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ADDITIVE EFFECTS IN SOLID PROPELLANT BURNING

H. SILLA, H. BURWASSER AND
H. F. CALCOTE

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Princeton, New Jersey

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PROPELLANT BURNING

H. Silla, H. Burwasser and H. F. Calcote

AeroChem Research Laboratories, Inc.

Princeton, New Jersey

Prepared for

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FOREWORD

This program was supported by the Office of Naval Research, Propulsion Chemistry Branch, Material Sciences Division, with funds supplied by Advanced Research Projects Agency. This is the final report and supersedes previous progress reports, AeroChem Technical Memorandums Nos. 14, 17 and 20, which may now be destroyed.

The authors wish to acknowledge the assistance of James Chambers in the experimental work.

SUMMARY

An experimental program has been carried out to determine the effect of additives on the burning rates of ammonium perchlorate-polyester-polystyrene solid propellant strands at one atmosphere and below. The object of this was to learn more about the mechanism of solid propellant burning. Additives were incorporated either by adding them to the gas in which the propellant burned or by admixing them with the solid. Admixture with the solid produced burning rates for 0.025 to 0.049 in/sec while the rate without additive was 0.031 in/sec. Burning the propellant in an oxygen atmosphere produced a tenfold increase in burning rate over burning it in nitrogen. Other oxidizers, e.g., ClO_3F , caused a similar increase while hydrogen and helium had no effect. The oxygen is effective for stoichiometric propellants, and controlling the oxygen flow controls the burning rate. The results are interpreted as showing that the fuel-oxidizer reactions in the gas phase of a burning propellant do not normally involve oxygen which may even act as a "catalyst". Burning rates in nitrogen atmospheres have a linear pressure dependence from 50 to 760 mm Hg. Comparison of this data with the Summerfield burning rate equation shows that his equation does not hold at sub-atmospheric pressures. A careful analysis of experimental errors were made with particular attention to the increase in burning rate due to a tilted burning surface.

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INTRODUCTION

The object of the work presented in this report has been to evaluate the role of additives in solid propellant burning as a means of obtaining some insight into the mechanism of solid propellant burning. Additives have been used in two general ways: by direct incorporation into the propellant, and by changing the gaseous environment of the burning strand.

The importance of understanding the nature of the chemical reactions is emphasized by the various current theories of composite propellant burning^{1, 2, 3}. The essential difference between the two main views is the choice of which chemical reactions are important. According to Chaiken, the important chemical reaction step involves the oxidation-reduction step of the oxidizer, while Summerfield feels that at pressures low enough so that chemical reactions are rate controlling the chemical reaction between fuel and oxidizer is rate controlling. It is through the use of additives, both gas phase and direct incorporation, that we hope to obtain some knowledge of which type of reactions do occur and their relative importance.

Since we have found it necessary to use a variety of different techniques, some of which were found inadequate, we will discuss the experimental aspects of the program first, thereby keeping subsequent sections to pertinent discussion of data.

Using two approaches, i.e., gas phase effects and solid additives, we discuss each aspect separately. As most of the effort has been concerned with gas phase results, the consideration of this phase will constitute a major portion of the discussion. This program has represented only a beginning on this approach and much more work remains to be done.

EXPERIMENTALPropellant Ingredients

Early in the program, it was decided that the propellant combination that would be used for this work would be $\text{NH}_4\text{ClO}_4^a$ for the oxidizer and Paraplex P-13^b for the fuel binder. This combination was chosen because NH_4ClO_4 is a common solid propellant oxidizer and the P-13 resin allowed for simple and safe processing of the propellant. This is also the combination employed at The James Forrestal Research Center of Princeton University, so that results from their program should be helpful in interpreting our data. The first strands used in these experiments were obtained through the courtesy of the Forrestal Research Center. Additional propellant ingredients were Nuodex^c (curing catalyst), lecithin^d (organic wetting agent), and lupersol^e (polymerizing agent).

Chemical analysis and particle size distribution for the "as received" NH_4ClO_4 is shown in Table I. A mix containing 70% "as received" NH_4ClO_4 and 30% fines as obtained from recrystallization was found to be more fluid than a mix containing 100% "as received" material. Such a mixture is known as a bimodal mix. Because it was thought that solid additives could be incorporated into the crystal structure of NH_4ClO_4 by coprecipitation, the fines were prepared in this manner rather than by grinding. The procedure followed was to rapidly cool a hot solution of NH_4ClO_4 in an acetone dry-ice bath, filter the precipitate in a vacuum flask, and then dry the precipitate at 65°C for a day.

-
- a From the American Potash and Chemical Corporation
 - b Trade name for a resin obtained from Rohm and Haas Company, solution containing 50% polyester and 50% styrene monomer
 - c From Nuodex Products Company, A Division of Heyden Newport Chemical Corporation, containing 6.0% cobalt
 - d From the W. A. Cleary Corporation of New Brunswick, New Jersey, under the trade name, Clearate B-60
 - e Lupersol DDM 60% methyl ethyl ketone peroxide in dimethyl phthalate from the Lucidol Division, Wallace and Tiernan, Inc.

TABLE I

CHEMICAL ANALYSIS OF NH_4ClO_4

NH_4ClO_4 assay (min.)	99.0
Moisture, surface	0.02
Water insolubles	0.10
Chloride as NH_4Cl	0.20
Sulfated ash	0.25
Bromate as NaBrO_3	0.04
Chlorate as NaClO_3	0.15
Sulfate as $(\text{NH}_4)_2\text{SO}_4$	0.2
Reaction to methyl orange	Neutral

Particle Size Distribution

Mesh	%
- 16	100
- 48	89-97
- 100	18-50
- 150	2-15
- 325	0-2

Propellant Mixing

Since the program involved trying a large number of additives and therefore preparing a small number of each variety of strand, a small mixer was needed. A 100 cc. mixer enclosed in a vacuum bell housing was purchased from the Brabender Corporation of Rochelle Park, New Jersey. An essential feature of this mixer is its ease of disassembly for cleaning.

The procedure adopted for preparing the propellant was to gradually add the NH_4ClO_4 , while mixing, to the resin containing the curing catalyst and the wetting agent. After addition of the NH_4ClO_4 , the mixer was evacuated to about 5 mm Hg. Mixing was continued for fifteen minutes without pumping, followed by an evacuation step and another fifteen minutes of mixing. It was found that continuous pumping would "dry" the propellant and that liquids would collect in a cold trap. Since no batch to batch variation in burning rates was noticed and our burning rate for one composition (77% NH_4ClO_4) compared with the burning rate obtained with Forrestal strands (Table II), this procedure was considered adequate. The final steps in the procedure were to break the vacuum, add the polymerizing agent, and mix for an additional fifteen minutes.

Propellant Casting

Following mixing, the propellant was cast in a wax mold by deairating through a slit which was merely a crimped piece of aluminum tubing. A photograph of the apparatus is shown in Figure 1. The procedure was to alternately deairate and tamp the propellant into the wax mold. After filling the wax mold, the propellant was cured in an oven at 80°C for a day. The cured block was then sawed into eight $1\frac{1}{4}$ inch square by 4 to 5 inch long strands.

Restrictors

Since the first phase of the additive work was to study the effects of various gaseous environments on solid propellant burning, it was believed that restrictors would hinder the diffusion of gases into the combustion zone.

