will describe the relationships between oxidizer combustion studies and the improvement of solid propellants. The general requirements for solid propellants are described and the importance of the oxidizer is highlighted.

1. Solid Propellants Defined

Solid propellants may be defined as materials that, upon receiving a minimum activating energy, undergo steady state pyrolysis and high temperature reaction of their pyrolysis gases, in equilibrium with their low molecular weight products at constant pressure, without requiring addition of mass or energy; but allowing a constant discharge of gaseous products. The overall process is called combustion, burning or deflagration.

The requisite "minimum activating energy" governs the type and amount of ignition material required to initiate combustion and is highly dependent upon the energy of activation for the thermal decomposition of propellant ingredients; heat of fusion, vaporization and sublimation; and heat capacity, thermal conductivity and radiation characteristics. Constant gas pressure, constant initial reactant (propellant) temperature and constant composition are the prerequisites for steady state combustion.

Higher combustion temperatures, with other factors held constant indicate higher thermal energy release and consequently higher

gas pressures for a given number of moles of products. This can then be translated into greater ability to do mechanical work. The low molecular weight stipulation also reflects the desirability of high pressure and the fact that the pressure of the gaseous products (for a given mass and temperature) is inversely proportional to their molecular weight. Higher pressures, for a given mass of combustion products, produce a greater net unbalanced force in a rocket combustion chamber, thus producing greater rocket acceleration.

Composite propellants, those prepared from liquid polymers, crystalline oxidizers and metallic or hydride additives, are an important example of the newer high energy propellants.

2. Propellant Burning Rate

When rating propellants, one of the most important performance variables is the burning rate of the propellant. Thrust, and the accompanying acceleration of a rocket-powered vehicle, can only occur when propellant is undergoing burning or combustion. Throughout the range of useful applications for solid rocket propulsion, desired thrust-times might vary from about 10 milliseconds to 100 seconds (boosters for space vehicles), or a time span of ten thousand fold. Burning rates for available propellants might vary from about .01 in./sec to 2 in./sec, or a range of 200 fold. Thus, it is obvious that rocket motors cannot be

designed solely to minimize stresses on the propellant and to maximize the volume of propellant contained, but major consideration must also be given to how the thrust-time can be achieved. If propellants could be chosen for their physical properties, and performance (in terms of specific impulse, pound-force seconds/pound-mass) and then the burning rate controlled through making minor (0 to 5 wt. %) changes in the propellant formulation, a distinct advancement in solid propellant technology would have been achieved.

Currently, it is known that for a given polymeric binder-fuel system, increasing the weight fraction of oxidizer (NH_4ClO_4, NH_4NO_3, etc.) in a formulation, below the stoichiometric point, and also reducing the average oxidizer particle size, increases the burning rate. Small percentages of transition metal compounds such as copper chromite and iron oxide will catalyze the burning rate. Also, for a given oxidizer weight fraction and given particle size distribution, varying the polymeric binder will vary the burning rate.

Although these factors appear to give control of burning rates, the maximum rate for a given oxidizer — binder system in most cases — is only of the order of two or three times that of the minimum rate. However, the most serious drawback is that alteration of the oxidizer weight fraction or the type of polymeric binder seriously changes the specific

impulse of the propellant. Thus, the use of this type of control is severely limited.

Since the progressively better oxidizers (from a specific impulse standpoint) seem to have inherently faster burning rates, greater research importance is attached to methods of achieving low burning rates (.01 to 0.1 inches/second) without sacrificing the performance achievable in propellants with rates in the range 0.1 to 1.0 inches/second. For a given base propellant and combustion pressure, no chemical compound, physical preparation of ingredients, nor method of energy alteration in the combustion process has been described in the literature that is capable of ten-fold burning rate reduction.

However, there are still very important propulsion problems that could be solved if much higher burning rates also could be achieved.

3. The Importance of Oxidizers

The philosophy used in undertaking this study has been that the biggest part of the answers to questions in solid propellant combustion can be found in a fuller understanding of oxidizer decomposition and combustion. Oxidizers now are, and look like they will remain to be the major ingredient on a weight or volume basis in solid propellants.

Further, it was felt that the best way to add to the fund of oxidizer knowledge is to study first the pure oxidizer and its perfect crystals, and then to progressively add varying factors and determine their combustion effects. A most desirable long range goal in this work is to develop an equation, or equations that will use common or easily estimated physical and thermochemical data for an oxidizer, and from that information be able to predict an approximate propellant burning rate versus pressure curve. At present this cannot be done, except by looking back at a vast amount of collected ammonium nitrate (A.N) and ammonium perchlorate (A.P.) propellant burning rates. When this is done, one can say that the rate for a new composite propellant will be in the range of 0.2 to 1.0 in./sec if A.P. is used; and 0.05 to 0.10 in./sec if A.N. is used. But this is hindsight and isn't much help for the future. What really needs to be answered are questions like: should cation substitution of nitronium for ammonium in the perchlorate give propellant rates of 0.5 to 1.0 in./sec; or should they be 1.0 to 2.0 in./sec? Should cation change to hydrazinium yield propellants that burn faster or slower than A.P. propellants? How about hydroxylammonium perchlorate propellants? Should hydrazine nitroformate or nitrate propellants be detonable? Can one synthesize an oxidizer that will give propellant rates of 5 to 10 in./sec? Can one catalyze A.P. positively to get rates of 10 in./sec; and negatively to get rates of 0.01 in./sec?

The answers to all these vital questions are bound up with the unknown factors affecting combustion, and the unknown mechanism of combustion. It was the intention of this study to develop a rather simple combustion test technique for the ready determination of the "intrinsic" burning rate response to pressure for monopropellant oxidizers. That is, the burning rate versus pressure curve for a single crystal burning one dimensionally in a direction normal to one of its faces. This was to be done by showing a relationship between powder and single crystal burning. The technique of powder burning was to comprise the "simple combustion test" referred to above. Such a technique could bring order out of the chaos caused by large quantities of test data now present in the literature that can't be correlated.

II. EVALUATION OF RESEARCH ON RELATED STUDIES

Combustion studies of monopropellant oxidizers have been conducted for over a decade. They have given good insight into the high temperature reactions of the chief ingredients in solid propellants. The majority of these studies were conducted with powders pressed into strands or sticks having nearly the crystal density. It was found to be much easier to do this than to obtain single crystals for combustion. However, it was ultimately found that no matter how well the samples were prepared, the particle size of the powder from which they were pressed affected the burning rate.

During the early planning of this combustion research effort little was known about the burning of single oxidizer crystals like ammonium perchlorate. In fact there seemed to be little interest in such experimentation. We felt that further research on pure oxidizer combustion would make an important contribution to solid propellant research. Whittaker[1] had tried a few experiments with the burning of modified habit single crystals of A.P. By 1965 the crystal growth work of McBride became known — and shortly thereafter the combustion tests by Hightower and Price[2].

By 1967, this interest has spread to such an extent that there are at

least a dozen laboratories in the U. S. and Europe studying oxidizer combustion. As shown in the following paragraphs, related work has been carried out in fields ranging from lower temperature decomposition reactions to theoretical explanations of observed burning rates.

A. Pressed Powder Combustion

Friedman[3,4,5], Adams[6], Shannon[7], Irvin[8], and Barrere[9] generally used high purity A.P. that had been separated into particle size fractions, and then pressed to a density of 1.90 g/cc in the form of strands 4mm square by 38mm long (or a convenient size in that general category). These samples were then ignited in a temperature conditioned strandburner under varying inert gas pressures. Friedman, Levy and co-workers, more recently vonElbe and McHale[10], have conducted the most sustained and thorough examination of pressed powder combustion. Starting with A.P., they have investigated most of the available oxidizers, and are currently studying hydroxylammonium perchlorate.

In the referenced studies, not only burning rate response to pressure, but the effects of varying the strand temperature prior to burning, varying catalysts, varying inert gas atmospheres, varying oxidizer particle sizes prior to pressing, added radiant energy and other effects have been examined.

In addition to burning rate as a reaction variable, the lower pressure limit at which A.P. combustion could be sustained (PDL) without added fuel, was measured for insulated and uninsulated samples.

The burning rate-pressure response band for strands made from particle sizes ranging from 50 to 200 microns is shown in Figure I. One of the difficulties encountered here was that although the data from a given laboratory showed a regular increase in burning rate with reduction in particle size of the powder from which strands were made; data for a similar material measured in another laboratory sometimes showed quite different values. Shannon's data, for the rate-pressure response of A.P. strands to varying initial temperature, shown in Figure II, illustrates the importance of both finer particle size and higher initial temperature in increasing rate at a reference pressure. The burning of these samples was generally unassisted (no fuel value added by sample holder), as opposed to the powder burning to be described later.

Some of the conclusions drawn by these investigators relevant to later discussions are listed below:

1) The lower pressure deflagration limit, PDL, (pressure below which stable burning was not maintained) was insensitive to sample size and to substitution of helium

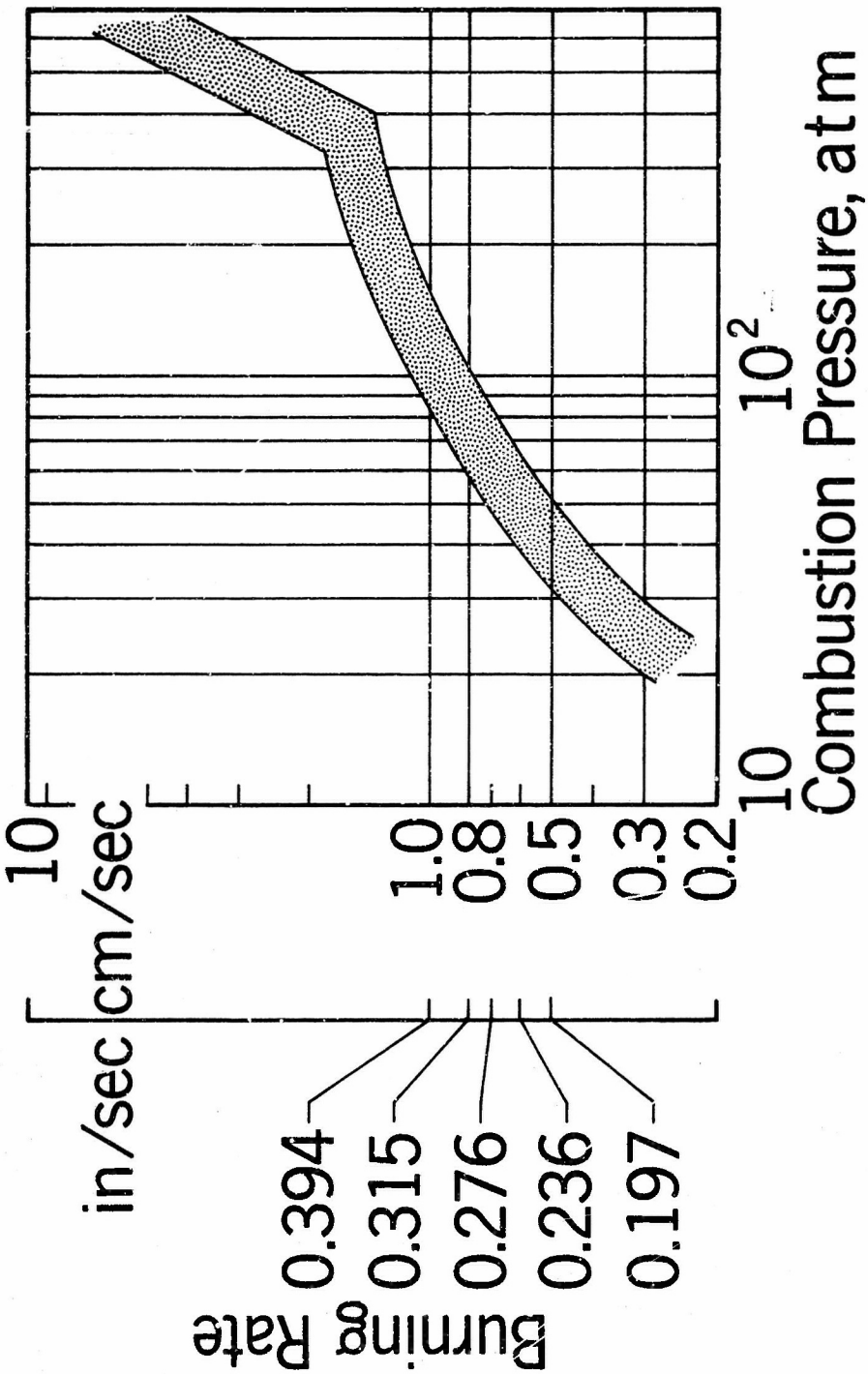

FIGURE I. AMMONIUM PERCHLORATE HIGH DENSITY POWDER BURNING RATES

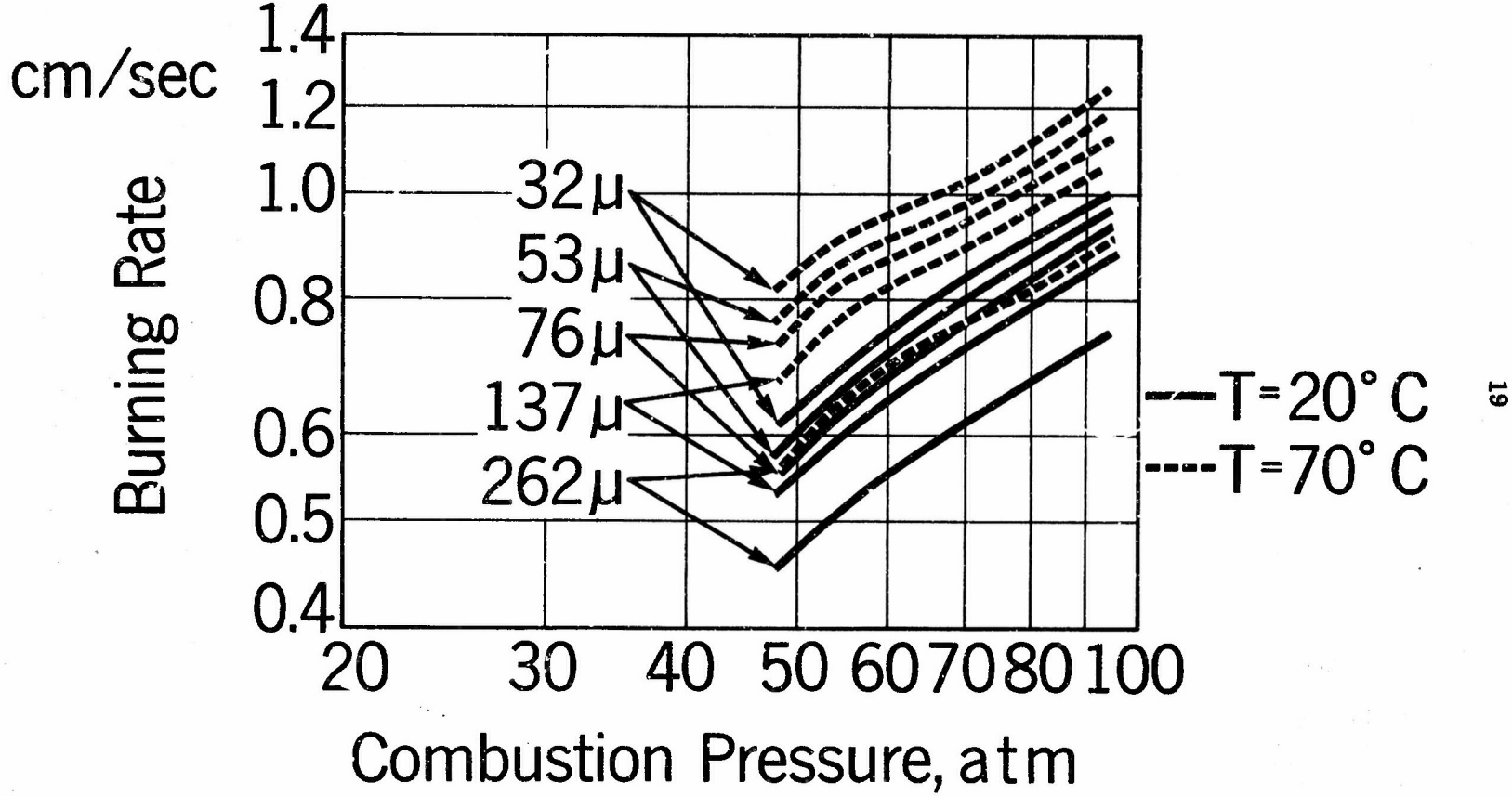

FIGURE II. PARTICLE SIZE AND TEMPERATURE EFFECTS ON AMMONIUM PERCHLORATE POWDER BURNING

for nitrogen as the strandburner pressurizing gas.

