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HIGH-TEMPERATURE SOLID PROPELLANT

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IIT Research Institute

Prepared for:

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(Final Technical Report)

HIGH-TEMPERATURE SOLID PROPELLANT

U.S. Naval Weapons Laboratory
Dahlgren, Virginia 22448

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HIGH-TEMPERATURE SOLID PROPELLANT

May 29, 1964, through August 29, 1965

Contract No. N178-8465

IITRI Project C6033

Prepared by

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U.S. Naval Weapons Laboratory
Dahlgren, Virginia 22448

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FOREWORD

This is Report No. IITRI-C6033-7 (Final Report) of IITRI Project C6033, Contract No. N178-8465, entitled "High-Temperature Propellants." The report covers the period from May 29, 1964, through August 29, 1965.

Mr. Allan J. Gaynor, Research Engineer, who was Project Leader, was assisted in the overall direction of the work by Dr. Morton J. Klein, Director of Applied Chemistry Research, and Mr. Charles K. Hersh, Manager of Propellant Research. Personnel who contributed to the project included: Mr. J. J. Finn, Associate Chemist, who performed the cross-linking studies and preparation of propellant polymer; Mr. James L. Austing, Research Engineer, who performed some of the propellant evaluations; Mr. George J. Macur, Assistant Chemist, who performed the metal-metal oxide studies; and Messrs. W. A. Able, Associate Engineer, and T. Stanley, Technician, who conducted the closed bomb studies and fabricated the propellant grains. The invaluable assistance of Mr. George Poudrier and Dr. Vincent Roach of the U.S. Naval Weapons Laboratory is gratefully acknowledged.

Data for this report are recorded in logbooks C14921, C14994, C15432, C15466, C15555, C15556, C15905, C15945, and C16091.

Respectfully submitted,

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ABSTRACT

HIGH-TEMPERATURE SOLID PROPELLANT

The program reached a successful conclusion with the attainment of propellant grains capable of withstanding an 800°F environment for one hour and performing as required from computed impetus values. Difficulties were experienced in cross-linking the carborane polymer as received from Reaction Motors Division of Thiokol. Conventional closed bomb evaluation of these typical slow-burning, high-temperature propellants was shown not to be applicable for these systems. Two pounds of pelletized propellant were furnished along with one and one-half pounds of unmixed granular propellant.

A secondary objective of the program was concerned with a study of the B-AgF_2 reaction. Results indicate the feasibility of using the above as a water-ignitable propellant system. Additional study is indicated to optimize the system and further elucidate the reaction mechanism.

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HIGH-TEMPERATURE SOLID PROPELLANT

I. INTRODUCTION

The objective of this program was the development of a power cartridge propellant that is stable to 900°F and provides an impetus of at least 100,000 ft-lb/lb of propellant at 70°F. Other criteria were as follows.

(1) The autoignition temperature should be 900°F or higher.

(2) The propellant should withstand exposure to temperatures ranging from -100 to + 800°F for 1 hr with no more that a ±10% change in form or dimensions.

(3) The propellant should have an impetus of at least 100,000 ft-lb/lb as measured by closed bomb techniques.

(4) The burning rate of the granulated propellant should be between 0.2 and 2.0 in./sec.

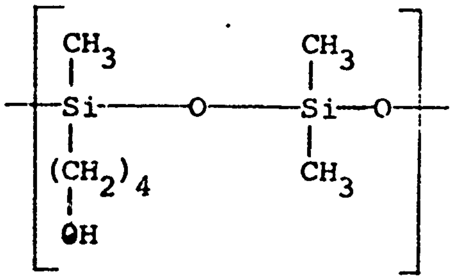
Previous work has shown the feasibility of using a metal-metal oxide as a heat source to produce the thermal energy required to decompose a thermally stable polymer. On decomposition, the binder produces gases that can do work. Thus one phase of the program was directed toward producing 3-1/2 lb of propellant by utilizing this concept.

The other phase of the program involved a study to elucidate the reaction mechanism of the water ignition of mixtures of boron and silver difluoride.