TABLE II

COMPARISON OF BURNING RATES OF STRANDS FROM DIFFERENT SOURCES

Pressure = 1 Atmosphere

Source	Strand Cross-section	Restrictor	Burning Rate in/sec
<u>Oxidizer-fuel ratio 77/23</u>			
AeroChem ^a	1/4" round	None	.0315 ± .0007
AeroChem	1/4" square	2 layers of butyrate dope	.031 ± .002
AeroChem	1/2" square	2 layers of butyrate dope	.031
Forrestal ^b	1/4" round	2 layers of butyrate dope plus 2 layers of vinylite	.031 ± .002
<u>Oxidizer-fuel ratio 80/20</u>			
R.M.D. ^c	1/4" square	None	.041 ± .001
R.M.D.	1/4" square	2 layers of butyrate dope	.033 ± .001
Forrestal	1/4" round	None	.042 ± .001

a See section on Extruding Propellants

b Strands furnished through the courtesy of The James Forrestal Research Center, Princeton University

c Strands purchased from the Reaction Motors Division of Thiokol Chemical Corporation

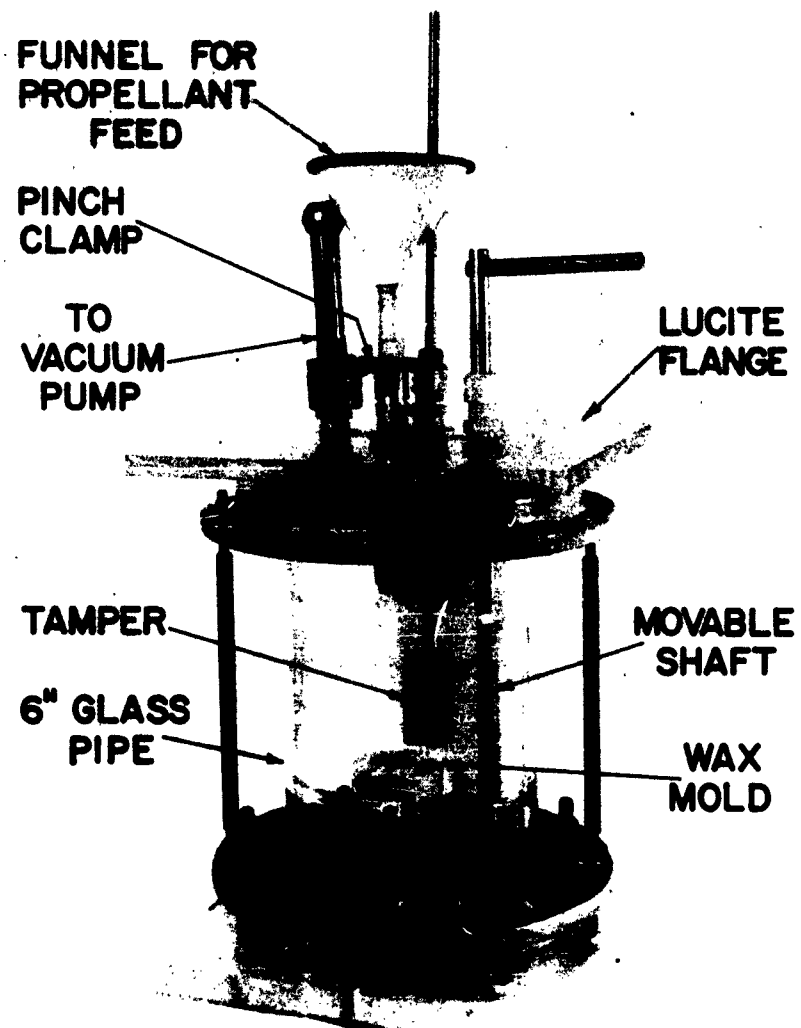


FIG.1 PROPELLANT DEAIRATOR

Some work was therefore done on unrestricted strands (O/F ratio = 80/20 by weight), but it was soon evident that the scatter of the data was greater in the case of the unrestricted than restricted strands as the following data shows for the case of strands burned in stagnant air at one atmosphere.

	<u>Burning Rate in/sec</u>	<u>Mean Deviation</u>	<u>No. of Tests</u>
Restricted	.039	.002	17
unrestricted	.054	.008	30

Furthermore, the weighted percent mean deviation of all restricted strands for all gases was about 5½% compared to 13% for all the unrestricted strands. It is also evident that the burning rate is faster for unrestricted strands.

The above discussion applies to data that was acceptable. In the case of strands burned in oxygen and oxygen mixtures, a large number of strands were rejected because of severe tilting or burning down the side. For these experiments, restrictors were even of greater necessity. Evaluation of various restrictors was made including: silicon grease, chromic oxide, aluminum oxide plus vinylite, copper oxide, silicon resin, and ammonium perchlorate. None of these were any more effective than butyrate dope in eliminating tilting and side burning. The restrictor employed was generally two coats of butyrate dope.

Strand Wiring

The final step in the strand preparation process was the strand wiring. Four wires were required for each strand, an ignition wire (No. 26 tinned copper wire), and three timing wires of either 1/2 amp. Buss fuse wires or .0065 inch diameter copper wires were used, depending on the experiment. It was found that for strands burned in nitrogen the 1/2 amp. lead fuse wire was adequate. However, for the experiments performed in O₂ and O₂-N₂ mixtures, pieces of propellant from violent ignition would sometimes prematurely break wires or the heat from the intense flames would prematurely melt the fuse wires. Copper timing wires were therefore used in the oxygen experiments.

The strand was marked off in one inch lengths with a divider and holes drilled with a No. 68 (.031 inch) drill. Originally, a manual hand drill was used, but it was difficult to drill clean holes. By using a small electric hand drill, cleaner holes were obtained, and considerably less time was expended in wiring strands.

Burning Rate Equipment

A photograph of the strand burning apparatus is shown in Figure 2. Two timings were obtained for each strand as a check on the uniformity of a given strand and also to increase the probability of obtaining at least one burning rate per strand.

Although initial experiments were performed with a distance of 1/2 inch from the ignition wire to the first timing wire, it was found later, and particularly in the case of the oxygen experiments, that this distance had to be increased to one inch due to surface irregularities caused by ignition. Frequently, these irregularities persisted as the strand was consumed by burning. The use of a wire for ignition, although simple, is not completely adequate. In future experiments a plane source of ignition, such as an energetic propellant or perhaps a flat coil of nichrome heater wire, should be tried.

During some of the last experiments, it was noticed that the burning surface of a strand would become irregular after passing a timing wire. Again, this disturbance was not as noticeable in 100% nitrogen as it was in oxygen mixtures. A good example of this effect was observed when sodium dichromate was used as an additive. In these experiments, it was noticed that the strand burned with a fairly constant tilt of 40° maximum until the burning surface crossed a timing wire. The burning surface then assumed a triangular shape which gradually disappeared after about 1/2 inch. Because of the disturbing effects caused by the use of a timing wire, another technique for measuring burning rates would be of value. It is suggested that some scheme based on using a photoelectric cell, resistance thermometer or thermocouples could be used.

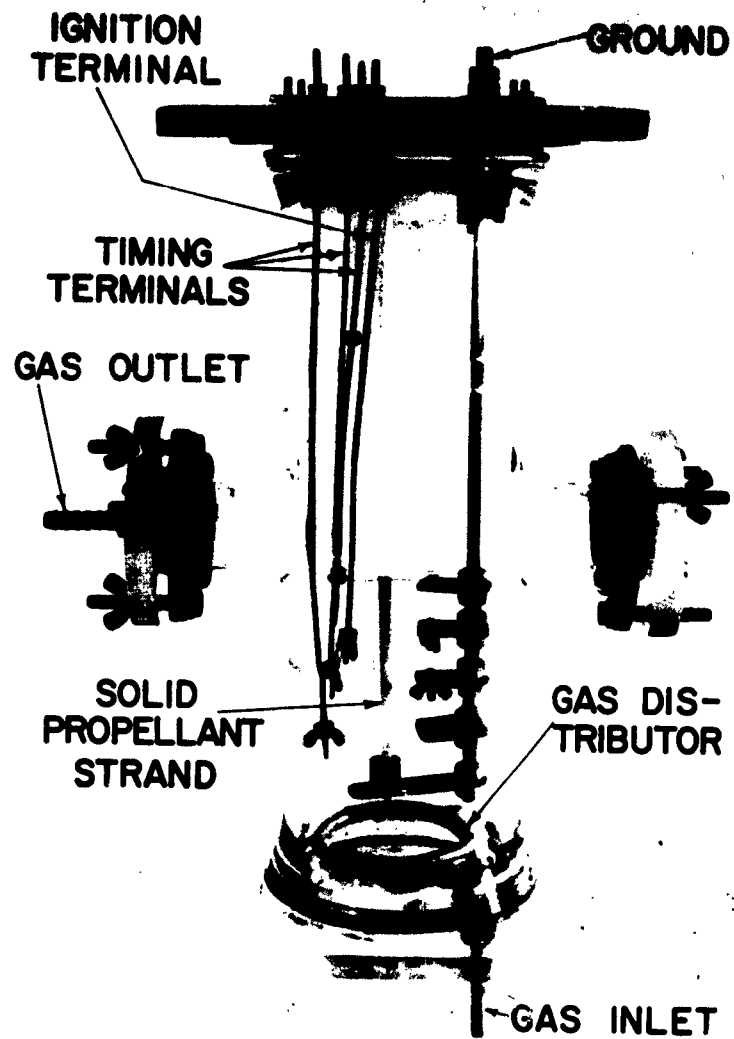


FIG. 2 STRAND BURNER

Comparison of Strands from Different Sources

Besides the strands prepared at AeroChem, other strands were obtained both from the Forrestal Research Center and Reaction Motors Division of Thiokol Chemical Corporation. The results are summarized in Table II. This data was taken with 1/4 inch strands, except where noted, at one atmosphere pressure with a flowing nitrogen atmosphere. No effect due to source, or strand cross-section were observed. However, the strands containing 80% oxidizer with no restrictor burned faster than the strands with restrictor.