2) PDL increases as the A.P. particle size (from which the strands were made) was decreased.

3) Preheating strands lowers PDL; and precooling raises it. The values below are only relative; they depend on a number of experimental variables.

PDL > 270 atmospheres at -18°C

PDL = 45 atmospheres at +21°C

PDL = 20 atmospheres at +70°C

4) A fraction of a percent of the well known propellant burning rate catalyst copper chromite greatly increases PDL at room temperature:

PDL = 22 atmospheres for pure A.P.

PDL = 170 atmospheres for A.P. + 0.5% copper chromite

5) PDL is raised when other black additives, like platinum black which may not be a catalyst in this system, are added.

6) Addition of external radiant energy drastically

lowers PDL at room temperature.

PDL without radiation = 22 to 45 atm.

PDL with radiation = 1 atm.

7) Considering all of the data in Figure I, a burning rate equation of $r = 1/4\ (P/1000)^{2/3}$, in in./sec, and pressure in psia gave a reasonably good correllation for average particle size of about 100 microns, in the 1000 to 2000 psia range.

8) Burning rates were increased for finer particle sizes, but the rate versus pressure slope remained nearly constant (see Figure II).

9) σ_p was equal to 0.24%/°F in the 70° to 160°F range.

Note: $$\sigma_p = \left[\frac{\delta\left(\frac{\Delta r}{r}\right) \times 100}{\delta T}\right]_p$$

where p = pressure, r = burning rate and T = temperature

10) Irvin found two combustion regimes with a transition at a pressure of 300 atm. Above 300 atm., the observed pressure exponent was of the order of

1.75. This rapid increase of deflagration velocity was attributed to flame penetration into cracks in the sample, which may arise from the high heat flux and large thermal gradients.

From the foregoing tests showing how preheating aids combustion, it was concluded that insufficient heat at the burning surface retards and limits combustion. Since flame zone maximum temperature calculations show that sufficient heat is available to sustain burning even at ambient pressure then heat loss must be the reason there is a lower deflagration limit, PDL. The experiments described above have attempted to pin down the loss pathway.

Since switching inert gases from nitrogen to helium (which has a thermal conductivity several times that of nitrogen) didn't affect PDL it was concluded that heat loss by either gas convection or gas conduction is not controlling. Since changing the strand sample size didn't affect the results, it would seem that edge cooling effects are not important. This leaves only solid conduction and solid or gas radiation as possible loss pathways. The effects of black additives led Friedman to the conclusion that the important heat loss mechanism is radiation, and the most important part of this loss is from the surface.

It was concluded from the high pressure tests of Irvin, that

physical changes in the sample under test, or changes in the ability of flames to penetrate existing voids, can markedly influence burning rate measurement. This has strong implications to the varying density tests conducted in the experimental portions of this work; where voids or cracks were "built into" the samples.

vonElbe, McHale, and co-workers are continuing the high density powder combustion tests with a range of other oxidizers. Their high magnification movies of the phenomena have brought the attention of other investigators to the physical processes that take place at the burning surface. Although no melting or liquid layer has been observed for A.P. in these powder tests, a layer has been observed for hydrazinium perchlorate, diperchlorate and hydrazine nitroform.

Another interesting powder combustion approach, not like that to be described in the experimental portion (III), is the loose granule burner developed by McAlevy[11] of Stevens Institute. The loose packing allows, for example, passing fuel gas through a bed of oxidizer to simulate propellant interactions. This approach would be particularly applicable to studies of nitronium perchlorate which would not be considered a monopropellant.

B. Single Crystal Combustion

Price, Hightower, and co-workers at Naval Ordnance Test Station, China Lake, California, (NOTS) have long been interested in combustion problems. Recently they have concentrated on the combustion of single A.P. crystals alone and bonded to PBAA type gumstocks. The latter samples were used as propellant models. They found evidence for the first time of a melt on the burning crystals. It is either ammonium perchlorate or a decomposition product. A most interesting conclusion from this work involved the relationship between powder and crystal burning. It has been shown above that for high and constant bulk density pressed samples of oxidizer powder, the smaller the particle size, the faster the burning rate. These investigators have proposed that a single oxidizer crystal be considered as composed of "zero particle size" particles — and thus it should burn faster than any pressed powder. Their data supports this hypothesis. Our data on low density powder in Section III supported an opposite hypothesis, i.e., that a single crystal may be considered an infinitely large particle, with a minimum surface area for reactions as compared with any other physical form, and thus it would be expected to have the lowest linear burning rate. However, the single crystal burning rates reported herein agreed remarkably well with the single crystal rates of Price. This caused an adjustment in our proposed model to account for the discontinuity in thermal conduction when going from pressed powders to single crystals with only a slight density change. Petersen[12], at the University of California, has been

studying the ignition and deflagration of single A.P. crystals and has confirmed the results of Price and the few observations of Whittaker made several years ago.

C. Surface Decomposition Reactions

During combustion of either powders or crystals, any given plane in the solid phase is progressively heated as the flame zone approaches it. There are a number of ways in which the solid A.P. can utilize this energy in addition to a simple temperature increase. Several of the ways are decompositions, and at about 460°C, A.P. rapidly decomposes. At 240°C there is an endothermic phase change from orthorhombic to cubic.

P. W. M. Jacobs of the University of Western Ontario summarized the latest work on A.P. activation energies at the Third ICRPG Combustion Conference, Kennedy Space Center, October 17, 1966. After examining large quantities of isothermal decomposition data he felt that there were more errors to contend with in the pressure rise type of measurements than in the weight loss measurements. The weight loss measurements give 30 K_{cal}/mole as the activation energy. Most interesting is the finding that this same energy holds for several temperature ranges and for several different types of decomposition that are postulated to occur in these ranges:

NH_4ClO_4 Decomposition Type, Temperature	Mechanism → Initial Products
Low Temp., 200°C	Electron transfer → NH_4 + ClO_4
Medium Temp., 200° – 300°C	Proton Transfer and Sublimation → NH_3 + $HClO_4$
High Temp., 300°C	Ion Formation → NH_4^+ + ClO_4^-

It is believed that most of the discrepancies in decomposition measurement in prior years, giving values ranging from 20 to 60 K_{cal}/mole, were due to gas phase reactions following the original surface decomposition. It is hoped that this surface decomposition activation energy value from weight loss measurements can be relied upon, and then further progress can be made by obtaining values for gas phase activation energies. The problem with gas phase determinations is how to get uniform molecular scale mixing at any temperature of ammonia or ammonium ions with perchloric acid or perchlorate ions so that true reaction rates can be measured. Thus far, tests with jets of ammonia passing into vaporized perchloric acid, and vice-versa, have produced quantities of solid ammonium perchlorate in the combination rather than the decomposition reaction. Also, this kind of reactant mixing is far from the molecular or ionic level.

D. Combustion Reactions and Temperatures

Levy and Friedman[4], and Arden, Powling and Smith[13] have described analytical and experimental investigations of A.P. combustion temperature profiles and the products of combustion. The diferences between high pressure (1000 psia) and atmospheric pressure results are summarized.

1. High Pressure Combustion (1000 psia)

In reference 4 the product gas temperature was calculated for the product distribution as analyzed, i.e., a N_2:NO:N_2O ratio of 1:0.87:0.45. Hydrogen chloride, chlorine, water and oxygen were assumed to be in thermodynamic equilibrium

$$Cl_2 + H_2O \rightleftharpoons 2HCl + \frac{1}{2} O_2$$

using the equilibrium constants of Sinke[14]. The stoichiometric equation then becomes:

$$NH_4ClO_4 \longrightarrow 0.265N_2 + 0.12N_2O + 0.23NO + 1.015O_2 + 1.62H_2O + 0.76HCl + 0.12Cl_2$$

The calculated flame temperature is 987°C. This is in fair agreement with their measured values of 930 to 970°C. The surface temperature is estimated to be between 700°C and 800°C. Precise measurements have not been made at high pressures due to the difficulty of placing a sensor in

such a thin zone or the difficulty of taking radiation measurements characteristic of the surface only when the flame zone is so close. Powling[15] has given an excellent discussion of the experimental problems involved in this measurement beyond about 4 atmospheres. However, he does conclude that the change in surface temperature at low pressures is compatible with equilibrium dissociation at the surface:

$$NH_4ClO_{4(s)} \rightleftharpoons NH_{3(g)} + HClO_{4(g)}$$

Powling used a ΔH sublimation value of 56 K_{cal}/mole, rather than the more recently accepted 30 K_{cal}/mole; however, the following relationships were valid in the range 30 mm Hg to 4 atmospheres.

$$\ln (Kp1/Kp2) = \ln (P_1^2/P_2^2) = \Delta H_s \ (1/T_2 - 1/T_1)/R$$

where Kp = equilibrium constant for the dissociation reaction

$$= P_{NH_3} \times P_{HClO_4}$$

and P = combustion pressure

ΔH_s = heat of dissociation or sublimation

T = surface temperature

Powling speculates that an equilibrium relationship such as this would not be expected at pressures significantly beyond 1000 psia. At high pressures the temperature at the surface would approach the flame temperature; and the partial pressures of NH_3 and $HClO_4$ would be expected to approach

zero. Under these conditions the surface reaction would be rate controlled.

2. Atmospheric Pressure Combustion

The product analysis at low pressure showed that all the chlorine was present as molecular chlorine. The stoichiometric equation was:

$$NH_4ClO_4 \rightarrow 0.55NO + 0.10N_2O + 0.125N_2 + 0.5Cl_2 + 2H_2O + 0.675O_2$$

This corresponds to a flame temperature of 967° C. The surface temperature as measured by an infra-red optical method[15] was 480°C. It was found that the burning of packed A.P. powders, partially fuel supported with a wide variety of fuels gave a surface temperature variation of only 450 ± 30°C. Burning rates were increased fourfold when the flame temperature was increased to about 1700°C by adding polystyrene powder as a fuel. The surface temperature in this latter case dropped to about 420°C. There was nearly a direct linear relationship between flame temperature (as manipulated by fuel addition) and burning rate.

3. Combustion Comparison

The decrease in NO when going from low pressure to high pressure (lower to higher reaction temperatures) is believed to be due to its lower oxidizing ability and less reaction with NH_3 or NH_2 radicals at the

lower temperature. This also explains the greater N_2 content at higher temperature:

$$NO + NH_2 \rightarrow N_2 + H_2O$$

The ammonia-nitric oxide flame temperature is 2640°C. Nitric oxide is an endothermic compound so that as more of it is formed — or remains in the product gases — the flame temperature is reduced.

It has been calculated that a flame temperature of about 930°C is required to support stable combustion. In the atmospheric tests described above A.P. would only burn by itself with added heat of about 10 cal/cm^2 sec (supplied as radiant energy) or 64 cal/gram (supplied as preheat). When some fuel was added — the higher temperature fuel-oxidizer flame provided the required energy. The oxides of chlorine are not found at either high or low pressure as they were the most powerful oxidizing agents present. No ammonia or amino radicals are found because they are the first species to be oxidized.

It may be that the nitric oxide reactions are so slow in taking place, that at atmospheric pressure the flame temperature is not established until it is too far from the burning surface to give a comparable effect to that at high temperature — although the difference in flame temperatures is only about 20°C.

Catalysts (copper chromate and chromite) have been found to reduce NO content at low pressure and N_2O content at high pressure, presumably by drawing the combustion reaction further toward completion (to N_2 and O_2) in both cases.

E. Burning Rate Theory

The most comprehensive analysis of the burning rate-pressure response of a monopropellant was prepared several years ago by Johnson and Nachbar[16]. They combined the applicable solid surface decomposition relations with laminar flame theory, and finally obtained the relation

$$p = \frac{1}{\bar{K}} (r^2 \Lambda)^{1/m}$$

where: p = pressure

r = burning rate

$\bar{K}$ = scaling factor

Λ = eigenvalue for particular conditions

m = order of the gas phase reaction

Even an abbreviated derivation of this final form is quite lengthy.

Although sample calculations were made only for ammonium perchlorate, the overall results are quite impressive. There was an

unaccounted for heat loss factor, and the gas phase activation energy was unknown. The measured burning rate at one pressure was fed in as a scaling factor and a reasonable estimate was made of the gas phase activation energy. A plot of the Johnson and Nachbar theoretical calculations for crystals burning adiabatically is included as the triangular data points and curve in the lower portion of Figure XI in Section III, C, 7.

The solution to the intriguing problem of burning rate prediction is still not complete, but the work of Nachbar and Johnson has opened a way. Barrere and Williams[9] have extended the work for certain non-adiabatic conditions; and have given an excellent review of burning rate theory and experiments.

Prior to 1960, there had been some attempts to relate burning rate of a homogeneous, condensed phase monopropellant to its physical and thermochemical properties. Combustion of a single crystal of ammonium nitrate or perchlorate represents a specific example of this general category. The most notable attempt was that of Schultz, Green, and Penner[17] given in 1958 for the linear pyrolysis rate of ammonium nitrate. Although this pyrolysis was not quite the same as a burning rate — it was very closely related — and showed more clearly than the earlier studies of lower temperature decomposition the kinds of problems to be faced. Solid pyrolysis rates were studied because it was generally agreed that condensed

unaccounted for heat loss factor, and the gas phase activation energy was unknown. The measured burning rate at one pressure was fed in as a scaling factor and a reasonable estimate was made of the gas phase activation energy. A plot of the Johnson and Nachbar theoretical calculations for crystals burning adiabatically is included as the triangular data points and curve in the lower portion of Figure XI in Section III, C, 7.

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phase reactions were the limiting factors in establishing burning rate or combustion velocity.

The biggest advantage of the linear pyrolysis test was that it gave a kind of burning rate measurement in which the surface temperature could be varied over a wide range, while holding pressure constant. These investigators then found the surface temperature at which the pyrolysis rate equaled the normal strandburner determined burning rate; and used that value as an estimate of the burning surface temperature.

They attempted using absolute reaction rate theory to predict the change in the rate of linear pyrolysis of a strand of pressed A.N., as they raised the temperature of a hot metal plate pressed against it. A number of assumptions were tried but the results were not encouraging because the experimental technique needed refinement, and too little was known about the configuration of the potential energy surfaces for the various rate processes they had proposed. The rate process they assumed to be controlling was the desorption HNO_3 (from NH_4NO_3 decomposition) from the pyrolyzing surface. This early groundwork in theory and experiment greatly aided later studies.

A considerable amount of continuing work has been done on the experimental technique, although attention from 1958 to 1966 was

directed to A. P. as the experimental compound. It now appears that more reliable results will come from the "porous plate" pyrolysis apparatus like that of either Barrere at ONERA or Coates[18] at Lockheed. An entirely new approach to heating the surface is being taken by Cole at Stevens Institute. Here a stream of hot gas is directed axisymmetrically at the oxidizer surface, and the temperature is sensed by an IR technique. A comparision of this data with the porous plate data will be most interesting. A recent analysis of the implications of absolute reaction rate theory has been given by Williams[19].

As more and more burning rate data, combustion mechanism data, and physical and chemical properties of oxidizers become available, there is an entirely different approach to testing the dependency of burning rate on any given independent variable. That is to use regression analysis on all suspected variables, and to allow correlation coefficients and other statistical tests to tell us which are most valuable. To determine the usefulness of this method, a trial analysis was run on a crystal property expected to be important to combustion characteristics. As shown in the Appendix the results were gratifying, and the method shows real promise for application in later burning rate studies.

III. EXPERIMENTAL WORK

It was planned originally that the experimental work would focus on the measurement of combustion properties of large single crystals of ammonium perchlorate. During the planning period for this research no such comprehensive study was reported. It was believed that single crystals of A.P. could be grown to a size large enough to study burning properties with relative ease from saturated solutions by evaporation or temperature lowering. Small scale experiments seemed to confirm this. However, during 1965, interest in this same problem seemed to flourish in several other laboratories throughout the U.S. By mid-1965 it became apparent that as yet unpublished work had been underway in the early 1960's at the Naval Ordnance Test Station laboratories at China Lake, California by McBride, at the University of California laboratories by Petersen and at Aerojet-Azusa by McGurk[20]. Also by that time it was evident that there was no simple way to grow large perfect A.P. crystals. No A.P. crystals were available commercially. Therefore, a major effort was begun to develop a sophisticated crystal growing bath and associated temperature controls. The people at the other laboratories reported difficulties in growing A.P. crystals even with rather elaborate systems. (Their studies

were directed toward comparisons with alkali perchlorates, ignition properties, and fundamental crystallographic studies respectively. They did however, recommend using techniques similar to those of J. N. Torgesen at the National Bureau of Standards, Crystal Chemistry Section. This was done, making several visits to Dr. Torgesen's laboratory and discussing theory and practice with him and his assistant, Mr. A. T. Horton.

By mid-1966 an apparatus was constructed at the University of Delaware and it had shown the capability of growing the kind of A.P. crystals that were needed.

During 1964-1965 however, it was realized that one important facet of crystalline oxidizer combustion that was not being studied by others was the combustion of low bulk density powders. All reported work dealt with the burning of powders pressed to nearly the crystal density of A.P. (1.95 g/cc). Low bulk density powders (1.0 g/cc), if they would burn would give previously unavailable information about flame penetration and the propagation of combustion reactions. As a sidelight, the low bulk density powder is an interesting propellant analog in that the inert gas or air voids are a special case of a no fuel value, low viscosity, low density, transparent binder.

Therefore, it was decided to put a major effort into determining the

feasibility of such burning and by mid-1966 it had been demonstrated that such powders would really burn reproducibly rather than detonate — or not burn at all.

By Spring 1967, crystals had been produced and combustion tests had been conducted on single crystals and a variety of oxidizer powders under a wide range of experimental pressures in order to describe the spectrum of crystalline oxidizer combustion.

The following three parts of section III describe how large single crystals were grown, how oxidizer powders were prepared, and finally the techniques and equipment for combustion testing and the data they provided.

A. Single Crystal Growth

It was found to be relatively difficult to grow single perfect crystals of A.P. By this it is meant that under a given set of crystal growth conditions it was far easier to grow many other types of large crystals. For example, sodium bromate was grown into large nearly perfect crystals quite early in the study, when many of the growth conditions were poorly controlled. The ease of growth seemed to follow the general rule of thumb that compounds of relatively higher solubility are relatively easier to grow as perfect crystals.

Since A.P. in contact with oxidizable materials is a potential fire hazard, great care was taken in the experimental work to prevent overheating, friction, contamination of A.P. with oxidizable materials and vice versa.

Two crystal growth baths were developed: a larger variety holding about 18 liters of solution, and a smaller one holding about three liters of solution. For large crystals, the large bath was superior. But for flexibility in studying technique changes the smaller type was also required. Work actually began on the smaller baths, but it was soon discovered that large crystals (that is, at least one cm. in one dimension) could not be grown in them. Tests then proceeded to the larger type.

Generally helpful information on crystal growth was obtained from the Russian work in three volumes by Shubnikov and Sheftal[21], and Gilman[22], and the earlier work by Buckley[23]. As a crystallography reference, Phillips[24] was used.

The ammonium perchlorate used in these experiments was "ultra high purity grade" as supplied by American Potash and Chemical Company. A typical analysis is shown in Table 1.

During the early parts of the studies, it seemed that evaporation techniques could be used. As the work progressed, however, it became evident that lowering the temperature of a saturated solution

TABLE 1

CHEMICAL ANALYSIS OF
ULTRA HIGH PURITY* AMMONIUM PERCHLORATE

CONSTITUENT	PERCENT BY WEIGHT
Ammonium Perchlorate	99.9
Sodium	0.0001
Potassium	0.0001
Chloride as NH_4Cl	Nil
Chlorate as $NaClO_3$	Nil
Total Moisture	0.182
Sulfated Ash	0.01
Sulfate as $(NH_4)_2 SO_4$	Very slight trace
Bromate	Nil
Water Insoluble	0.0020
Iron as Fe_2O_3	0.000
pH	4.4

*American Potash and Chemical Corporation grade, Lot No. W-1987-27A, supplied as recovered from crystallizer. 97.4% of particles are larger than 100 mesh (149 microns) and largest fraction is in 297-420 micron range.

was best for A.P.

1. Three Liter Crystal Growth Apparatus

The three liter bath was ultimately developed and produced excellent results, with a minimum of sophisticated controls. The rotation mechanism and base heating is identical to the large bath to be described later. However, the temperature control was maintained by a Magnaset thermoregulator and mercury relay which controlled the base heater system. Temperature reduction was achieved by driving the thermoregulator balance temperature down through a belt attached to an electric clock drive. The belt slowly turned the knurled knob of the thermoregulator and lowered the control point uniformly by 0.01 to 0.10 °C per day depending on the drive wheel size. These details are shown in Figure III.

2. Large Cryst Growth

Large crystals are defined as those having at least one dimension equal to a centimeter. It is important to get sizes in this range, and larger, so that samples for combustion tests may be cut from them. The combustion test samples for use in a window-bomb should be at least 0.5 cm x 0.5 cm by several millimeters.

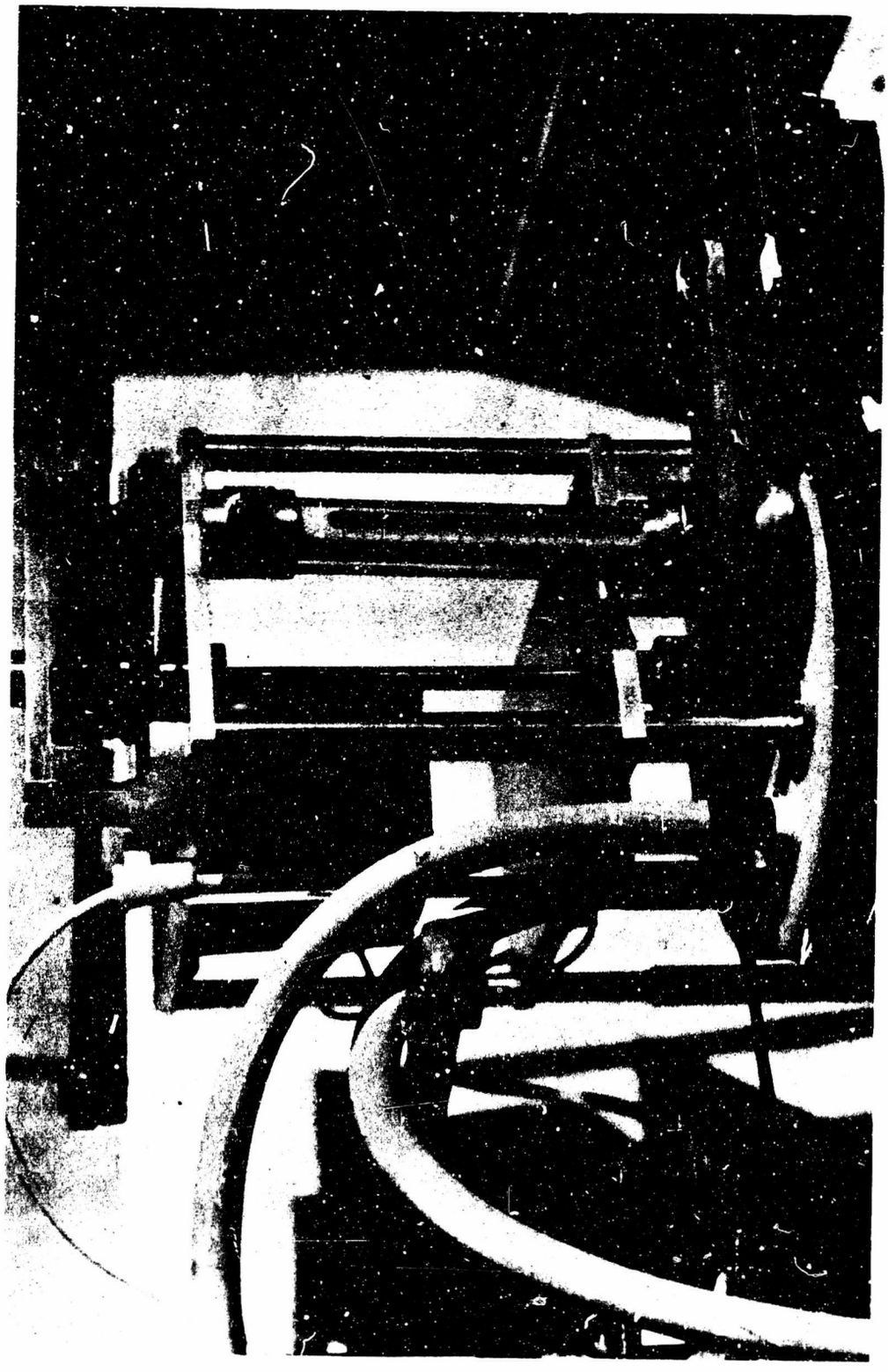

FIGURE III. THREE LITER CRYSTAL BATH CONTROLS

Since the large crystals are grown on cylindrical pins of several millimeters in diameter, there are unavoidable defect areas formed in the central portion of the crystal which must be cleaved out. The crystals are readily cleaved along their crystallographic axes by a sharp razor blade tapped with a mallet.

The single crystals of ammonium perchlorate for combustion studies were grown from saturated aqueous solution at about 45°C in a closed bath. The three chief components are: 1) the bath itself with provisions for stirring, heating, insulation, etc., 2) temperature acquisition and recording equipment, and 3) the temperature controller and programmer. The equipment arrangement for the large, 18 liter bath is shown in Figure IV. To the left is the Quartz Thermometer mounted atop a digital recorder. In the center is the bath with insulating jacket opened. On the right is the controller and programmer.

a) Crystal Growing Bath

Single crystals are grown from solution contained in a large glass jar 12-inches in diameter, 12-inches in height, and approximately 4-1/2 gallons in capacity following the technique of Torgesen and Horton at NBS[25]. Essentially the changes made at the University of Delaware dealt with:

FIGURE IV. EIGHTEEN LITER CRYSTAL GROWING APPARATUS

1) materials of construction

2) method of sealing the bath for compatibility with A.P.

3) temperature sensing and

4) additional insulation of the bath itself and the temperature sensitive portions of the electronic controls.

Jar covers of teflon support the rotation mechanism the finger heaters, and temperature sensing devices. The jars are supported in stainless steel frames which contain bottom heaters to distribute heat uniformly over the entire bottom surface and inhibit volunteer crystal growth. The bottom heater consists of 25 small (15 watt) lamps evenly distributed over the base of the frame on a sheet of Transite.

The crystals are supported on lucite pins that are press fit into holes near the ends of the branches of a "crystal tree." The general aim is to provide support offering a minimum of interference with the external growth surfaces. The crystal tree is constructed of nylon rod and has three rows of four branches each, thus accommodating a total load of 12 crystals. It was felt that glass would be too brittle and

subject to breakage and lucite would soften at higher bath temperatures. Lucite because it is transparent, was used wherever possible. Neither nylon nor lucite appeared to be attacked by the A.P. solution.

To promote efficient stirring of the bath and produce uniform solution temperature and concentration, the crystal tree is provided with rectangular vanes of lucite. The vanes hang from the tree branches and generally swing freely. The vanes change position depending on the direction of rotation and continuously promote a transfer of solution from top to bottom in the jar. It is believed on the basis of small bath tests, that considerably more stirring than this arrangement provides would be advantageous.

A stainless sleeve attaches the crystal tree "trunk" to the shaft of the rotation mechanism. An adjustable seal at the lid of the bath provides good contact between the nylon trunk and the Teflon lid and prevents the loss of solvent vapor, contamination of the solution from the outside, and corrosion of bearings and other metal parts of the rotation mechanism.

The photograph (Figure V) taken during an actual growth operation with the fiberglass filled insulation jacket opened shows the overall bath arrangement. The jacket has a zipper closure for ready