Strands of Greater Than 80% Oxidizer

The above mixing procedure was found to be satisfactory for mixtures containing less than 80% oxidizer by weight. Because of the dry mixes obtained for oxidizer contents greater than 80%, the mixing was done by kneading a polyethylene bag containing the propellant.

The dry mixes obtained for oxidizer contents greater than 80% also prevented the propellant from being deaerated in the manner described above. Instead a small portion of the propellant was placed loosely in the wax mold, evacuated, and then tamped. This operation was repeated three or four times until the wax mold was filled. Strands prepared in this manner were mechanically weak, and only a small number of useful strands were recovered from each cured block. Because of the weakness of the strands, burning rates were obtained by marking the strands with a red grease pencil and timing the interval with a stopwatch.

Extruding Propellants

During the initial stages of the program, some effort was devoted to developing a technique for extruding propellants into a straw with a caulking gun. The advantages of such a technique are that additives which would interfere with the curing could still be used, and secondly, the curing step could be by-passed. This technique had to be abandoned due to frequent jamming of the propellant in the nozzle. Pressures up to 100 psig, the maximum operating pressure of the caulking gun, were used in order to extrude the propellant, but with little success. On disassembling the gun, it was found that the propellant remaining in the gun was "dry". Apparently, the applied pressure acts to separate the fuel from the oxidizer.

Fortunately, it was found that none of the solid additives tried interfered with the curing with the exception of sulfur. However, it is believed that more difficulties would be encountered with organic additives.

EXTERNAL ENVIRONMENTEffect of Tilted Burning Surface

A most serious question relating to the significance of the results with added gases is that of the complication of tilted burning surfaces. It was found that, even with four coatings of restrictor on strands burned in oxidizing atmospheres, tilting surfaces could not be eliminated, and in fact for the data shown in Figure 3 was culled from a set of which an average of 50% of the results obtained had to be rejected because of obvious tilting of the burning surface. The rejected results were those where tilting could be detected. This was found to be a tilt where the length of the burning side is about 10-20% of the strand diameter. On the average, approximately 50% of the results obtained with oxygen-nitrogen mixtures were thereby rejected.

An estimate of the effect of tilting on burning rates was therefore made to evaluate the reliability of the results. It was assumed that the linear burning rate normal to the surface is a constant — this is the principle upon which strand burning is based when the burning surface is flat. Then the mass consumption rate which is proportional to the observed burning rate obtained by the breaking of two wires is given by $\rho r A$, where ρ is the density of the propellant, r is the burning rate normal to the surface, and A is the surface area. Thus, the observed burning rate is A/A_0 times the burning rate in nitrogen where the surface area A_0 is perpendicular to the axis, i.e., a flat surface bounded by a circle for a cylindrical strand. Estimates of surface area effects have been made for the following models: (1) cylindrical burning down the side, (2) a tilted surface to form an ellipse, (3) cone burning, and (4) hemi-spherical burning. The results of these calculations are presented in Figure 4. The detectable — and thus rejected data — angle in terms of $L/D = 0.2$ (length of burning side = 20% of the diameter) would give an error for the various shapes of