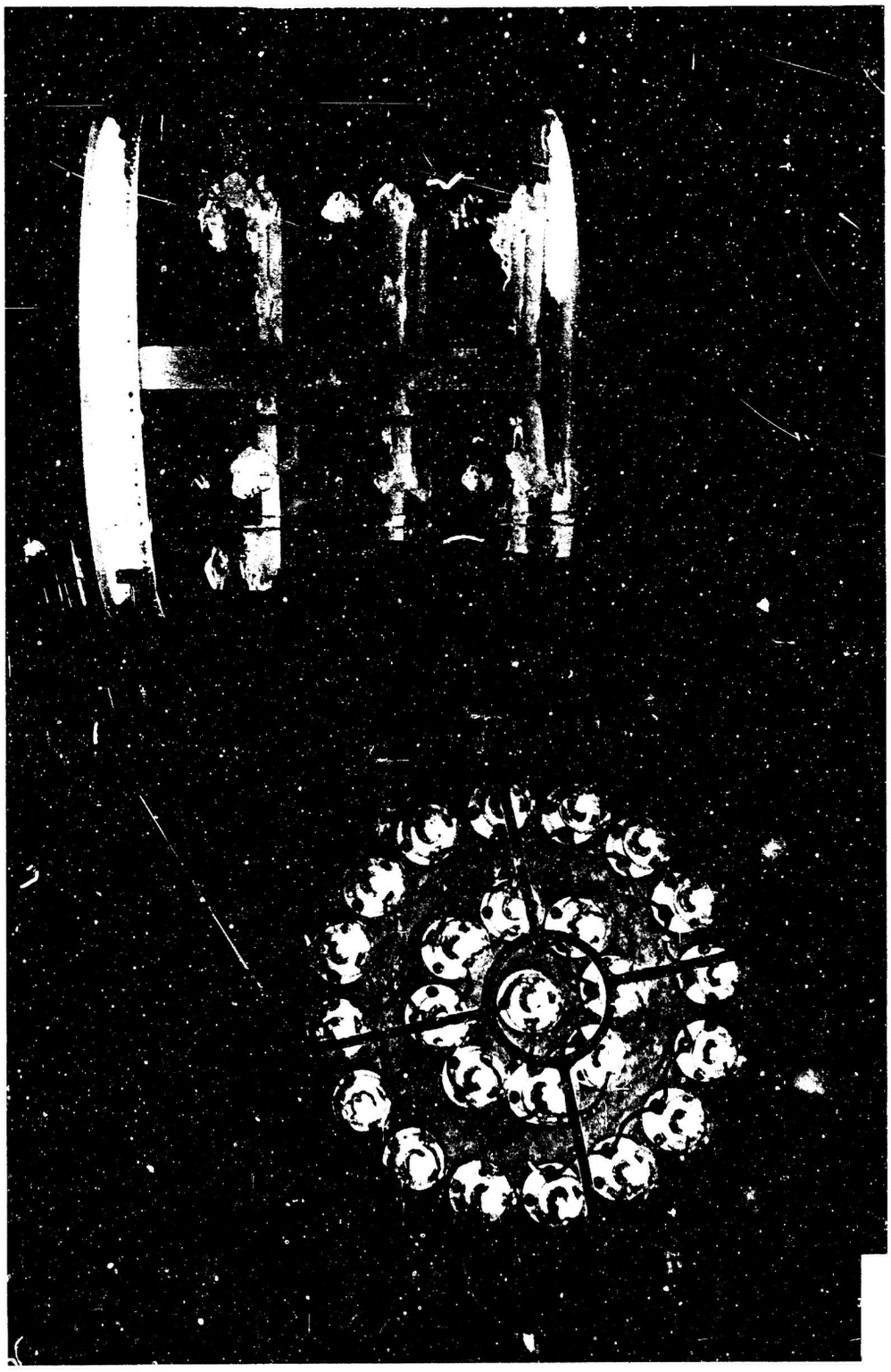

FIGURE V. CRYSTAL BATH DETAILS

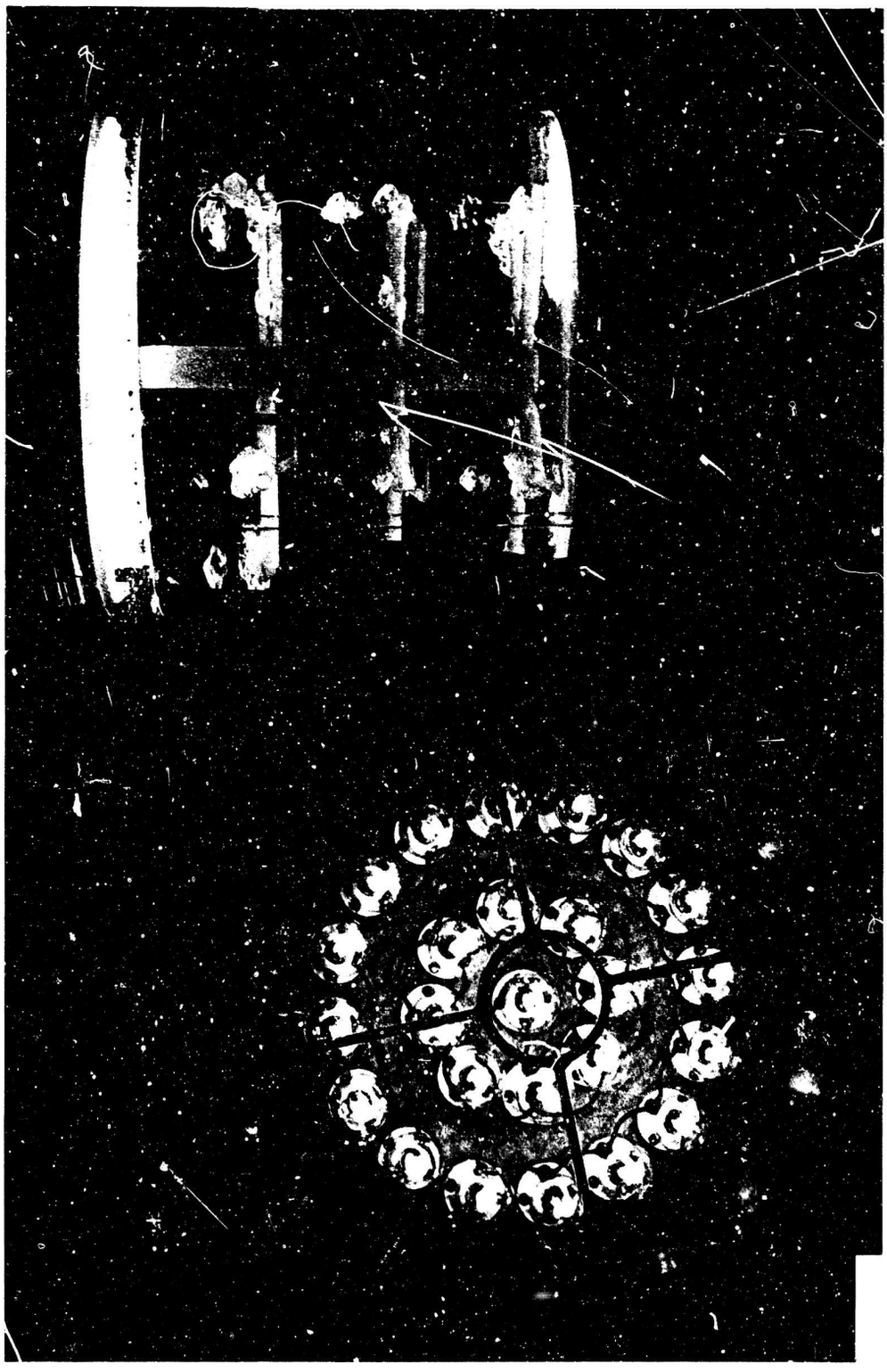

FIGURE V. CRYSTAL BATH DETAILS

inspection of the crystals during growth.

In order that all surfaces of the growing crystal may be washed approximately equally with the solution to promote uniform growth, it is necessary to provide a mechanism for rotation of the crystal tree in both directions. The rotation device employs a rack-and-pinion mechanism. The gear-rack, moved back and forth by eccentric attachment to the shaft of a slow speed motor, imparts, through the pinion gear on the tree shaft, an approximately sinusoidal rate of rotation to the crystal tree. The arrangement gives gradual deceleration and acceleration on either side of the reversal point and avoids undue mechanical stress in the gorwing crystals and the equipment assembly.

The arrangement currently used provides a maximum speed of approximately 25 rpm and the crystal tree is rotated through about four complete revolutions between changes of direction. Good quality motor lubrication oil and vaseline or gear-grease were found to be essential for smooth operation and to prevent motor failure. Ball bearings are used for the crystal tree and driver-arm shafts.

The motor used was a Hurst Company Model EA which provides 300 inch-ounces of torque at 2 rpm. These are the most powerful synchronous totally-enclosed, ball bearing motors available for low (less

than 10) rpm operation on a continuous basis. Less powerful 100 to 200 inch-ounce motors were found to fail due to torque overload within a few weeks.

b) Bath Temperature Readout and Recording

When it was found that bath temperature changes of 0.001°C were important, and that a knowledge of the variations at the 0.0001°C level would help correct other portions of the system, the need for a highly sophisticated temperature acquisition system was indicated. In addition, since it was necessary to know what the temperature history of the bath was on a nearly continual basis, the need for a recording system was also indicated. It is of interest that during the period that our need developed, the Quartz Thermometer was introduced by Hewlett Packard. After an exhaustive analysis of the relative merits and economics of conventional resistance thermometers versus quartz thermometry the latter was chosen. The Quartz Crystal Thermometer was judged superior on the following counts:

-somewhat lower overall cost (about $1000 less)

-faster direct readout (10 seconds versus one or more minutes)

-better accuracy (0.0001°C versus 0.001°C)

-better system stability and lower laboratory space requirement.

The particular model used was the DY-2801A with special long, low mass, sensing probes.

A Model 562A Digital Recorder was coupled with the thermometer to give printout of bath temperatures to 0.0001°C every 17 seconds.

c) Temperature Control and Programming

Precision control of temperature is of primary importance during the growth of single crystal specimens of high quality from solution. As has been clearly pointed out by Torgesen, momentary temperature fluctuations will result in interrupted and accelerated growth rates, and will produce veils of mother liquor inclusions which lie parallel to the crystal faces on which deposition occurs. We have found it essential to follow all of the guidelines laid down by Torgesen and Horton. When the temperature-changing technique is used, we have found that finite changes in temperature of a few hundredths of a degree will again induce the inclusion of mother liquor pockets. The close control of temperature at a given instant, together with a slow and continuous change in the temperature to maintain a uniform degree of super-saturation, can do much to minimize this effect.

The control apparatus constructed was essentially a duplication of that described by Torgesen et. al.

An order of magnitude improvement in temperature stability was obtained by placing a large lucite box over the entire bath to provide a lagging effect. A small fan was included inside the box to minimize temperature gradients. Temperature recordings showed that with this apparatus, control of temperature to $\pm$ 0.0008°C was obtained. In working with a potentially hazardous material like A.P. however, it was felt that this total enclosure of the bath and its motors was unwise.

The greatest single problem causing bath temperature fluctuation was drifting of the room temperature. Oddly enough when air conditioner or room heating got out of control, the bath temperature drifted inversely to room temperature. This was due to room temperature changes affecting the resistances in the control circuit. The effect of a 4°C rise in room temperature was to lower the controlled point of the bath by 0.060°C. That is the bath temperature range of variation was ten times greater than with a stable room temperature. When the room temperature was constant ($\pm$ 1°C) the bath temperature range was $\pm$ 0.003°C without the lucite bath cover.

The performance of the equipment was highly

satisfactory for the several week or even several month periods required in crystal growth experiments. It is composed of common electronic components which are subject to failure, and realizing that failure of temperature control is disastrous to crystal growth experiments, electronic tubes, mechanical relays, switches, motors, etc., of the best quality were used as NBS had recommended.

d) Properties of Single Crystals Grown

Visually perfect single A.P. crystals, with the largest dimension greater than one centimeter have been grown in these experiments. In tests conducted by Dr. J. N. Maycock, they were found to be transparent in the visible and near ultraviolet. At about 200 millimicrons a sharp absorption band front appeared indicating high purity and the transition of electrons from the valence to conduction band. In his tests of electrical conductivity at varying temperatures, the separate regimes of conduction for the two different forms were easily identified. It was interesting that the phase transition: orthorhombic to cubic appeared closer to 255°C rather than the 240°C reported in the literature.

A typical crystal is shown in Figure VI. Figure VII gives three views of a typical crystal with the faces labelled. Table 2 describes the faces and their intersections and uses the values given by

FIGURE VI. AMMONIUM PERCHLORATE SINGLE CRYSTAL

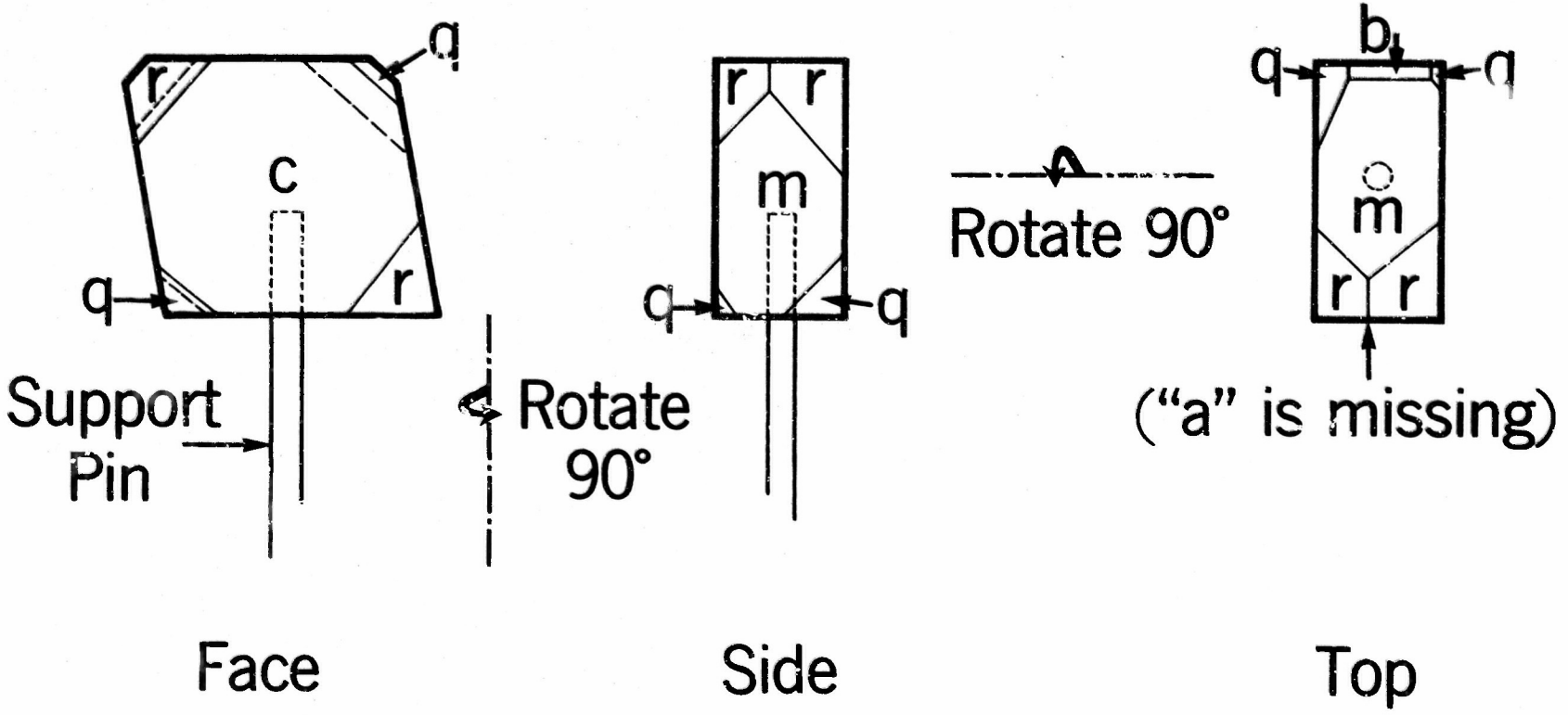

FIGURE VII. AMMONIUM PERCHLORATE SINGLE CRYSTAL HABIT (ORTHORHUMBIC)

TABLE 2

AMMONIUM PERCHLORATE SINGLE CRYSTAL CHARACTERIZATION
(ORTHORHOMBIC)

Faces	Indices	Observations
c	001	Largest faces, two always formed
b	010	Smallest face, usually only one formed
a	100	Not found
m	110	Second largest faces, four always formed; pairs of m faces are parallel two forming acute angles and two forming oblique angles
r	101	Third largest faces, the coigns at the ac intersection
q	011	Fourth largest faces, the coigns at the bc intersection

Face Intersection	Angle	Observations
cm	90°	
mm	76°	At the acute intersection
	104°	At the oblique intersection
bm	51°	
ar	51°	
rr	102°	
bq	38°	
qc	52°	

Tutton[26]. In most cases, the "c" or "m" faces were the largest, and generally the "c" faces were the largest of the two. The "r" faces were next largest; followed by the "q" faces. When an "r" face was not developed its neighboring "r" face was generally large. One "b" face was usually developed, but quite small, and no "a" faces were formed.

In a few crystals the "r" and "q" faces were larger than the "m" faces but never larger than the "c" faces.

The availability of perfect crystals opens up new vistas for research, not only in combustion, but also in such diverse fields as mechanical properties improvement of propellants. Here the wetting and bonding forces between crystals and binders may be studied.

B. Single Crystal Combustion Tests

Single crystals of A.P., prepared as described above, were cleaved along natural face boundaries to prepare wafer-like samples for combustion. The crystal dimensions for combustion samples were 0.2 x 0.2 x 0.08 inches (or 5000 x 5000 x 2000 microns). The combustion tests were conducted in a special micro window-bomb by Dr. William Wood at the Rohm and Haas Redstone Research Laboratories. Color films were taken at a speed of about 2000 frames per second. Upon analysis of these movies, which contained millisecond timing marks, it was possible to

accurately determine burning rates. At pressures of 900 and 1500 psi burning rates of 0.314 in./sec and 0.415 in./sec respectively were obtained. These data were in excellent agreement with the results, previously referred to, obtained by Hightower and Price[2]. Figure VIII is a photograph of a single crystal of A.P. burning at 0.415 in./sec and a window-bomb pressure of 1500 psia.

The crystals were mostly perfect with a few internal voids and cracks. There were enough clear portions in each crystal, however, to get the perfect crystal burning rate. Tests were conducted in a nitrogen atmosphere. Figure IX shows the burning rates obtained and for comparison, the solid line is taken from the data of Price. The agreement between two sets of results is excellent, and lends credence to the proposal that there is an intrinsic burning rate for oxidizer crystals that can be confirmed by different investigators. The interpolated value, obtained at both laboratories for r_i at 1000 psi is 0.33 in./sec.

Most of the observations made by Hightower and Price were confirmed. The previously unreported observations are recorded here. Internal voids caused minor erruptions when the reaction zone reached them. However, the crystals showed surprisingly good resistance to cracking from thermal shock. Ignition was by hot wire and a magnesium flash powder.

FIGURE VIII. AMMONIUM PERCHLORATE SINGLE CRYSTAL BURNING AT 100 ATMOSPHERES

FIGURE VIII. AMMONIUM PERCHLORATE SINGLE CRYSTAL BURNING AT 100 ATMOSPHERES

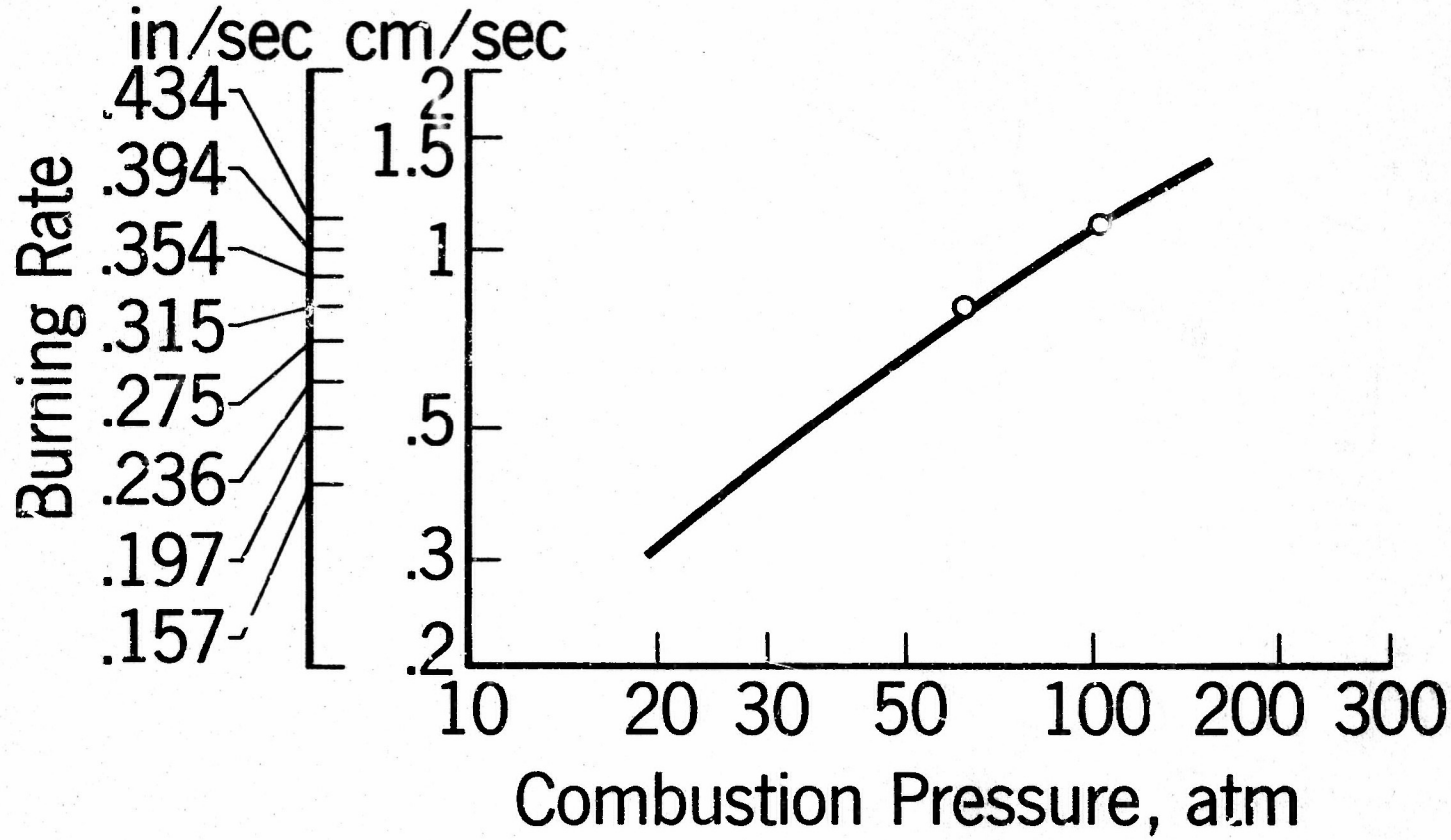

FIGURE IX. SINGLE CRYSTAL AMMONIUM PERCHLORATE BURNING RATE (r_1) VERSUS PRESSURE

An examination of the reacting surface in these films seems to indicate that the solid phase reaction zone is extremely thin, less than 100 microns, and that cracks in the crystals do not readily allow a forward propagation of the reaction. The gases are transparent near the surface but within a distance of about 500 to 1000 microns become a dense white cloud due to product condensation. As this cloud passed over the still red hot ignitor wire there was no noticeable reaction taking place. At the time these observations were taking place the ignitor wire was approximately one centimeter above the reacting surface. The reaction rate appeared to be somewhat slower at the crystal edges undoubtedly due to loss of heat by conduction and convection to the nitrogen atmosphere. In one sequence a globule formed near the crystal edge that had a glassy or molten surface. It finally broke free and tumbled off to the side apparently undergoing vigorous surface combustion all the while. The existence of some liquid phase also confirms Hightower's observation. In no case did the burning crystal surface appear to be a smooth flat plane. However, we could not detect any regular surface features. At the highest pressure the burning surface appeared to be the most smooth.

C. Low Bulk Density Powder Combustion

A number of previous investigators as described in Section II, A have reported on the combustion of A. P. powder pressed to nearly the

crystal density. This work was not repeated.

Interest developed in low bulk density studies when it was realized that bulk density as a combustion variable had not been investigated previously. In addition it was found that bulk density as a detonation variable was being studied at Stanford Research and the correlation between detonation and combustion was felt to be of theoretical interest. For many years it had been believed that powdered oxidizers that were monopropellants (like ammonium perchlorate) would burn erratically — or possibly — when in the low bulk density state explode. However, it was felt that under the right conditions combustion might be made to take place reproducibly over a wide range of pressures. It was soon found that when using a non-fuel insulating sample holder, combustion would not take place below several hundred psi. This confirmed the results of Friedman and others. However, when the sample holder provided some fuel value together with insulation, it was found that combustion readily took place even at sea level pressure. In later discussions with E. Price of Naval Ordnance Test Station it was found that their studies of firing of rocket motors loaded with pure A.P. had shown the same results. When the A.P. in the rocket motor was lined with even a few percent of a combustible insulation, combustion took place in the range of 50 psi. When the combustible material, which was only present as a small percentage of the A.P. was removed,

combustion did not take place until the pressure was raised to several hundred psi.

It was postulated that the reason for being able to sustain combustion at lower pressures was the higher flame temperature (caused by the fuel-oxidizer combination) feeding back a greater energy flux to the surface. This greater energy flux is necessary to counteract a greater radiant energy loss from the surface at low pressures.

Thus, the plan for this investigation was to devise a suitable powder sample holder, determine the precision of combustion measurements, and then to measure the combustion rates of various oxidizer powders.

1. Powder Sample Preparation

Oxidizer powder samples were prepared from pure crystallized material that had been dried, ground, and carefully screened to get specific particle sizes. Powders were dried by allowing them to come to equilibrium in a dry box maintained at less than 5% relative humidity at 75°F. U. S. Standard Sieves were used in the screening operations. Most of the powders used were passed through 40 mesh and retained on 50 mesh giving them an average particle size of about 360 microns.

2. Sample Holder Selection

Combustion of A.P. powders having a bulk density of about 1.0 g/cc was conducted at pressures ranging from 100 to 1000 psia; 100 psia was chosen as a standard pressure for the first experiments in order to give a longer sample burning time. The rate was determined as an average over a four inch long sample. Various kinds of soda straws and plastic tubes were tried. Neither metal nor glass tubes were considered because of their high thermal conductivity and heat capacity. In addition, as the powder burned down deep into such a tube, it was felt that the high velocity flow of product gases could alter the static pressure at the burning surface. It was realized that plastic and cellulosic materials offered some fuel value; but it was felt that the advantages given above were compensating factors.

The second citation under reference 10 gives an excellent discussion of these problems, and presents experimental data for A.P. powder burning in glass tubes. In those tests PDL was much higher by comparison, and burning rates were much lower. It is believed that a large portion of this difference is due to heat abstraction by the glass tubes.

After investigating a large number of kinds of tubes and straws, five representative types were chosen. Then 10 replicates of each of the 5 kinds were loaded with -40 +50 mesh Ultra High Purity A.P.

and tested in a strandburner. On the basis of the tests summarized in Tables 3, 4, and 5, the 4 mm inside diameter, common waxed paper soda straw was chosen as the best. It uses a reasonable size sample (about 2 grams), is conveniently handled, and gives good precision for the rates measured.

The linear burning rate, measured normal to the ignited surface, such as is measured for solid propellants, was 2.24 inches per second for the powder at 100 psi. A "reduced" burning rate was determined by multiplying the regular burning rate by the ratio of bulk density to crystal density. (Considering as the limit the burning of a single crystal, this would be 1.0.) The "reduced" rate was 1.20 inches per second. This correction puts all measurements on an equal mass per unit volume basis.

The strandburner average pressure was between 105 and 110 psia (due to starting the test at 100 psia and encountering a rise due to combustion products up to about 120 psia). The measure of precision used was the range of the burning rates taken as a percentage of the average rate. An examination of the 4 mm paper straw data showed that this percentage was the smallest by far indicating the least scatter and best precision. Table 3 shows the interaction of straw material and size on burning rate. The paper straws were felt to enter least into the

TABLE 3

SAMPLE HOLDER SELECTION:
INTERACTION OF MATERIAL AND SIZE ON BURNING RATE

Holder Material and Size	Burning Rate, in./sec
Waxed Paper	
4.0 mm	2.24
6.5 mm	2.54
Plastic	
3.5 mm	1.40
4.5 mm	2.14
6.0 mm	2.61

TABLE 4

SAMPLE HOLDER SELECTION:
EFFECT OF INERT MATERIAL FRACTION ON RATE

% Inert	Burning Rate, in /sec
14.5 (6 mm plastic)	2.61
16.3 (6.5 mm waxed paper)	2.54
17.2 (4.0 mm waxed paper)	2.24
18.5 (3.5 mm plastic)	1.40
30.5 (4.5 mm plastic)	2.14

TABLE 5

SAMPLE HOLDER SELECTION:
EFFECT OF HOLDER TYPE ON PRECISION

Holder Type	Burning Rate Range as % of Average
4.0 mm paper	17.4
6.5 mm paper	27.6
4.5 mm PVC	50.9
3.5 mm cellophane	62.1
6.0 mm polyethylene	53.3

combustion reaction.

3. Burning Rate Versus Pressure Tests (Constant Bulk Density)

For the data shown in Table 6 constant particle size was maintained at -40 +50 mesh UHP-A.P. and the packing density for all 50 samples was 1.11 ± 0.03 g/cc. The nitrogen pressure in the strandburner was varied from 100 to 1500 psia. The burning rates increased from 2.11 in./sec to 12.31 in./sec in this range. The precision of the individual data points was good at all pressures, but best (± 6%) at 1000 psia. The tests at 100 psia were a check for repeatability over a period of time against tests with the same material run at 100 psia one month previously. The two values for reduced rate were 1.20 in./sec and 1.22 in./sec; or a difference in the averages of eight samples of 0.02 in./sec. This degree of precision was considered excellent for purposes of this study.

This set of data showed that the correction to "reduced rate," where control of sample bulk density is good, is not useful. It had been first postulated that mass burning rate might be constant, but this was now proven incorrect.

It also showed conclusively that there was a relation between powder and single crystal burning. This will be treated under Discussion of Results (Section IV).

TABLE 6

LOW BULK DENSITY A.P. POWDER BURNING RATES VERSUS PRESSURE
(Constant Bulk Density; Ave = 1.11 g/cc; -40 +50 mesh, 360 micron powder)

Sample No.	ρ Bulk	ρ Bulk / ρ Crystal	Test Pressure psia	Rate in./sec	Reduced Rate in./sec	Avg. Rate in./sec n Samples	Average Reduced Rate in./sec n Samples	Rate Range and % of Avg.	Reduced Rate Range and % of Avg.
C-1	1.14	0.585	1520	--	--	12.31	7.06	10.47	6.06
C-2	1.12	0.574	1520	--	--	for	for	to	to
C-3	1.13	0.579	1520	10.47	6.06	8	8	13.38	7.68
C-4	1.13	0.579	1525	12.54	7.26	samples	samples	or	or
C-5	1.12	0.574	1520	11.49	6.60			12.31	7.06
C-6	1.13	0.579	1520	12.74	7.38			-1.84	-1.00
C-7	1.12	0.574	1530	13.38	7.68			+1.07	+0.62
C-8	1.10	0.564	1520	12.82	7.23				
C-9	1.13	0.579	1520	11.91	6.90			25.6%	22.9%
C-10	1.10	0.564	1520	13.12	7.40				

TABLE 6 (Continued)

Sample No.	ρ Bulk	ρ Bulk / ρ Crystal	Test Pressure psia	Rate in./sec	Reduced Rate in./sec	Avg. Rate in./sec n Samples	Average Reduced Rate in./sec n Samples	Rate Range and % of Avg.	Reduced Rate Range and % of Avg.
C-11	1.09	0.559	1015	9.15	5.11	9.49	5.37	8.93	5.11
C-12	1.09	0.559	1015	9.28	5.19	for	for	to	to
C-13	1.08	0.554	1050	--	--	9	9	10.00	5.74
C-14	1.10	0.564	1015	9.48	5.35	samples	samples	or	or
C-15	1.12	0.574	1015	10.00	5.74			-0.56	-0.26
C-16	1.11	0.569	1015	8.93	5.08			+0.51	+0.37
C-17	1.11	0.569	1015	9.83	5.58				
C-18	1.10	0.564	1015	9.50	5.36			11.3%	11.7%
C-19	1.12	0.574	1015	9.95	5.71				
C-20	1.09	0.559	1015	9.30	5.20				

TABLE 6 (Continued)

Sample No.	ρ Bulk	$\frac{\rho \text{ Bulk}}{\rho \text{ Crystal}}$	Test Pressure psia	Rate in./sec	Reduced Rate in./sec	Avg. Rate in./sec n Samples	Average Reduced Rate in./sec n Samples	Rate Range and % of Avg.	Reduced Rate Range and % of Avg.
C-21	1.10	0.564	650	--	--	6.67	3.73	5.90	3.42
C-22	1.09	0.559	615	6.86	3.83	for	for	to	to
C-23	1.11	0.569	615	6.23	3.54	9	9	7.41	4.14
C-24	1.09	0.559	615	6.59	3.68	samples	samples	or	or
C-25	1.11	0.569	615	6.73	3.83			6.67	3.73
C-26	1.13	0.579	615	5.90	3.42			-0.77	-0.31
C-27	1.09	0.559	615	7.41	4.14			+0.74	+0.41
C-28	1.01	0.518	615	6.96	3.61				
C-29	1.10	0.564	615	6.76	3.81			22.6%	19.3%
C-30	1.08	0.554	615	6.62	3.67				

TABLE 6 (Continued)

Sample No.	ρ Bulk	$\frac{\rho \text{ Bulk}}{\rho \text{ Crystal}}$	Test Pressure psia	Rate in./sec	Reduced Rate in./sec	Avg. Rate in./sec n Samples	Average Reduced Rate in./sec n Samples	Rate Range and % of Avg.	Reduced Rate Range and % of Avg.
C-31	1.11	0.569	315	4.43	2.52	4.52	2.60	4.15	2.38
C-32	1.08	0.554	315	--	--	for	for	to	to
C-33	1.14	0.585	315	4.55	2.66	9	9	5.30	3.10
C-34	1.14	0.585	315	5.30	3.10	samples	samples	or	or
C-35	1.11	0.569	315	4.30	2.45			4.52	2.60
C-36	1.11	0.569	315	4.62	2.63			-0.37	-0.22
C-37	1.14	0.585	315	4.91	2.87			+0.78	+0.50
C-38	1.13	0.579	315	4.17	2.41				
C-39	1.12	0.574	315	4.22	2.42			25.4%	27.7%
C-40	1.12	0.574	315	4.15	2.38				

TABLE 6 (Continued)

Sample No.	ρ Bulk	$\frac{\rho \text{ Bulk}}{\rho \text{ Crystal}}$	Test Pressure psia	Rate in./sec	Reduced Rate in./sec	Avg. Rate in./sec n Samples	Average Reduced Rate in./sec n Samples	Rate Range and % of Avg.	Reduced Rate Range and % of Avg.
C-41	1.12	0.574	250	--	--	2.11	1.22	1.77	1.02
C-42	1.12	0.574	105	2.11	1.21	for	for	to	to
C-43	1.11	0.569	105	2.12	1.21	8	8	2.41	1.37
C-44	1.13	0.579	105	1.77	1.02	samples	samples	or	or
C-45	1.12	0.574	105	2.33	1.34			2.11	1.22
C-46	1.13	0.579	105	2.13	1.23			-0.34	-0.20
C-47	1.11	0.569	110	--	--			+0.30	+0.15
C-48	1.13	0.579	105	2.00	1.16				
C-49	1.13	0.579	105	2.04	1.18			30.3%	28.7%
C-50	1.11	0.569	105	2.41	1.37				

NOTE: Of the seven samples out of 50 that did not burn like the others, the two major difficulties were sample damage and rapid deflagrations — or mild detonations. In the latter case the recorded test pressure was significantly higher showing the presence of a shock wave.