Cone.....	8%
Ellipse.....	2%
Cylinder.....	80%

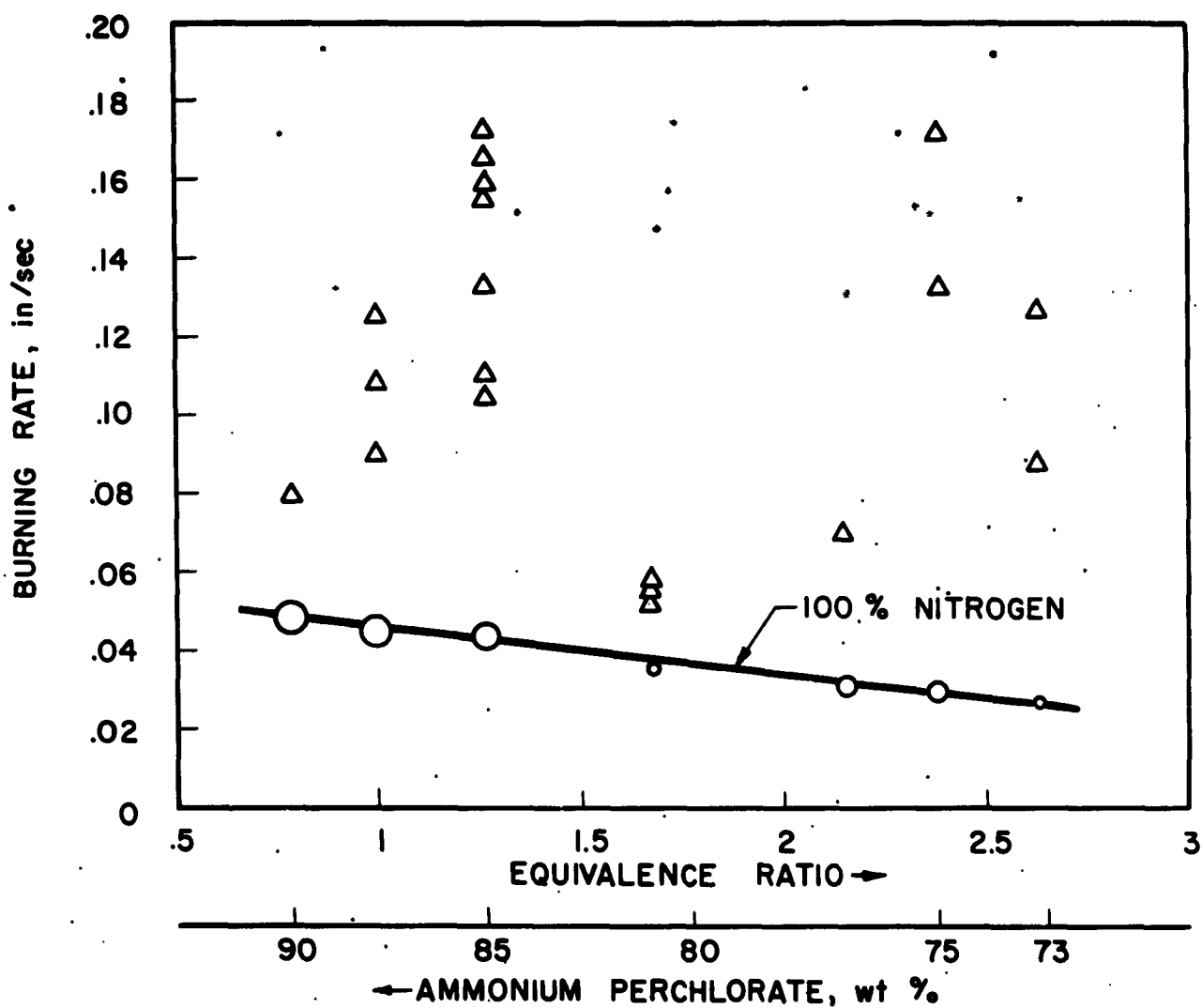


FIG.3 EFFECT OF 40% O₂ - 60% N₂ ATMOSPHERE
ON BURNING RATES OVER RANGE OF EQUIVA-
LENCE RATIOS

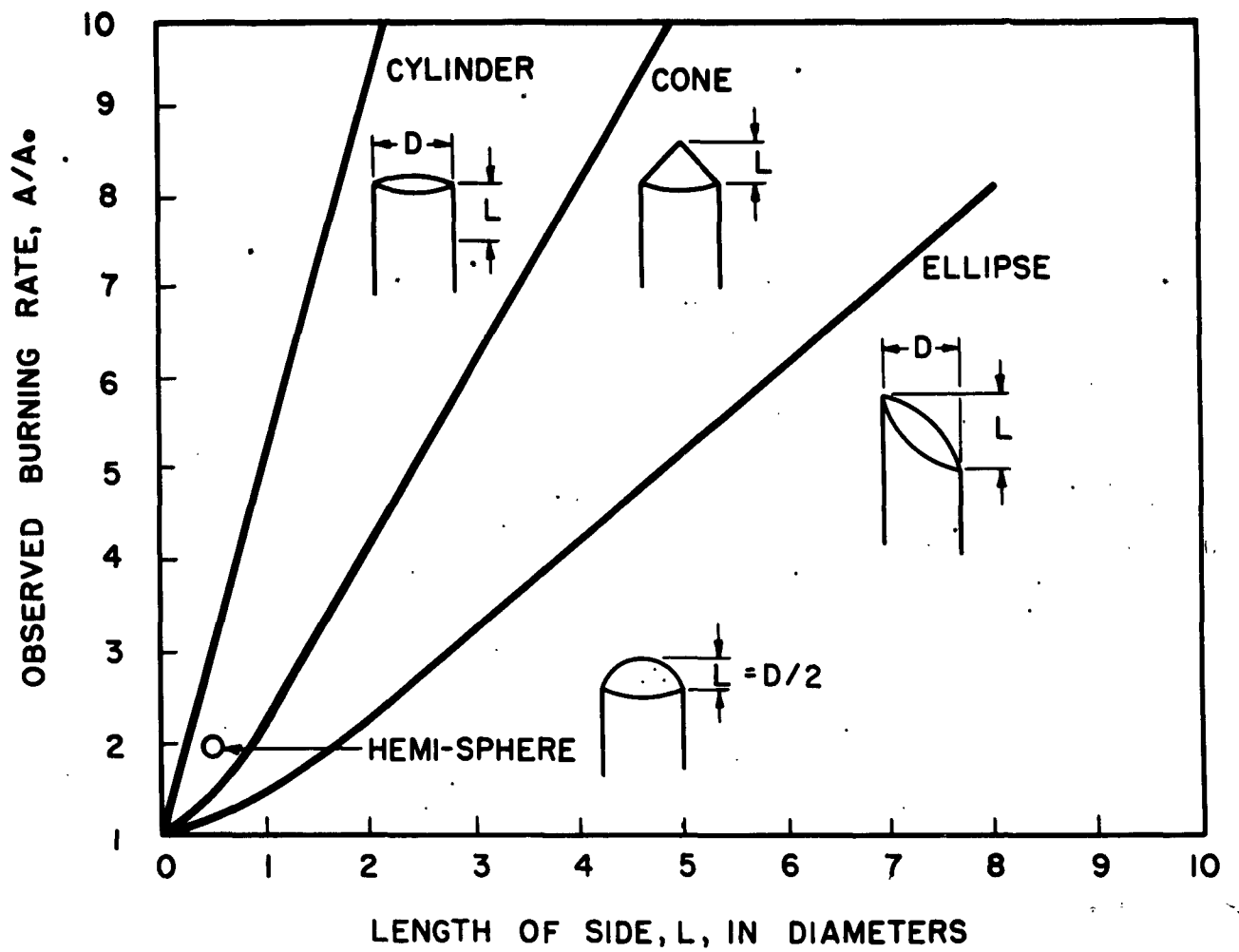


FIG. 4 EFFECT OF NON-IDEAL BURNING ON OBSERVED BURNING RATE

The cylindrical burning, i.e., down the side was easily detected, so probably few of these found their way into the "accepted data". Hemispherical burning was not actually observed; L/D would be one, and it would lead to an observation of twice the real burning rate. The cone or elliptical burning forms would have given a maximum error in the burning rate of 8%. We therefore conclude that surface changes may give, with oxygen present, burning rates too great by less than 10%. It was noted that in some instances burning rates obtained from a tilted surface agreed with burning rates obtained from what appeared to be a flat burning surface.

Screening

The results of screening experiments with twenty-two gases are summarized in Table III. The greatest change is seen to occur in the presence of oxidizing gases. This will be subject to more detailed discussion below, but some of the results with other gases bear brief comment.

Some interesting visual observations were made as follows: burning with propylene, methyl bromide and Freon produced heavy dark deposits on the walls of the burner housing, indicating mixing with gases which are at temperatures sufficient to prolyse these hydrocarbons. Hydrogen sulfide was similarly affected, decomposing to produce heavy yellow deposits on the wall. Both boron trichloride and boron trifluoride produced a clearly visible green color in the upper portion of the flame zone, as well as producing white deposits on the walls.

As discussed above, the most common experimental error, namely, "tilted surfaces" due to increased surface area yields consistently higher burning rates than would occur with a normal surface. Therefore, for a series of experimental values of burning rates, the minimum values can be taken to be more significant. On this basis, BCl_3 shows very definite inhibitory behavior. Although averages are reported, two different strands burned within 2% of .0256 in/sec, roughly 30% below values with nitrogen. BF_3 showed no such decrease. On the other hand, the other chlorine containing compounds showed no effect or produced an increase. No obvious reason for this result is apparent.

TABLE III

RELATIVE BURNING RATES OF RESTRICTED STRANDS^a

Pressure = 1 Atmosphere

Oxidizer-Fuel Ratio 80-20

Gas	Burning Rate in/sec	Mean Deviation	No. of Tests	Relative ^b Burning Rate
BCl ₃	0.033	± .005	5	0.92
N ₂	0.036	.001	6	1.0
HCl	0.036	.001	4	1.0
CH ₃ Br	0.036	.001	3	1.0
He	0.036	.001	5	1.0
H ₂ S	0.036	.001	5	1.0
HBr	0.036	.002	6	1.0
CCl ₂ F ₂	0.036	.001	4	1.0
COCl ₂	0.036	.001	2	1.0
H ₂	0.037	.001	4	1.0
CH ₃ NH ₂	0.037	.001	4	1.0
BF ₃	0.037	.001	2	1.0
SO ₂	0.037	.001	5	1.0
C ₃ H ₈	0.038	.001	5	1.1
NO	0.039	.005	14	1.1
CO ₂	0.039	.001	8	1.1
NH ₃	0.039	.001	6	1.1
Air ^c	0.039	.002	17	1.1
CO	0.040	.004	10	1.1
Air	0.041	.002	4	1.2
Cl ₂	0.046	.006	7	1.3
N ₂ O	0.13	.03	3	3.7
O ₂	0.39	.02	5	11.0

^a Strands furnished by the Forrestal Research Center, Princeton University^b Relative to nitrogen^c Burning rate determined in stagnant air

Comment also should be made on the lack of effect of H_2 , He and HBr. Workers⁴ at JPL have reported the effects of added gases where H_2 and He increase burning rates of NH_4NO_3 composite propellants in the pressure range from 500 to 1000 psia. Extrapolation to 100 psia shows only H_2 having an effect. With added CO_2 , NH_3 , and CO, strands sometimes extinguished or failed to ignite. At these pressures, the mean free path is very small, diffusion is slow, and yet the gases were able to diffuse into the reaction zone at sufficient concentration to affect the burning rate. A lack of effect of He or H_2 would be expected in a pressure regime where chemical reaction rates are rate controlling as contrasted to a pressure regime where transport properties are rate controlling.

Addition of NH_3 produced a dense white fog depositing presumably as NH_4Cl on all parts of the apparatus. This indication of the presence of significant amounts of HCl in the product gases is to be contrasted with Friedman's findings⁵ in the deflagration of pure ammonium perchlorate that although HCl is a major chlorine carrier at high pressures, at one atmosphere HCl is completely absent as a product.

Assuming diffusion of HBr is adequate, its lack of effect is indication of the absence of a combustion system with oxygen. The effect of halogen containing gases on combustion has been investigated rather extensively by Rosser and co-workers at Stanford Research Institute⁶. They have shown that bromine and iodine compounds are equally effective as hydrocarbon-oxygen combustion inhibitors, and both are much more effective than chlorine containing compounds. In a more recent report⁷, Rosser has extended the investigation of flame inhibition to nitrogen-oxide supported flames. Halogen additions to these flames proved to be no more effective than nitrogen gas acting as a diluent. Similar lack of effect was noted for NH_3 -NO flames, and for flames wherein the fuel contained nitro groups. They conclude therefore that halogens as inhibitors are effective only in chain mechanisms where H, O or OH are chain propagators. For the work reported here, therefore, we conclude that either (1) HBr has not diffused into the flame zone to any critical extent or (2) if a chain mechanism is operative in the flame zone, oxides of nitrogen are a

significant fraction of the oxidizing gas or (3) the HCl already present masks the effect of HBr. The second alternative is reasonable in view of experimental evidence of the decomposition of NH_4ClO_4 ⁶. Most of the oxygen present in the perchlorate eventually is evolved in the form of NO or N_2O , thereby limiting an inhibiting effect of halogen containing gases. In connection with this gas phase work, no decrease in burning rate was observed when NH_4Br was added as a solid directly into the strand. Since NH_4Br sublimes at 500°C , it is a reasonable expectation that the HBr should be present directly in the flame zone above the strand surface. There is no way at present to decide between this and the masking effect of HCl.