4. Photographic Observations

Since the data given above showed that burning rates at 1000 psia for the powder samples were two to five times higher than any rates that have been measured for solid propellants, it was felt important to get a photographic record of this burning. In solid propellant strand burning the surface generally does not depart more than 45° from an orientation normal to the axis of burning. The same situation was found with these samples.

The burning of these powders, even at high rates proceeds at a "deflagration" speed (measured in inches or centimeters per second, rather than in hundreds or thousands of meters per second as is found in detonations) and nearly as a plane wave as can be seen in Figure X. Although there are multitudes of free channels in the loosely packed powders that conceivably could allow the flame to flash from top to bottom of the sample almost instantaneously — this does not occur. This shows that there is an important flame propagation factor that is operative. This is approximately a ten power enlargement photograph taken of a powder sample enclosed in a tube of 6 mm inside diameter burning at 9.30 inches per second and 1000 psia. The justification for using an adiabatic assumption in the theoretical analysis of this burning is that the tube holding the sample is not consumed until long after the flame passes — and thus the tube provides

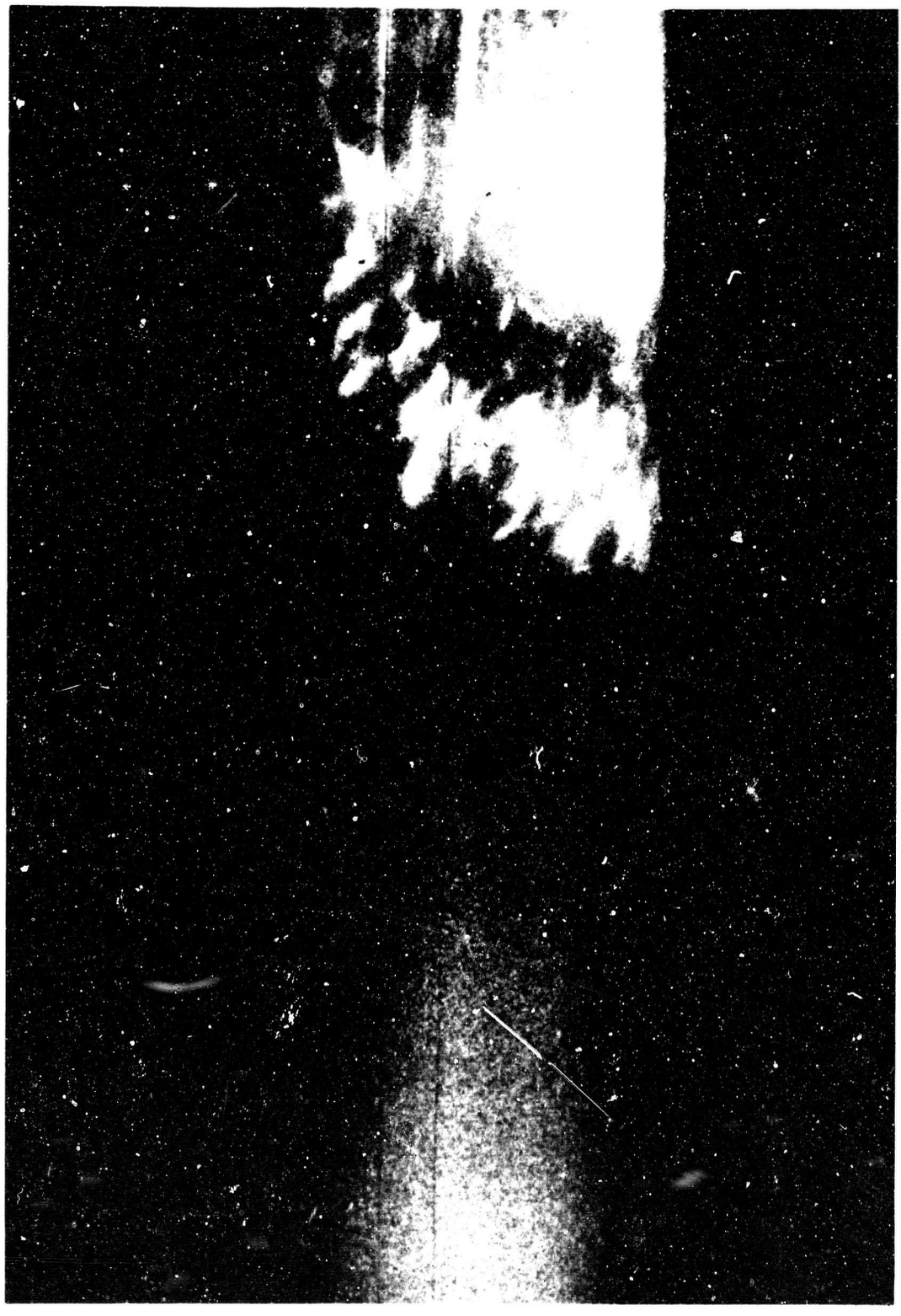

FIGURE X. AMMONIUM PERCHLORATE POWDER SAMPLE BURNING INSIDE INSULATING TUBE AT 68 ATMOSPHERES

good insulation against conductive or convective heat loss. At the same time the tubing material cannot be contributing too greatly to the combustion reaction since it is seen to remain largely intact during the critical period.

Analysis of film taken 10 milliseconds after Figure X against a light background, shows much the same burning zone structure. The entire solid-gas zone seems to be about one diameter or six millimeters in thickness. The sample holder used in this test to improve visibility was a translucent plastic straw. Other photographs taken of the 4 mm paper straws, under the same conditions, indicated the same type of burning — but the characteristics of the zone were not easily distinguishable.

5. Ambient Pressure Tests

These tests were conducted in the standard laboratory open-air environment of 14.7 psia and 75° F. Burning rates were determined from burning times measured visually with a stopwatch as the burning surface passed between two benchmarks four inches apart. The data is given in Table 7. In these tests the sample tube burned completely about one millimeter behind the A.P. burning surface, and thus did not provide as much insulation as in the tests at high pressures. Reproducibility was higher than at the higher pressures. The range of values for ten samples

TABLE 7

LOW BULK DENSITY A.P. POWDER BURNING RATES VERSUS PARTICLE SIZE
(Constant Pressure, One Atmosphere)

Sample No.	Type	Bulk Density g/cc	Rate in./sec	Average Rate n-samples	Rate Range and % Avg.	Comments
Z-1	UHP A.P.	1.05	0.0315	0.0333	0.0315	Samples dried in dry N_2 gas steam
Z-2	-40 +50	1.05	0.0330	for	to	Ave. bulk density 1.05 g/cc
Z-3	Mesh	1.05	0.0316	10	0.0348	
Z-4		1.04	0.0348	samples	or	
Z-5		1.03	0.0345		0.0333	
Z-6		1.06	0.0333		+0.0015	
Z-7		1.07	0.0332		-0.0018	
Z-8		1.04	0.0334			
Z-9		1.04	0.0339		10%	
Z-10		1.05	0.0341			

TABLE 7 (continued)

Sample No.	Type	Bulk Density g/cc	Rate in./sec	Average Rate n-samples	Rate Range and % Avg.	Comments
Z-11	UHP A.P.	1.24	0.0302	0.0311	0.0301	Samples dried in dry N_2 gas steam
Z-12	-70 +120	1.21	0.0311	for	to	Ave. bulk density 1.20 g/cc
Z-13	Mesh	1.17	0.0313	10	0.0327	
Z-14		1.22	0.0312	samples	or	
Z-15		1.23	0.0301		0.0311	
Z-16		1.21	0.0327		+0.0016	
Z-17		1.15	0.0316		-0.0010	
Z-18		1.21	0.0307			
Z-19		1.18	0.0311		8.4%	
Z-20		1.16	0.0308			

was 10% of the mean value (σ equal to about 5%). The pure A.P. samples of -40 +50 mesh (360 micron average particle size) at a bulk density of 1.05 g/cc gave a rate of 0.033 in./sec. As is shown in the following section on particle size-bulk density interactions, a fraction of smaller particle size, -70 +120 gave a higher average density, 1.20 g/cc, but nearly the same burning rate, 0.031 in./sec.

The good reproducibility of rates under ambient conditions, and the ease of conducting the tests, suggest that the above method is a good way to run preliminary screening of oxidizer combustion. The test is only applicable to those oxidizers like A.P. that will burn at this low pressure under the influence of the small amount of added fuel provided by the sample tube.

Since the ambient pressure tests took place in air rather than nitrogen, it was realized that the straw or sample holder material could burn without the oxidizer. It was found that the flame zone of an empty burning straw moved at about 0.055 in./sec, or nearly twice as fast as the burning surface when the straw was loaded with A.P. However, combustion was not complete, and charred or carbonized straw remained after burning as a warped black cylinder.

6. Bulk Density-Particle Size Effects on Burning Rate

The interest in bulk density effects is prompted by the need to know more about flame reaction propagation through a heterogeneous medium.

Referring to Table 8 it can be seen that where bulk density is modified by changing the particle size fraction of the powder that is burned, there is little effect on burning rate because the particle size (surface area) effect works in opposition to the density effect. Therefore, one other method was tried, that of variation of the ratio of coarse to fine particles in bimodal blends. In this type of test, it was still true that increasing the fines proportion increased the density, but the interesting factor was that there still remained a significant proportion of the coarse granules to exert their effect as shown in Table 9. As will be seen from the data, this distinction was important. Under these conditions, for the three powder blends tested, and using average rates for at least seven samples, there was the kind of an inverse relationship that might be expected between bulk density and burning rate. The same relationship held at 1000 psia and at 100 psia. It is interesting that the effect is the reverse of what is found in propellant burning. However, this emphasizes the importance of voids in combustion propagation.

TABLE 8

A.P. UNIMODAL POWDER COMBUSTION
BULK DENSITY-PARTICLE SIZE EFFECTS AT 500 PSIA

(34 Atmospheres)

Mesh Fraction	Average Particle Size Microns	Average Bulk Density g/cc	Average Burning Rate in./sec
-30 +40	508	1.00	5.97
-40 +50	359	1.11	5.92
-50 +60	274	1.26	5.29
-60 +70	230	1.31	5.02
-70 +120	168	1.36	5.32

TABLE 9

A. P. BIMODAL POWDER COMBUSTION
BULK DENSITY-BIMODAL BLEND EFFECTS

Composition, Wt. %

-30 +40 Mesh 508 Microns	-70 +120 Mesh 168 Microns	Average Bulk Density g/cc	Pressure psia	Average Burning Rate, in./sec
75.0	25.0	1.08	1050	15.44
66.7	33.3	1.14	1050	11 53
60.0	40.0	1.17	1050	10.78
75.0	25.0	1.08	100	2.54
66.7	33.3	1.14	100	1.82
60.0	40.0	1.17	100	1.71

7. Chemical Modifications of Burning Rate

In the study of chemical modifications of monopropellant oxidizers, it was planned that screening of burning rates be carried out using powder burning rates as the method for detecting gross burning rate changes. The studies described above gave confidence that where samples were carefully prepared, real and important differences in burning rate could be found.

Those chemical modifications that greatly changed the combustion environment were found to cause large changes in burning rate; comparable to the large changes found when powder bulk density was changed by 10 to 20% or combustion pressure was changed by about 50%.

For these tests, bulk density as a percent of crystal density, and particle size were held constant. The data is plotted in Figure XI together with the data for pure A.P. 360 micron (1.11 g/cc bulk density) and also the theoretical curve for pure A.P. single crystals taken from the data of Johnson and Nachbar[16]. The brackets marked "range" show the range in rate obtained for powder samples with particle sizes and densities as shown in Table 8.

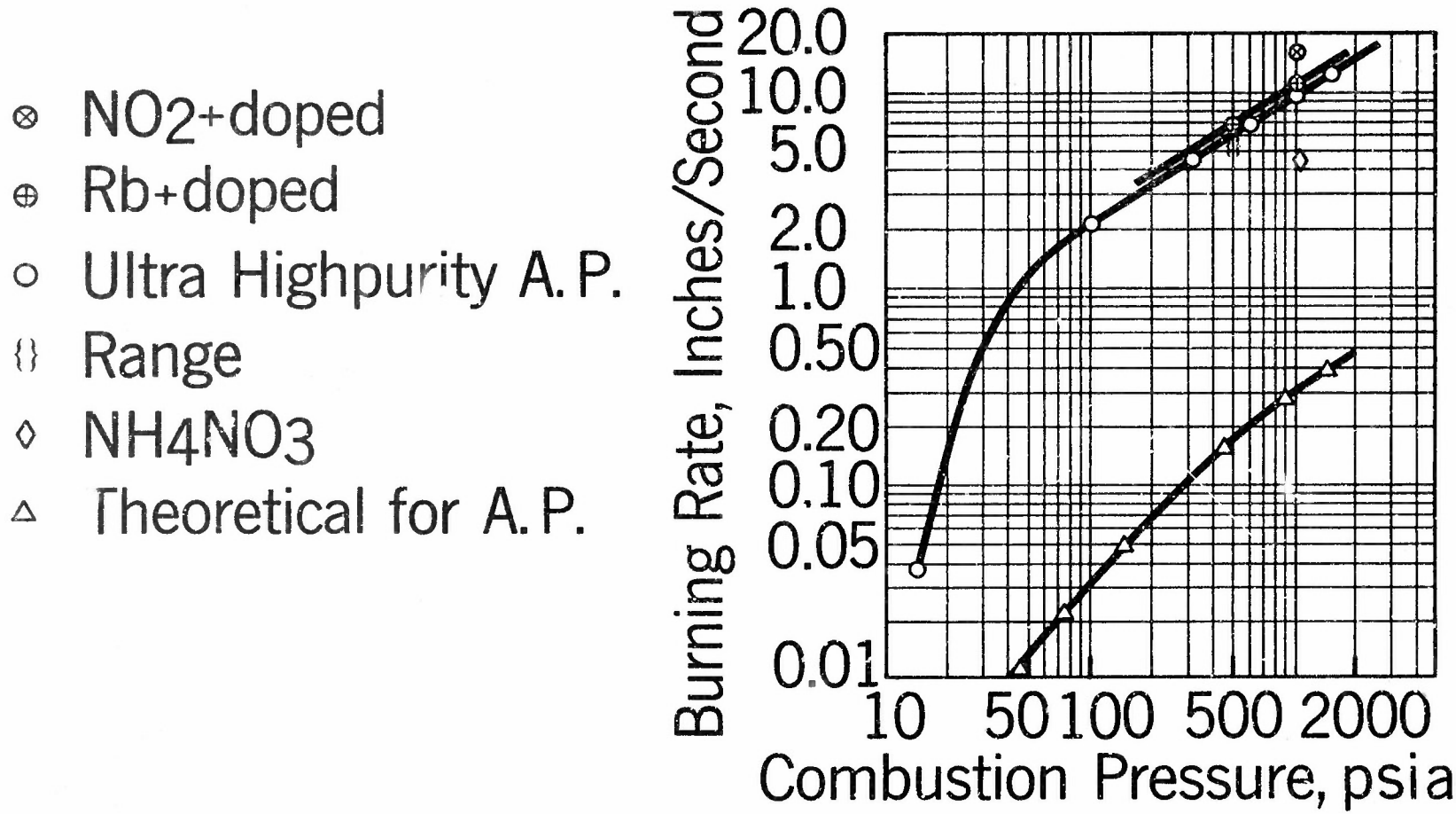

FIGURE XI. COMPARISON OF OXIDIZER POWDER (r_p) AND SINGLE CRYSTAL (r_l) BURNING RATES

(1) Rubidium Ion Doping of A.P.

Fine crystals of pure A.P. doped with 0.2% rubidium ion were prepared. Flame photometric analysis showed that the rubidium ions had entered the lattice in the same proportion as that in the crystallizing solution. This was to be expected because of the nearly identical crystal unit cell parameters of each of the two pure perchlorates. Combustion was conducted in air at ambient pressure, 14.7 psia.

The difference in burning rate between rubidium doped and pure A.P., other factors held constant, was negligible at 14.7 psia (0.034 in./sec doped versus 0.033 in./sec pure).

To test for possible elevated pressure interactions, combustion was conducted at 1500, 1000, 500, 200, and 100 psia. These latter samples were 10% lower in bulk density and as can be seen from Figure XI, gave a higher burning rate as would be expected. Only the 500 and 1000 psia points are plotted.

(2) Nitronium Ion Doping of A.P.

Considering the much greater chemical reactivity of nitronium salts when compared with ammonium salts, it was felt worthwhile to determine the burning rate of nitronium doped A.P. A sample of

about 0.01% NO_2^+ ions in A.P. crystals was supplied by J. N. Maycock of RIAS. The crystals were prepared from saturated nitric acid solution of A.P. with a small amount of NO_2ClO_4. Twenty-two samples were tested for impact sensitivity; and the doped material was found to be considerably more sensitive than pure A.P. In a falling ball (modified JPL) type apparatus the value obtained was 41.4 inch-pounds as the maximum energy which could be imparted by impact for 10 successive trials without visible reaction or decomposition. This value is lower than either A.P. (greater than 100 inch-pounds) or N.P. (about 75 inch-pounds).

Combustion tests were run at 1000 psia and the average rate was 15.0 in./sec. The average bulk density was about 10% lower than the pure A.P. line, and the rubidium doped results would give the better comparison.

(3) Ammonium Nitrate

Ammonium nitrate was recrystallized several times, and then prepared as -40 +50 mesh granules similarly to the A.P. samples. The intent here was to get combustion rates for an NH_4^+ oxidizer in which the perchlorate ion had been completely replaced.

The oxidizer powder, as prepared, was in the same particle size range as the A.P. reference material and had the same ratio

of bulk to crystal density (about 0.55). It is well known that ammonium nitrate is difficult to ignite, as are ammonium nitrate oxidized propellants. Previous investigators have added ammonium dichromate to the nitrate which has improved ignition. In the test reported herein, the pure material was used, although propellant was added at the ignition wire to help initiate burning. It was still found that burning would not take place below 1000 psia. At 1000 psia, a rate of 4.45 in./sec was found; approximately one-half the rate obtained for A.P.

IV. DISCUSSION OF RESULTS

On the basis of the crystal and powder tests that have been conducted it has been concluded that two combustion variables should be analyzed and included in future oxidizer studies; and a third should be measured in some way. The first variable is the intrinsic burning rate, r_i; that is, the pure single crystal linear burning rate in an inert atmosphere at a reference pressure of 1000 psia. The second is the ratio of the actual burning surface area (within the burning zone) of an oxidizer powder to the plane surface area of a burning single crystal of the same dimensions as the powder sample. It is designated as the characteristic burning surface, A*. Once the variation of A* with powder physical properties is known, r_i can be calculated and used as a fundamental variable in burning rate equations. The third important variable is the minimum flame zone thickness, designated Z_f, which will allow stable combustion at a given pressure. Z_f has not yet been measured, but order of magnitude estimates can be made.

A. Intrinsic Burning Rate, r_i

This value, measured as the linear burning rate of single crystals at 1000 psia (68 atm.) provides a fundamental rate value for oxidizer

combustion. It is an overall rate determined by the following concurrent processes: high temperature decomposition of a crystal lattice, desorption or vaporization of the fragments into the gas phase, and finally the flame or combustion reaction of the oxidizing and reducing species to form stable gas products. It is most interesting that for a given closed system initial temperature and constant inert gas pressure, the only variable remaining is the chemical composition of the oxidizer. It is believed that obtaining r_i for a variety of oxidizer chemical compositions will open the way for relating burning rate to chemical composition. Probably the most important physical characteristics that affect crystal burning are thermal conductivity and condensed phase changes. A high thermal conductivity will allow rapid heat transfer away from the burning surface and tend to raise the temperature of the solid region just below the burning surface. This is thought to be the major reason for single crystals burning slightly faster than any powders pressed to high density. The pressed powder presents an intermittent gas-solid path for heat conduction and thus offers greater resistance to heat flow, and keeps the subsurface layers cooler. Although the thermal conductivity has not been measured, an analogous variable, the sound velocity, has been measured by Evans[27] and co-workers for both single crystals and pressed powders of A.P. The value jumps from 2.18 to 3.90 mm per microsecond when going from powder to crystal, with a concurrent density increase of only a few percent.

B. Characteristic Burning Surface, A*

Since far more data can be readily collected on the burning of powders (as compared with single crystals) under a wide variety of conditions, it is important to relate powder burning to the more fundamental single crystal burning rate, r_i. The most direct way of doing this is proposed to be the assignment of a relatively greater surface area in the powder burning case. Based upon the high speed photographs of powder burning, there is a zone into which flames penetrate during burning of several millimeters, and the zone thickness for a given type of sample is relatively constant. If one assumes the combustion mechanisms to be nearly the same in either powder or crystal burning, then the chief reason for a difference in linear (or mass) burning rate lies in the greater available surface area for burning in the powder samples.

The dimensionless measure of this greater area is proposed to be A* = powder burning surface area ÷ crystal burning surface area, when both samples present a unit area plane surface normal to the burning axis. In the following derivation, ρ = density, r = linear burning rate, and $\dot{m}$ is the mass generation rate of combustion products for a unit area plane surface normal to the burning axis. The subscript "i" stands for the single crystal intrinsic burning case and "p" for the powder burning case. The units used need only be consistent in both cases. The equilibrium

combustion pressure is taken as 1000 psia, or 68 atm. A* is obtained from burning rate data as follows:

For the crystal burning case,

$$\dot{m}_i = (\rho_i)\ (r_i) \tag{1}$$

and for the powder burning case,

$$\dot{m}_p = (\rho_p)\ (r_p) \tag{2}$$

also,

$$\dot{m}_p = (\rho_i)\ (r_i)\ (A^*) \tag{3}$$

then,

$$(\rho_p)\ (r_p) = (\rho_i)\ (r_i)\ (A^*) \tag{4}$$

and

$$A^* = \frac{(\rho_p)\ (r_p)}{(\rho_i)\ (r_i)} \tag{5}$$

Using A.P. 360 micron powder as an example with densities in g/cc and rates in in./sec, we obtained:

$$A^* = \frac{(1.11)\ (9.30)}{(1.95)\ (0.33)} = 16.05$$

To obtain an estimate for the A* value of ammonium nitrate (A.N.) 360 micron powder burning under the same conditions, data of Schultz, Green, and Penner[17] was used. They gave a value of 0.103 in./sec for the pressed powder rate of A.N. at 1000 psia. Making the assumption that the crystal burning rate for A.N. is higher than the pressed powder rate in the same proportion as found for A.P., an estimated A.N. crystal rate of 0.125 in./sec is obtained. Then substituting in equation (5) above, this rate, together with the low density powder rate taken from Figure IX, and the bulk density for that rate:

$$A^* = \frac{(0.97)\ (4.54)}{(1.73\ \ (0.122)} = 20.85$$

Although a number of estimates and assumptions have been made, these two calculations indicate that a similar fraction of the available surface takes part in the combustion reactions of both A.P. and A.N. powders.

C. Minimum Flame Zone Thickness, Z_f

The fact that powder burning is many times faster on a linear basis than single crystal burning, and that it becomes slower as density increases, indicates that some minimum unobstructed dimension is required normal to a solid surface to establish a stable flame zone. For the tightly packed powders, although there are voids present, apparently they are not

of sufficient dimensions to allow flame propagation or else even the tightly packed powders would have a mass burning rate considerably greater than the single crystals.

Although we have no accurate measurement of this dimension, for the tightly packed powders which respond nearly like a plane surface, the voids would be on the order of a micron. For the low density powders, high speed photographs have shown that there is considerable flame penetration, approximately 5,000 to 10,000 microns, where the voids cross section is of the order of 100 microns. These rough estimates would indicate that for A.P. there is a minimum flame zone height, Z_f of the order of tens of microns.

It is of interest that in independent tests of the ability of flames to penetrate into prepared A.P. propellant cracks; it was found that at 500 psia (34 atm.) no burning would proceed into cracks of less than 25 microns.

D. Comparison Between Powder Combustion and Detonation

Evans in reference 27, studying the detonation characteristics of A.P. powders, has measured the longitudinal sound velocity (the limiting wave velocity for a wave of infinitesimal pressure and material velocity) in those powders. The sound velocity is zero at minimum bulk density, the "pour" density. The velocity, though dependent on particle size, rises

to five to ten times its minimum value at about 1.10 g/cc as density is increased to 1.90 g/cc from the pour density which is near 1.00 g/cc. However, when increasing density to the single crystal value, 1.95 g/cc, the velocity value increases by 1/3, a rather large jump for the small density increase.

In combustion on the other hand, at the minimum bulk density, the velocity (burning rate) is probably approaching a maximum. The combustion velocity decreases to about one-thirtieth the low density value at 1.90 g/cc bulk density. Then as density is increased to the single crystal state, the burning rate increases about 10%.

This comparison of tests seems to point up certain differences between burning rate and detonation rate. In the burning case, larger void space increases rate. In the detonation case larger void space decreases rate. In both cases, however, larger surface area at a constant bulk density tended to increase rates.

V. CONCLUSIONS

1. Single crystals of A.P. burn at 0.33 in./sec at 1000 psia, whereas high density packed powders burn at 0.28 in./sec, and low density powders burn at 9.30 in./sec.

2. Low bulk density ammonium perchlorate powders burn stably over a wide pressure range when insulated and partially fuel assisted. A.P. powders burned stably in the range from one atmosphere to one hundred atmospheres.

3. "Doping" of A.P. can produce easily detectable changes in powder burning rate. NO_2^+ (Nitronium) ion added to the A.P. lattice at about the 0.01% level increased the rate by about 50%.

4. Differences between oxidizers can be readily detected. Ammonium nitrate powder burned only 1/2 as fast as an equivalent particle size A.P. powder at the same pressure. These powder rates ranked in the same order as the crystal or high density rates.

5. The burning rate versus pressure slopes for both A.P. powders and crystals were about the same, and equal to approximately 2/3 over the

range 500 to 1500 psia.

6. The mass burning rate is not constant for varying densities. At densities of less than 80-90% the importance of flame penetration into the packing voids becomes important.

7. Increasing void fraction at constant particle size increases rate.

8. Decreasing particle size (increasing surface area) at constant void fraction increases rate.

9. The natural packing characteristics of finer particle size fractions which give higher bulk densities (less voids) compensates for the greater surface area of the finer particles and the linear rate stays approximately constant.

10. A*, the characteristic burning surface, for both NH_4ClO_4 and NH_4NO_3 is nearly the same when the oxidizers are burned as physically similar powders; thus Z_f, the minimum flame zone thickness is the same for both.

VI. RECOMMENDATIONS FOR FUTURE RESEARCH

The overall goal of future studies should be to give further definition to the combustion characteristics of crystalline oxidizers. Emphasis should be placed on identifying those physical and chemical properties which govern crystal burning rates and the pressure range in which burning is stable. Special attention should be given to the combustion effects of oxidizer variations in: crystal lattice structure, ion chemical type, ion sizes, ion charges, decomposition activation energy, crystal surface structure, particle size, packing density and physical state changes during combustion.

The following are typical specific tasks that should be accomplished:

1. Prepare "doped" crystals of A.P. with the NH_4^+ ion replaced with ions like NH_3OH^+, $NH_3CH_3^+$, NO_2^+, or PH_4^+, or similar ions to study effects of chemical environment and ion size changes.

2. Study the effects of using ions like Sr++ or Al+++ to affect electron transfer reactions at the beginning of crystal lattice decomposition. Relate effects to electrical conductivity changes.

3. Determine minimum crack width into which A.P. crystal flames will penetrate. Determine whether the flames will be extinguished if two crystals are brought tight together at their burning surface. Obtain better estimates of Z_f.

4. Run combustion tests on single crystal A.P. samples in a window-bomb and record burning results with high speed motion picture photography in the pressure range 2000 to 10,000 psia. This is to determine whether or not there will be a change in combustion mechanism in this range which is usually critical for propellants.

5. Correlate crystal lattice chemical composition and physical structure with r_i, the intrinsic burning rate, and determine A* values by conducting powder tests.

6. Prepare deuterated A.P. to determine whether oxidation of ND_4 during combustion will be slowed to the extent that overall burning rate will be reduced.

7. Observe the combustion of oxidizers that liquify to determine how the flame propagates when powders are in the low density state. Compare A* results with those of oxidizers which sublime or decompose without melting.

8. Determine whether or not there are key surface or gas phase reactions that are catalyzed by specific wavelengths of radiation that could be made available in the gas phase by addition of specific dopants.

9. Utilizing these experimental results, determine how the remaining parameters that have been empirically fitted into currently used equations can be better estimated from other physical and chemical data; in particular, the gas phase activation energy for the A.P. combustion reaction, since this is the most important yet undetermined parameter.

10. To be able to predict burning rates, modify the theoretical treatment and equations of Nachbar and Johnson with regard to energy losses and to make them more applicable to single crystals and powder burning. Apply equations to oxidizers other than A.P.

11. Rank all oxidizers and modifications studied with regard to burning rate and combustion properties at a reference pressure.

12. By extrapolation and interpretation of above data, predict structures for new oxidizers or those crystal modifications that will give higher and lower burning rate (extended range) oxidizers.

VII. BIBLIOGRAPHY

1. Whittaker, A. G. and Barham, D. C., "Burning Rate of Ammonium Perhlorate Single Crystals" A.R.S. Journal, p. 1273, (1962).

2. Hightower, J. D. and Price, E. W., "Combustion of Ammonium Perchlorate," 11th Combustion Institute Symposium, University of California, August 1966; (to be published by Combustion Institute in 1967).

3. Friedman, R., Levy, J. B., and Rumbel, K. E., "The Mechanism of Deflagration of Pure Ammonium Perchlorate," Atlantic Research Corporation, AFOSR TN-58-173, AD NO 211-213, Alexandria, Virginia, (February, 1959).

4. Levy, J. G., and Friedman, R., "Further Studies of Pure Ammonium Perchlorate Deflagration," Eighth Symposium (International) on Combustion p. 663, The Williams and Wilkins Company, Baltimore, (1962).

5. Friedman, R., Nugent, R. G., Rumbel, K. E., and Scurlock, A. C., "Deflagration of Ammonium Perchlorate," Sixth Symposium (International) on Combustion p. 612, Reinhold Publishing Corporation, New York, (1957).

6. Adams, G. K., Newman, B. H., and Robins, A. B., "The Combustion of Propellants Based Upon Ammonium Perchlorate," Eighth Symposium (International) on Combustion, p. 693, The Williams and Wilkins Company, Baltimore, (1962).

7. Shannon, L. J., and Peterson, E. E., "Deflagration Characteristics of A.P. Strands," AIAA Journal, 2 p. 168, (1964).

8. Irvin, O. R., Saltman, P. K., and Anderson, W. H., "Deflagration Characteristics of A.P. at High Pressure," Ninth Symposium (International) on Combustion, Academic Press, New York, p. 358, (1963).

9. Barrere, M., and Williams, F., "Analytical and Experimental Studies of the Steady State Combustion Mechanism of Solid Propellants," O.N.E.R.A. T.P. NO. 240, Paris, France, (1965).

10. vonElbe, G. and McHale, E., "Branched Chain Reactions in the Decomposition of Hydrazine-Based Oxidizers," 3rd Combustion Conference Paper, p. 85, CPIA Publication No. 138, Vol. 1, (February, 1967). Also, with Byrne, J. R., "Research on the Deflagration of High-Energy Solid Oxidizers," Quarterly Report No. 5, AF49(638)-1645, Atlantic Research Corporation, Alexandria, Virginia, (March 31, 1967).

11. McAlevy, R. F., III, and Lee, S. Y., "Further Studies of Ammonium Perchlorate Composite Propellant Deflagration by Means of Burner Analog Techniques," 3rd Combustion Conference Papers, p. 95, CPIA Publication No. 138, Vol. 1, (February, 1967).

12. Petersen, E. E., "Ignition and Deflagration of Single Crystals of A.P.," Paper presented at AFOSR Chemical Kinetics of Propulsion Meeting, Stanford Research Institute, (August 12, 1966).

13. Arden, E. A., Powling, J., and Smith, W. A. W., "Observations on the Burning of Ammonium Perchlorate," Combustion and Flame V-1, p. 21, (1962).

14. Sinke, G. C., "Thermodynamic Properties of Combustion Products," Dow Chemical Company Report No. AR-IS-158, (April 1, 1959).