Oxidizing Environments

An interesting effect related to comparing oxidizing gases is seen to occur when oxygen is replaced on a volume basis by perchloryl fluoride (ClO_3F)* in nitrogen containing mixtures (see Table IV and Figure 5). The sizeable effect should be compared with the absence of any effect when Freon (CCl_2F_2) was used as a gaseous environment. The lack of effect with Freon (note lack of effect with BF_3 as well, although only two experiments were performed) may be due to increased strength of the fluorine bond in Freon as compared with the fluorine bond in the perchloryl fluoride. It should be noted that anhydrous perchloryl fluoride is thermally stable up to 500°C . It also has a smaller diffusion coefficient than oxygen ($32/102.5$)⁷. It is most likely decomposed in the hot boundaries of the flame, allowing the lighter components to diffuse into the combustion zone. In particular, one should note the significant increase over the results with oxygen when the oxygen is replaced by perchloryl fluoride on a mole basis. However, since a molecule of perchloryl fluoride contains three atoms of oxygen, the burning rate line for perchloryl fluoride in Figure 5 is converted to an "equivalent oxygen line". This conversion results in translating each point on the perchloryl fluoride line horizontally to the right. The result is the dashed line in Figure 5. The coincidence of this line with the oxygen line is evidence that ClO_3F is effective by furnishing oxygen.

* A sample of this gas was submitted to us through the courtesy of the Pennsalt Chemical Corporation, Philadelphia, Pennsylvania.

TABLE IV

EFFECT OF OXYGEN AND PERCHLORYL FLUORIDE ON STRAND BURNING RATES

Pressure = 1 Atmosphere

Oxidizer in N ₂ Atmosphere Volume %	Burning Rate in/sec
0	.031 ± 0.002*
20 O ₂	.039
30	.042
40	.076
50	.090
70	.13
100	.28
30 ClO ₃ F	.075
50	.114

Strands: 77 wt.% oxidizer loading with two coats of butyrate dope plus two coats of vinylite

* Number of experiments: 9. The remaining results contain one or two experiments each.

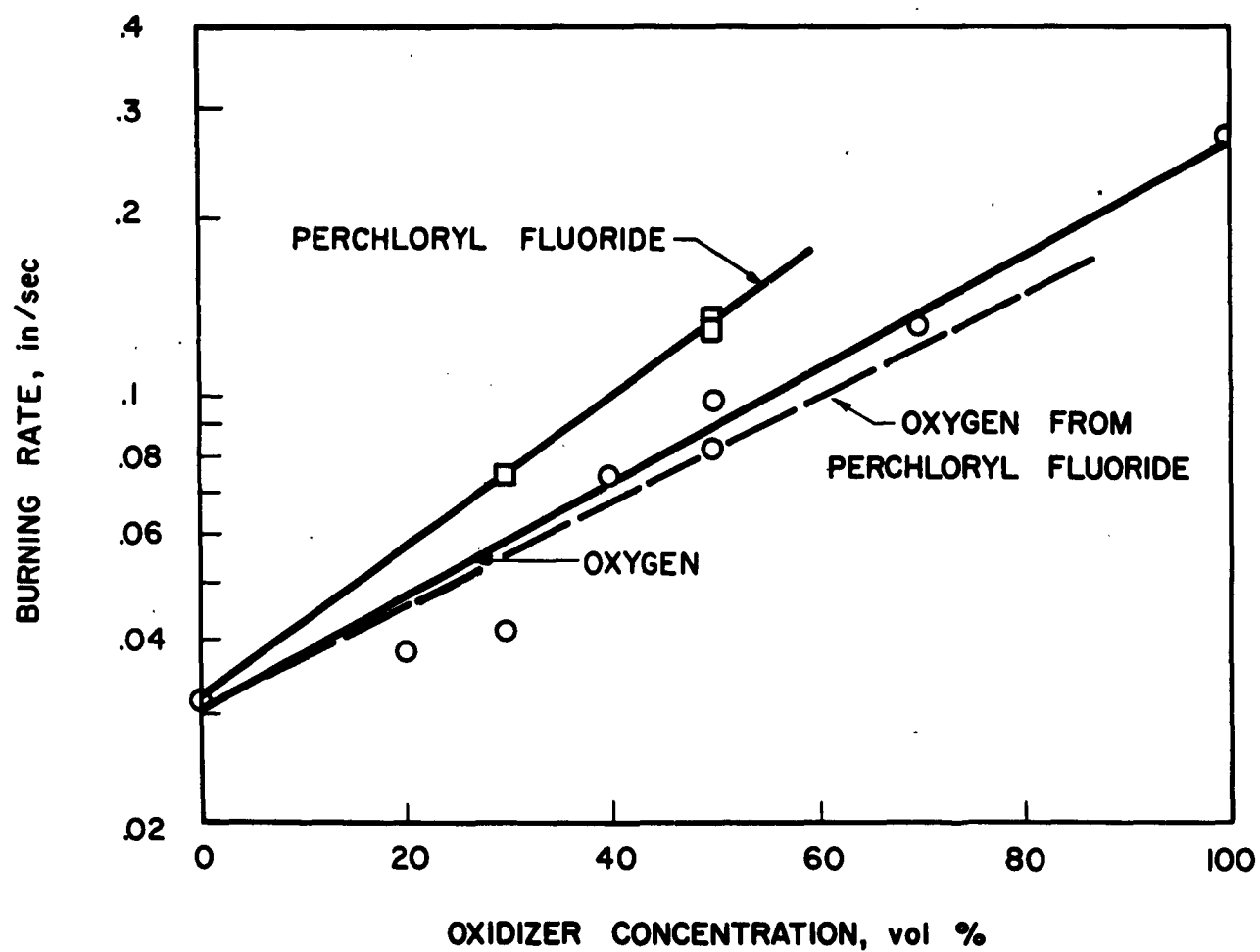


FIG. 5 EFFECT OF OXIDIZER CONCENTRATION IN THE AMBIENT ATMOSPHERE ON THE BURNING RATE STRANDS CONTAIN 77% NH_4ClO_4

Oxygen Effects

Table IV. and Figure 5 illustrate the effect of varying oxygen content on burning rate. Table V and Figure 3 present the data with varying equivalence ratio and constant oxygen atmosphere. Although the results with oxygen (Figure 3) show considerable scatter, nevertheless, the pertinent fact is that all of the oxygen points are higher than the 100% nitrogen curve by more than the expected error due to tilt of the burning surface. The size of the points on the 100% nitrogen curve represents the experimental reproducibility.

The sensitivity of burning rate to oxygen indicates another possible source of error affecting the scatter shown in Figure 3. The better data fit of Figure 5 as compared to Figure 3 might be attributed to the fact that the strands used for Figure 5 were restricted with two coats of butyrate dope plus two coats of vinylite while only two coats of butyrate dope were used in Figure 3. Another difference which might effect the results was the fact that the strands used for Figure 5 were circular, while those for Figure 3 were square. It should be noted, however, that with nitrogen flow, strand shape was not a factor (see Table II). The gas flow which was not carefully controlled might also affect the scatter. All the data in Figures 3 and 5 were obtained with a constant flow of about 110 cc/sec (STP). To answer the question of flow effect, an experiment was performed at 56 cc/sec which resulted in a burning rate of approximately one-half that obtained at the higher flow rate. No effort was made to pursue this further, other than establishing that increasing total flow of an oxygen containing gas increased the burning rate.

The oxygen effect was further noted in the following experiment. A strand was ignited in a 50% O_2 - N_2 mixture and noted to burn very rapidly. The oxygen was shut off, and the nitrogen flow increased. The burning was observed to slow up considerably. Turning on the oxygen again caused an increase in

TABLE V

EFFECT OF STOICHIOMETRY ON BURNING RATES IN TWO ATMOSPHERIC ENVIRONMENTS

Pressure = 1 Atmosphere

Oxidizer Loading, wt.%	Equiva- lence Ratio	100% N ₂			40% O ₂ - 60% N ₂		
		Burning Rate in/sec	Mean Devia- tion	No. of Experi- ments	Burning Rate in/sec	Mean Devia- tion	No. of Experi- ments
73	2.64	.0266	.0006	5	.11		2
75	2.38	.030	.002	15	.15		2
77	2.14	.031	.002	9			
81.1	1.67	.0361	.0008	9	.058	.002	3
85	1.26	.044	.003	3	.15	.02	8
87.7	1.0	.046	.004	5	.11	.01	3
90	.795	.049	.004	4	.080		1

burning. The relative times in this experiment eliminate the possibility that the oxygen is absorbed by the strand. This experiment was performed at one atmosphere and also at reduced pressures (see below).

Sub-atmospheric Burning Rates

Some exploratory experiments were made at sub-atmospheric pressures with the same apparatus by simply attaching the exhaust line from the burner housing to a water aspirator. The advantages of low pressure studies are evident from several points of view. Of major significance for this work is the relation of pressure to flame thickness. As the ambient pressure decreases, the mean free path of the gas molecules increase, thus favoring increased rates of diffusion while the chemical rates of bi-molecular processes will decrease. This slowing up of rate causes a thickening of the flame zone, facilitating any attempts to traverse this zone. At these pressures, bi-molecular chemical reactions can be assumed to be sufficiently slow compared to transport phenomena so as to be rate controlling. Additives supposed to affect chemical reactions should have major effects in this regime. Furthermore, a decrease in burning rate can be expected, increasing the precision of the measurements, and minimizing "tilting" effects associated with fast burning strands.

Low pressure experiments should also allow determination of pressure coefficients in a regime that has been almost completely neglected. At lower pressures, it would be worthwhile to re-examine the effects of certain gaseous additives whose negligible effect at higher pressures could be attributed to poor diffusional mixing. The first experiments performed at reduced pressures were attempts to investigate further the oxygen effect by observing this at reduced pressure. As might be expected in such a crude apparatus, rapid burning, as in the presence of oxygen, produced pressure fluctuations making quantitative measurements of burning rates meaningless. Nevertheless, certain interesting observations were made. At 50 mm Hg, ignition of a 1/4 inch round strand having an oxidizer fuel ratio of 77/23 could not be achieved except in the presence of oxygen. Increasing oxygen flow greatly increased the burning rate. Shutting the oxygen off during burning produced flame extinguishment in some cases.

A series of experiments in flowing nitrogen were performed at various pressures down to the low pressure ignition limit for the propellant used. The strands contained 80 wt.% NH_4ClO_4 oxidizer and 20% polyester-styrene co-polymers, and were 1/4 inch square. They were not restricted and were observed to burn with fairly flat surfaces (Figure 6). The results are shown in Figure 7.

The sub-atmospheric data were compared with Summerfield's burning rate equation. The Summerfield equation⁹ can be written in the form

$$\frac{P}{r} = a + b (P^{2/3})$$

where P is the pressure, r is the burning rate, and "a" and "b" are empirically determined constants, "a" is related to a "reaction time", i.e., its magnitude is determined primarily by chemical reactions in the combustion zone, and "b" is related to a "diffusion time". At low pressures the mean free path increases to the point where diffusion becomes rapid relative to chemical rates, therefore chemical rates become rate controlling, and $b(P^{2/3})$ should become small compared to "a". As predicted, r versus P (Figure 7) is a straight line from which the slope $1/a$ can be obtained — $b(P^{2/3})$ must be small; "a" calculated from the slope yields a value of 340 psia/in/sec. This value of "a" is very close to the values given in Summerfield's paper, namely, 160-365 psia/in/sec. However, if we plot P/r against $P^{2/3}$, to determine the constants "a" and "b", the data are fitted by a straight horizontal line (Figure 8). The slope "b" is therefore zero or very small. Since "b" should have a finite constant value (27.0 and 17.3 for an average particle size of 120 and 16 microns respectively)² as determined by high pressure data, the values $b \approx 0$ determined at the low pressure implies that "b" is pressure sensitive. No further work was done to substantiate this dependence of "b" on pressure since the primary purpose of the experiment was to determine if sub-atmospheric pressures were suitable for further study.

Diffusion into Combustion Zone

To understand the gaseous environment effect with oxygen, some effort was made to estimate the rate of diffusion into the flame zone. A crude estimate of mixing can be made by following the method of Drew⁹. The model is that of diffusion into a laminar jet in "rod-like" or plugged flow. In the case of the burning strand, there is a temperature profile from the surface to the final

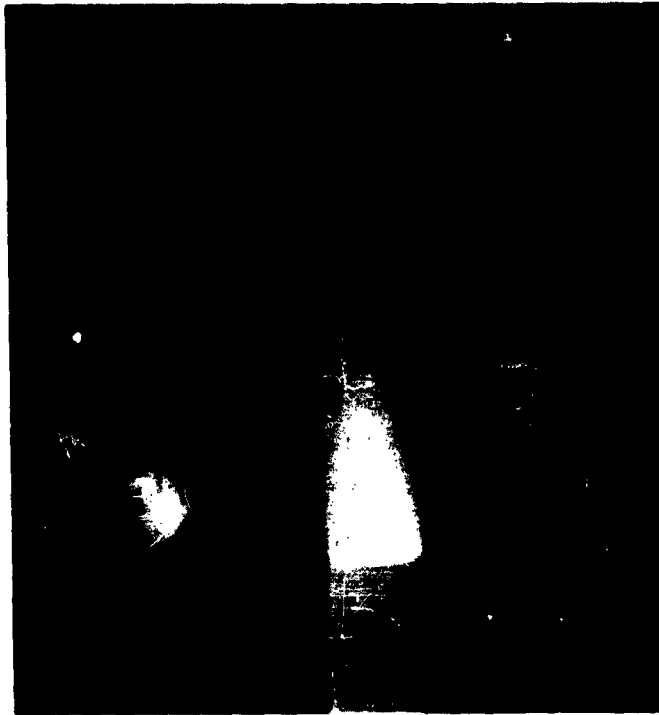


FIG. 6 STRAND BURNING IN PARTIAL VACUUM

Atmosphere — nitrogen

Pressure — 33 cm Hg

Oxidizer — Fuel Ratio — 80/20

Restrictor — None

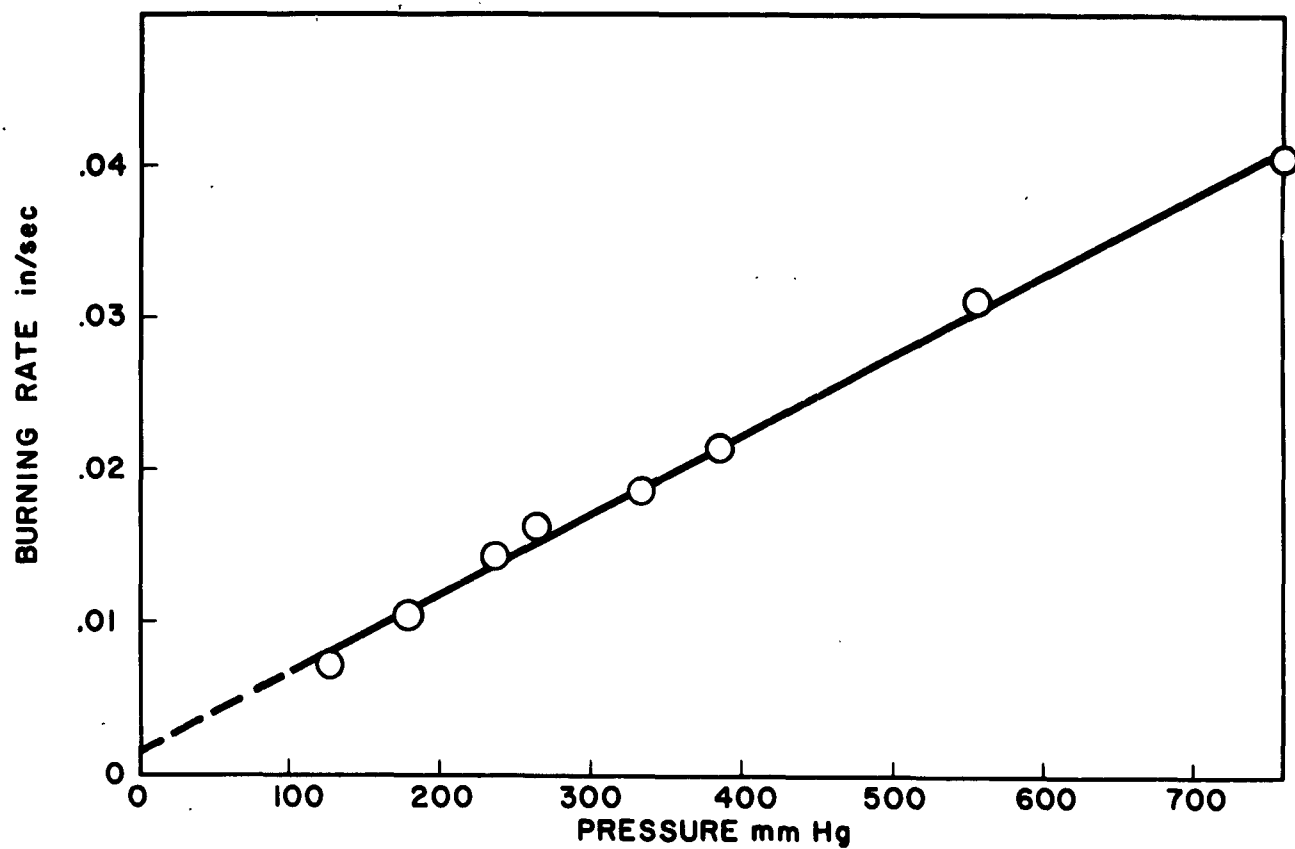


FIG. 7 BURNING RATES AT LOW PRESSURES IN NITROGEN
Oxidizer-Fuel Ratio - 80/20
Restrictor - None