15. Powling, J. and Smith, W. A. W., "The Surface Temperature of Ammonium Perchlorate Burning at Elevated Pressures," Tenth Symposium on Combustion, p. 1373, The Combustion Institute, Pittsburgh, Pa., (1965).

16. Johnson, W. E., and Nachbar, W., "Deflagration Limits in the Steady Linear Burning of a Monopropellant With Application to A.P.," Eighth Symposium on Combustion, p. 678, The Williams and Williams Co., Baltimore, (1962).

17. Schultz, R., Green, L., Jr., and Penner, S. S., "Combustion and Propulsion, Third AGARD Colloquim," p. 372, Pergamon Press, New York, (1958).

18. Coates, R. L., "Linear Pyrolysis Rate Measurements of Propellant Constituents," AIAA Preprint No. 65-55, (January, 1965).

19. Williams, F. A., "Combustion Theory," p. 202, Addison-Wesley, Reading, Mass., (1965).

20. McGurk, J. L., "Crystallographic Changes in Ammonium Perchlorate Related to Different Rates of Heating," ICRPG Third Combustion Conference, CPIA Publication No. 138, Vol. 1, p. 51, (1967).

21. Shubnikov, A. V., and Sheftal, N. N., Editors, "Growth of Crystals," translated from the Russian by Consultants Bureau, Inc., New York, (1959).

22. Gilman, J. J., Editor, "The Art and Science of Growing Crystals," John Wiley and Sons, Inc., New York, (1951).

23. Buckley, H. E., "Crystal Growth," John Wiley and Sons, Inc., New York, (1951).

24. Phillips, F. C., "An Introduction to Crystallography," John Wiley and Sons, Inc., New York, (1963).

25. Torgesen, J. L., Horton, A. T., and Saylor, C. P., "Equipment for Single Crystal Growth from Aqueous Solution," Journal of Research, National Bureau of Standards, 67C, 25, January-March, (1963).

26. Tutton, A. E. H., "The Alkali Perchlorates and a New Principle Concerning the Measurement of Space Lattice Cells," Roy. Soc. Proc., CXI-A, p. 462, (1926).

27. Evans, M. W., Reese, B. O., and Seely, L. B., "Detonation Characteristics of Low Density Granular Materials," Stanford Research Institute Annual Report, (January 15, 1967).

VIII. APPENDIX — PREDICTION EQUATIONS; A TRIAL ANALYSIS

Referring to goal number 5, "the study of reaction mechanisms," (under Part I, Introduction) it is useful to be able to take expected variables and determine their interdependence. The best method of doing this is a step-wise plan. First, a guess is made as to the most important variables based upon a model description of the phenomena. Then, the results are analyzed to determine how good a correlation there is between variables. Then by examining results of this analysis, an improvement can be made in the model. This is done by either rejecting some variables or by adding new ones; or by changing the kind of relationships between variables in the model equation.

To study ways of using this method to improve models and theory, two new prediction equations for lattice energy were developed. The correlation between variables was analyzed by multiple regression analysis. U_o (lattice energy) values have been measured for many compounds, and many equations have been set up for their calculation. The lattice energy of an ionic crystal is defined as the increase in internal energy at absolute zero when the component ions are separated from each other at such a

distance that there are no longer any interactions between them. The forces holding the lattice together are non-coulombic.

A. The Kapustinskii Equation

The more rigorous methods of calculation of lattice energies are restricted to salts for which the crystal structures are exactly known[1]. For less simple structures than those of the alkali halides the extended calculation of lattice energies becomes increasingly laborious as the symmetry decreases. If however, only the first two terms (out of four known terms) in the lattice energy are considered, that is, U_o is taken to be $U_m - U_r$ (Madelung term — repulsive term) then U_o may be written as:

$$U_o = \left(\frac{N_a v}{2}\right)\left(\frac{\alpha z_1 z_2 e^2}{r_o}\right)\left(1 - \rho/r_o\right)$$

This is the form of the original Born equation, developed around 1920. The number of ions in the chemical molecule is v, the number in a mole is $N_a v$ and $\alpha = M/v/2$. The madelung constant, M, a measure of the electrostatic interaction of the ions in the lattice, is proportional to the number of ions in the chemical molecule and hence α is independent of this. z_1 and z_2 are the

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[1] Waddington, T. C., "Lattice Energies and Their Significance in Inorganic Chemistry," of "Advances in Inorganic and Radiochemistry," 1, p 157, Academic Press, New York, (1959).

ion valencies, e is the charge on the electron, r_o is the equilibrium distance between unlike ions in the crystal and ρ is a constant. Although α is not identical for different lattice types, Kapustinskii found empirically that in passing from one lattice type to another the change in the constant α was proportional to the change in the interatomic distance. Every crystal may then be considered to transform into a rock-salt lattice without change of lattice energy if the coefficients α and r_o are simultaneously modified so as to have the values corresponding to the ions in a rock-salt lattice. U_o can now be found either by measuring r_o and the crystal structure and calculating M and hence α or by putting $r_o = r_A + r_c$, the sum of the Goldschmidt ionic radii for coordination number 6, and taking $\alpha = 1.745$, its value for a rock-salt lattice. The substitutions $r_o = r_A + r_c$ in Ångstrom units, $\rho = 0.345$ Å, $\alpha = 1.745$, and $N_a e^2 = 329.7$ $K_{cal}/Å$ give Kapustinskii's formula:

$$U_o = \frac{287.2\ v\ z_1 z_2}{(r_c + r_A)} \left[1 - \frac{0.345}{(r_c + r_A)}\right] \quad K_{cal}/\text{mole}$$

If the ions are nonspherical there is considerable difficulty in specifying radii; this is particularly true with complex ions.

Referring to the Born equation, Kapustinskii's replacement of r_o, the interatomic distance, by $r_A + r_c$ introduces some error. There are many salts in which the unlike ions are not "touching," for example, NaI,

where the lattice spacing is determined by I^- to I^- contacts. Also, the assignment of ionic radii can only be regarded as approximate even in the alkali metal halides. In spite of these objections the Kapustinskii formula remains a useful guide to approximate lattice energies, especially in those cases where the structure is unknown. As shown in Table IV, the values for lattice energies given by the Kapustinskii equation fall on the low side of the experimental value obtained from the Born cycle.

B. New Lattice Energy Prediction Equations

In looking for new variables (those not explicitly used in available equations) for a U_o prediction equation, it became evident that molecular weight (M) was important by examining a listing such as Table I. Beyond that, it was postulated that the ability of the ions to pack together was important, and thus a factor such as the ratio of ion sizes (f_g) should be considered. Next it was felt that some measure of density could indicate the strength of the lattice in pulling itself to minimum volume. The normal crystal density (ρ_x) and an "ultimate" density (ρ_j) were used. The ultimate density is just the molecular weight divided by the volume of the ions in a mole, assuming they are hard spheres with their ionic radii. It was felt that the boiling point (t_b) and the solubility (s) in a common solvent such as water would give a measure of the difficulty in breaking up the lattice and separating the ions.

Table I shows these values for the alkali halides.

Table II shows the form for the simple model equation proposed, and the results of the regression analysis performed on the 20 sets of data given in Table I.

An examination of the "t" test values shows that molecular weight and ρ_j, a measure of the ultimate density of the material, were important. It also showed by the negative coefficient that the relationship between molecular weight and U_o was inverse. Based on this information, a second equation was set up and another regression analysis run with the results as shown in Table III. The coefficient of correlation increased from about 0.85 to 0.91 showing that an improvement in prediction of U_o had been made. In Table IV it is shown that the average error in estimating U_o had been reduced from 6.8 percent in the first prediction equation to 5.7 percent for the second equation. For this particular set of data the Kapustinskii equation gives an average error of 4.5 percent. Thus, we have a valid estimation equation of U_o for alkali halide compounds. This equation was also tried for sodium nitrate, another univalent ions compound, and whereas the Kapustinskii value was 176 K_{cal}/mole the value for the number two equation was 175 K_{cal}/mole, a surprisingly close check.

TABLE I

U_o PREDICTION EQUATION DATA FOR ALKALI METAL HALIDES

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	(M) Molecular Weight	(f_g) Radius Large / Radius Small Ion Sizes (Å)	(ρ_x) Crystal Density g/cc	(t_b) Boiling Point in °K (°C)	(ρ_j) Ultimate Density g/cc (m.w./2.521 $\Sigma r3$)	(s) Solubility in g/100 ml H_2O at 0°C
LiF	241.2	25.94	1.36/0.60=2.27	2.60	1949 (1676)	3.77	0.25
LiCl	198.2	42.40	1.81/0.60=3.02	2.068	1626 (1353)	2.74	35.0
LiBr	188.5	86.86	1.95/0.60=3.25	3.464	1538 (1265)	4.51	142.7
LiI	175.4	133.86	2.16/0.60=3.60	4.061	1463 (1190)	5.16	
NaF	216.0	42.00	1.36/0.95=1.43	2.79	1973 (1700)	4.94	4.0
NaCl	183.8	58.45	1.81/0.95=1.91	2.165	1686 (1413)	3.42	35.7
NaBr	175.9	102.91	1.95/0.95=2.05	3.203	1663 (1390)	4.94	79.5
NaI	164.5	149.92	2.16/0.95-2.27	3.667	1573 (1300)	5.44	158.7

TABLE I (Continued)

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	(M) Molecular Weight	(ξ_g) Radius Large / Radius Small Ion Sizes (Å)	(ρ_x) Crystal Density g/cc	(t_b) Boiling Point in °K (°C)	(ρ_j) Ultimate Density g/cc (m.w./2.521 Σ r3)	(s) Solubility in g/100 ml H_2O at 0°C
KF	191.5	58.10	1.36/1.33=1.02	2.48	1773 (1500)	4.74	85.0
KCl	166.8	74.55	1.81/1.33=1.36	1.984	1773 (1500)	3.57	30.0
KBr	160.7	119.01	1.95/1.33=1.47	2.75	-	4.83	53.5
KI	151.0	166.02	2.16/1.33=1.62	3.13	-	5.30	127.5
RbF	183.6	104.48	1.48/1.36=1.09	-	1683 (1410)	7.20	120.0
RbCl	162.0	120.94	1.81/1.48=1.22	2.76	1663 (1390)	5.23	77.0
RbBr	155.2	165.40	1.95/1.48=1.32	3.35	1613 (1340)	6.16	95.0
RbI	146.5	212.40	2.16/1.48=1.46	3.55	1573 (1300)	6.33	140.0

TABLE I (Continued)

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	(M) Molecular Weight	(f_g) Radius Large / Radius Small Ion Sizes (Å)	(ρ_x) Crystal Density g/cc	(t_b) Boiling Point in °K (°C)	(ρ_i) Ultimate Density g/cc (m.w./2.521 $\Sigma r3$)	(s) Solubility in g/100 ml H_2O at 0°C
CsF	171.0	151.91	1.69/1.36=1.24	3.586	1523 (1250)	8.21	-
CsCl	153.2	168.37	1.81/1.69=1.07	3.97	1563 (1290)	6.21	161.7
CsBr	148.3	212.83	1.95/1.69=1.15	4.44	1573 (1300)	6.90	100.0
CsI	140.3	259.83	2.16/1.69=1.28	4.51	1553 (1280)	6.91	44.0

TABLE II

MULTIPLE REGRESSION ANALYSIS FOR $U_o = f(M, f_g, \rho_x, t_b, \rho_j, s)$

Final Equation: $U_o = -0.423\ M + 5.12\ f_g + 3.21\ \rho_x + 0.006\ t_b + 6.04\ \rho_j - 0.044s + 169.1$

Square of multiple correlation coefficient = 0.855*

Variable	Coefficient	Variance of Coefficient	"t" Test for Significance	Comments
M (Molecular Weight)	-0.423	0.009	4.53	Important variable
f_g (Ratio of ion sizes)	5.12	18.7	1.19	Not significant
ρ_x (Crystal density)	3.21	15.5	0.816	Not significant
t_b (Boiling point)	0.006	0.00003	1.10	Not significant
ρ_j (Ultimate density)	6.04	10.7	1.85	Significant variable
s (Solubility in H_2O)	-0.044	0.003	0.803	Not significant

*This means that 85.5% of variation in U_o is accounted for by this model

TABLE III

MULTIPLE REGRESSION ANALYSIS FOR

$$U_o = f\left(\frac{1}{M}, \frac{1}{M^2}, \rho_j\right)$$

Final Equation: $U_o = \frac{5357}{M} - \frac{56,305}{M^2} + 4.94\ \rho_j + 96.6$

Square of Multiple Correlation Coefficient = 0.912*

Variable	Coefficient	Variance of Coefficient	"t" Test for Significance	Comments
$\frac{1}{M}$ (recip. of molecular wt)	5,357	1,053,700	5.22	Highly significant variable
$\frac{1}{M^2}$ (recip. of molecular wt squared)	-56,305	531×10^6	2.44	Significant variable
ρ_j (ultimate density)	4.94	4.15	2.43	Significant variable

*This means that 91.2% of the variation in U_o is accounted for by this model.

TABLE IV

COMPARISON OF PREDICTION EQUATION VALUES WITH EXPERIMENTAL LATTICE ENERGY VALUES

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	Difference (U_o Expt - U_o Pred. #1)	Difference (U_o Expt - U_o Pred. #2)	Difference (U_o Expt - U_o Kapustinskii)
LiF	241.2	28.64	3.2	13.5
LiCl	198.2	0.16	-6.9	6.1
LiBr	188.5	-1.85	15.4	-1.0
LiI	175.4	-8.49	16.4	5.0
NaF	216.0	6.89	-0.6	4.5
NaCl	183.8	-6.51	-4.9	3.9
NaBr	175.9	-6.78	8.2	0.4
NaI	164.5	0.07	7.8	3.5

TABLE IV (Continued)

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	Difference (U_o Expt - U_o Pred. #1)	Difference (U_o Expt - U_o Pred. #2)	Difference (U_o Expt - U_o Kapustinskii)
KF	191.5	-1.76	-4.0	3.0
KCl	166.8	-14.98	-9.2	4.1
KBr	160.7	-1.22	-0.8	-0.6
KI	151.0	7.38	-2.0	4.2
RbF	183.6	4.79	5.3	1.9
RbCl	162.0	-9.24	-0.9	3.8
RbBr	155.2	-4.16	-2.2	5.5
RbI	146.5	6.84	-5.3	5.5

TABLE IV (Continued)

Halide	(U_o) Born Cycle Ex'pt'l U_o K_{cal}/Mole	Difference (U_o Expt - U_o Pred. #1)	Difference (U_o Expt - U_o Pred. #2)	Difference (U_o Expt - U_o Kapustinskii)
CsF	171.0	-10.41	1.0	0.6
CsCl	153.2	-2.71	-3.9	3.8
CsBr	148.3	2.36	-6.3	4.4
CsI	140.3	10.97	-10.2	5.6

It appears that the multiple regression analysis technique will be of valuable assistance in getting models showing the dependence of crystal burning rate on the variables believed to be important in combustion studies

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13. ABSTRACT

A fundamental understanding of the combustion characteristics of crystalline oxidizers like ammonium perchlorate is important if complete knowledge pertaining to the combustion and stability characteristics of composite solid propellants is to be attained. This research involved theoretical and experimental studies of the burning of crystalline oxidizers ranging in physical form from large single crystals to low bulk density powders. Single crystals, visually perfect throughout most of their mass, were grown from saturated water solution by a temperature lowering technique using a bath-control system-data acquisition combination that maintained temperatures to ± 0.001°C. Electrical conductivities and UV absorption measurements showed them to be of high purity. A strand-burner, window-bomb and high-speed cinematography were used to obtain burning rate versus pressure. The study of large single crystal burning removed particle size, shape and bulk density factors as complications. The intrinsic burning rate, r_{ij}, of a single crystal was defined and postulated as a fundamental combustion variable. Low bulk density powder combustion was shown to be feasible. The characteristic burning surface, A_b^*, for powder combustion was defined and shown to relate powder burning to single crystal burning. The explanation proposed for the large difference found between physical surface area available in the burning zone and the actural burning surface area, is the necessity for a minimum flame zone height, z_{ij}, above a stable burning surface.

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Combustion and stability characteristics of composite solid propellants						