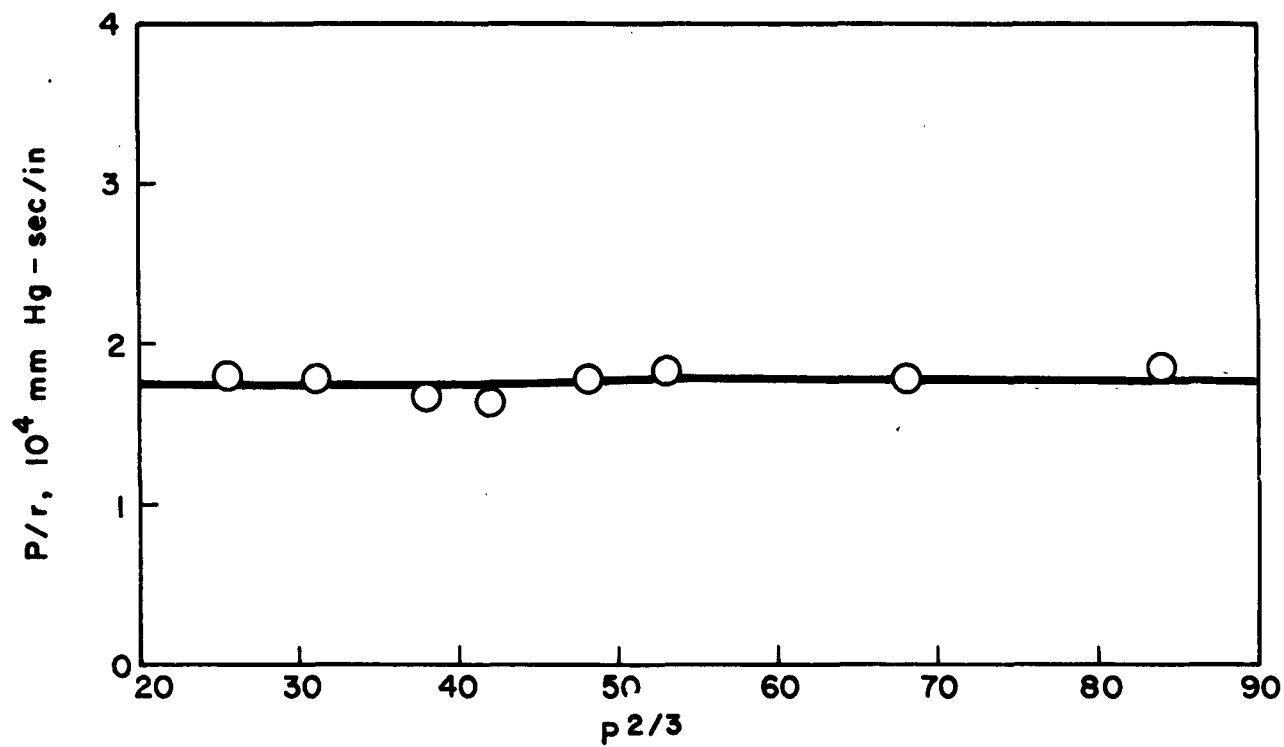


FIG. 8 BURNING RATE EQUATION

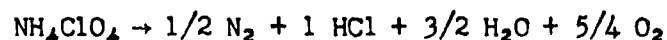
$$\frac{P}{r} = a + b(p^{2/3})$$

reacted gases. Drew's treatment applies only to a system of uniform plug temperature with no chemical reaction. Taking Summerfield's value for a surface temperature of 1000-1100°K as the minimum temperature for which this calculation would be significant, "plug impregnation" by oxygen has been calculated assuming a constant plug temperature of 1200°K. The calculation was repeated for the maximum temperature of 2500°K, and the results are reported in Table VI. Distances are given for various impregnations into the flowing gas stream above the surface of 1/4 inch and 1/2 inch diameter strands. The degree of average impregnation is the concentration with respect to ambient. There will, of course, be a concentration gradient from the outer periphery stream to the center. Induced gas flow around the periphery may increase the effective rate of diffusion and will also cause non-ideal (i.e., non-flat) burning. If diffusion is causing oxygen to penetrate into the flame zone, increasing strand diameter should produce a decrease in the magnitude of the oxygen effect. That this is the case is shown by the following data for square strands of 77/23 oxidizer-fuel ratio, restricted with two coats of butyrate dope and burning in a 40% oxygen atmosphere.

<u>1/4 inch square</u>	<u>1/2 inch square</u>
.066 ± .008 in/sec	.039 ± .001 in/sec*

Values chosen were from strands burning with virtually flat or slightly tilted (less than approximately 5°) surfaces.

If the combustion zone thickness is the order of 10^{-2} cm (reference 2) at 200 psi, then the average degree of oxygen penetration in Figure 3 is only 40% of 5 to 10% or about 2 to 4%. In a propellant if we assume "ideal" decomposition of ammonium perchlorate to be:



the oxygen concentration would be 29 mole percent. In a stoichiometric propellant, assuming the fuel to decompose to four molecules, the oxygen concentration would be 15%. The significant observation is that the oxygen concentration due to diffusion only becomes comparable to the "ideal" original concentration of oxygen at a distance above the fuel surface perhaps four times greater than the assumed combustion zone thickness. It must be kept in mind that the above reasoning applies to stoichiometric propellants having greater and less than the stoichiometric quantity of oxidizer. All strands were found to give increased burning

* The burning rate in N_2 for this 1/2 inch strand was .031 in/sec (Table II).

TABLE VI

OXYGEN DIFFUSION INTO PROPELLANT REACTION ZONE

Pressure = 1 Atmosphere

Concentration % of Ambient	Distance Above Strand Surface, cm.	
	1/4 inch Diameter Strand	1/2 inch Diameter Strand
<u>1200°K</u>		
6	2.2×10^{-2}	8.7×10^{-2}
10	5.9	24
20	24	95
30	52	200
<u>2500°K</u>		
6	1.6×10^{-2}	6.3×10^{-2}
10	4.2	17
20	17	68
30	37	150

rates in oxygen (see Figure 3) so that the oxygen from the ambient atmosphere is not simply altering the stoichiometry.

Oxygen flow into the burning zone might also be induced because of the velocity difference between the burning gases and the atmosphere. Unless this greatly increases the degree of mixing, an explanation of the oxygen effect must therefore assume either:

1. The flame thickness, i.e., where significant reactions occur, must be greater than previously supposed,
2. Oxygen diffusing in differs from oxygen from decomposition, or
3. The oxygen has a catalytic effect and oxygen diffusing in differs from oxygen from decomposition.

The second view seems more reasonable. In experimental studies of the decomposition of NH_4ClO_4 , much of the oxygen eventually is evolved in the form of NO or N_2O (references 5 and 8). Furthermore, experimental studies of pre-mixed N_2O , NO, and NO_2 , hydrocarbon flames¹⁰ show that burning velocities of these flames are less than those with oxygen. It is difficult to speculate with present information as to whether the oxygen acts as simply a more efficient oxidizer than the gaseous oxidizer resulting from the decomposition of NH_4ClO_4 or whether it has a catalytic effect on the chemical rates. The decision as to which explanation is the correct one is not trivial because in one instance greater quantities of oxidizer would be required than in the other. The significance of this should become apparent in the next section of this report.

In order to answer some of these questions, temperature and composition profiles through the flame zone would be of great value.

Proposed Application

The increase in burning rates obtained by the addition of various gaseous oxidizers has suggested a means by which burning rate control and, possibly, thrust termination of a solid propellant rocket might be accomplished. The proposed system would contain a composite propellant and an auxiliary tank of liquid oxygen or other oxidizer, which acts as the controlling medium. By regulating the flow of liquid oxidizer into the combustion chamber, the burning might be increased or decreased. The quantity of oxidizer required would, of course, depend upon

whether it was acting as an oxidizer or catalyst. This system would be comparable to a hybrid system if large quantities of oxidizer were required.

. The significance of these suppositions depends on assuming that the oxygen actually diffusing into the combustion zone is small, which seems reasonable, and that the effect, if catalytic, will persist at rocket chamber pressures. This latter assumption is more questionable because at higher pressures the chemistry becomes less important as a rate controlling process.

INTERNAL ENVIRONMENTAdditives

Following the procedures already outlined, a variety of solid additives were tried, keeping the oxidizer-fuel ratio constant. Data are presented in Table VII. With few exceptions, the additives produced changes in the burning rate in agreement with those found in the literature for ammonium perchlorate propellants. However, values in the literature are usually quoted at pressures in excess of 1 atmosphere and the fuels used may differ as well. Thus, for example, urea produced an 11% decrease in burning rate in our system while ammonium oxalate had no effect. Adams and co-workers¹¹ found a 10-1/2% decrease for 4 wt.% urea in a stoichiometric NH_4ClO_4 polystyrene propellant burned at 1000 psi, an effect similar to the one obtained in this work. However, in their work ammonium oxalate produced a 14% reduction in burning rate, while no effect was observed in the work reported here. The difference in these results is difficult to explain as ammonium oxalate can be expected to yield similar decomposition intermediates to those of urea. There is an obvious need here for chemical analysis of the combustion products of the two compositions.

The greatest increase in burning velocity was obtained with sodium dichromate, but these strands all showed "tilt" to the extent of 30 to 40°. As already discussed, tilt might cause the observed burning rate to be large while no change exists in the burning rate normal to the surface. Assuming no change in burning rate normal to the surface, a 40° elliptical tilt should give an observed rate of 0.041 in/sec. The angle of tilt necessary for the observed burning rate of 0.049 in/sec is 50° — considerably larger than that estimated for the observations. To determine whether the observed increase was due to tilt or a real change in burning rate, a series of strands were photographed while burning and the tilt angle estimated more

TABLE VII

INFLUENCE OF SOLID ADDITIVES ON BURNING RATES^{a, b}

Pressure = 1 Atmosphere

Oxidizer-Fuel Ratio 77/23

Additive	Burning Rate in/sec	Mean Deviation	No. of Experiments
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	.0252	.0008	9
$(\text{NH}_4)_2\text{CO}$	.027	.001	9
CaCO_3	.028	.001	6
Na_2SO_3	.028	.001	9
KHCO_3	.0282	.0006	8
Na_2CO_3	.0289	.0007	10
$\text{NH}_4\text{H}_2\text{PO}_4$	.029	.002	8
$(\text{NH}_4)_2\text{SO}_4$	.0293	.0008	7
HSO_3NH_2	.030	.001	8
None	.031	.002	9
NH_4Br	.031	.002	11
$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	.0314	.0004	8
NH_4Cl ^{c, d, e}	.0314	.0008	4
None ^d	.0315	.0007	6
$(\text{NH}_4)_2\text{SO}_4$ ^c	.032	.001	9
$\text{Mg}(\text{ClO}_4)_2$	.032	.001	8
CuO	.033	.002	6
NH_4Cl ^{c, d, e}	.034	.001	7
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	.049	.002	8

a 1/4 inch square cross-section strands, restricted - unless specified

b 1.5 wt.% additive in strand

c Coprecipitated

d 1/4 inch diameter round cross-section strands, no restrictor

e Two separate propellant batches

closely from the photograph. These photographs are presented in Figure 9 and the burning rates shown below:

<u>Burning Rate in/sec</u>	<u>Figure 9</u>
.053*	A
.050	B
.052	
.051	C
.053	
.051	D
.063	E
.062	F

The first three pairs of measurements have a mean deviation of 0.001 in/sec or 2%. The elliptical tilt angle required to give 0.052 in/sec is about 50°. It can be observed in the photographs that the angle is more nearly 30° except for E and F where the burning rate is also greater. It can thus be concluded that the sodium dichromate causes a real increase in burning rate.

Recently, considerable data on burning of ammonium perchlorate propellants with polyester acrylate fuel has been submitted by a group at Aerojet¹². Although the work concerned itself with reduction of temperature sensitivity, effects on burning rates at 1000 psi were examined as well. Correlations were made showing that additives which are effective in promoting the thermal decomposition of NH_4ClO_4 and in catalyzing the oxidation of CO and of hydrocarbons (C_2H_6) will greatly increase the solid propellant burning rates. Additives which greatly inhibit the low temperature (270°C) decomposition of NH_4ClO_4 appear to decrease burning rates. Some additive

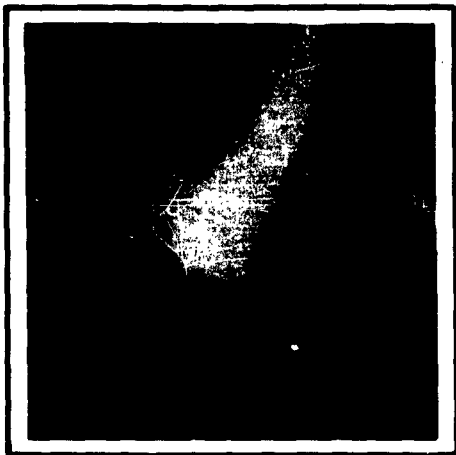
* Paired rates represent two measurements on same strand.



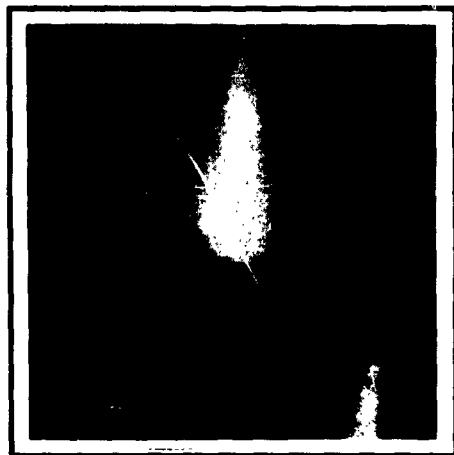
A



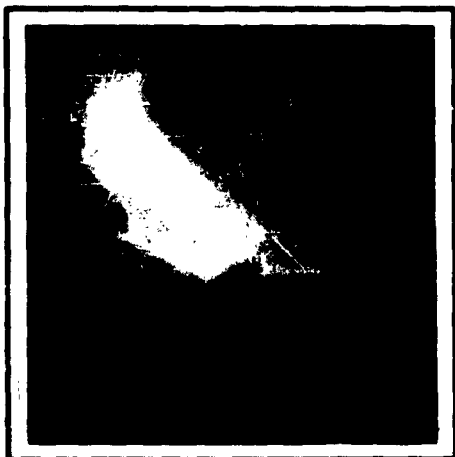
B



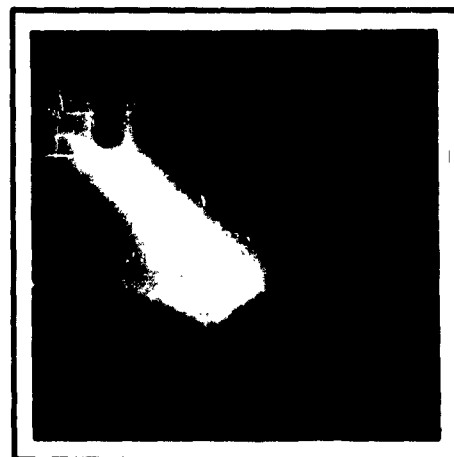
C



D



E



F

FIG.9 STRANDS CONTAINING 1.5% $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$
 1 atm. N_2 O/F = 77/23
 Restrictor-2 Coats Butyrate Dope

effects relevant to our experiments are given below. The fuel used was polyurethane and all experiments were performed at 1000 psi in a burning rate bomb.

<u>Additive</u>	<u>% Change in Burning Rate</u>
CaCO_3	-15
LiF^a	-30
CaC_2O_4	0
$\text{Ca}_3(\text{PO}_4)_2^b$	up to +100

a No burning rate data is given for NH_4Cl , although it yields similar inhibitory effect on decomposition of pure ammonium perchlorate, as does LiF .

b $\text{Ca}_3(\text{PO}_4)_2$ shows no effect on decomposition rate of pure ammonium perchlorate and no effect on oxidation rates.

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