II. PROPELLANT PREPARATION

A. Cross-linking of Propellant Polymer

A thermally stable boron polymer, characterized as



$$\left[-\underset{\underset{\underset{\Theta H}{|}}{(CH_2)_4}}{\underset{|}{\overset{\overset{CH_3}{|}}{Si}}} - O - \underset{CH_3}{\underset{|}{\overset{\overset{CH_3}{|}}{Si}}} - O - \right]$$

where $\Theta = C_2H_{10}B_{10}$, was purchased from the Reaction Motor Division (RMD) of the Thiokol Chemical Corporation. The previous program had demonstrated that this material would function very effectively as the gas generator when used in conjunction with a metal-metal oxide heat source. Upon receipt of the polymer from RMD during the third month of the program it was noted that the viscosity of this material was considerably higher than that of the previously supplied material. This difference in viscosity created an unforeseen problem of mixing to obtain a cross-linked material. The material as received was shown by infrared spectroscopy to be identical to the original sample. The increased viscosity was apparently due to a higher-molecular-weight material than was previously supplied. This was confirmed by contact with RMD personnel.

The procedure recommended to accomplish cross-linking by RMD involved mixing the polymer with 5 wt % ethyl silicate and adding 0.75% tin octoate as a catalyst. This procedure worked quite well with the original material when the polymer was the consistency of vaseline. The addition of 5% ethyl silicate to the new sample of polymer did not lower its viscosity sufficiently to permit hand-mixing.

The first attempt of kneading the catalyst into the RMD polymer, which contained 5% ethyl silicate, was performed in a Carver press. The mass was flattened between two Teflon sheets, and the process was repeated about 20 times. Subsequent heat treatment, 48 hr at 80°C followed by 48 hr at 150°C, did not give a 400°C melting polymer. Mulling the polymer with 5% ethyl silicate and catalyst in a polyethylene beaker was equally unsatifactory.

The addition of a small amount of benzene to reduce the viscosity was tried; this resulted in a product that melted at 384°C. Methylene chloride was then tried as a solvent. The solvent was evaporated at 80°C followed by a cure at 150°C. This operation gave a product that melted at 390°C. Further heating lowered the melting point. A fivefold scale-up did not produce a polymer that melted above 400°C.

The cross-link reaction was conducted in a Parr bomb in order to contain the RMD polymer-ethyl silicate-catalyst mixture in methylene chloride. After treatment at 80°C the material was taken out of the bomb, heated to 150°C, and maintained there for one day. This treatment also resulted in a material with a melting point lower than 400°C.

The safety of heating methylene chloride with the RMD polymer plus ethyl silicate and catalyst was explored. One gram of RMD polymer, 1 cc dichloromethane plus a few drops of ethyl silicate, and one drop of catalyst were sealed in a thick-walled test tube and heated at 150°C for 24 hr. The mixture proved safe, resulting in a material with a melting point range of 370 to 384°C. A second experiment was performed by using some bomb fittings as an additional precaution; this resulted in a material with a melting point range of 372 to 388°C.

Another experiment was performed in the Parr bomb on a 10-gram batch by using dichloromethane as the solvent. After being heated 27 hr at 80°C, the solvent was removed, and the material was again heated at 150°C for 48 hr. The product melted between 310 and 370°C. Two grams of the product were broken up and extracted with acetone. After 1/2 hr the product was filtered. The residue of the liquor melted below 70°C and weighed 1.6 grams. The extracted material (0.4 gram) melted between 365 and 375°C. The untreated product was reheated for an additional 27 hr. Two grams of this material was extracted with acetone. The extract contained 1.6 grams of material that melted between 52 and 70°C. The extracted residue melted between 362 and 378°C.

The extraction of unreacted or lower-molecular-weight moieties was disturbing. Two possibilities were suggested;

additional amounts of ethyl silicate are required to achieve cross-linking, or the solution of the RMD is not sufficiently dispersed, i.e., it contains large globules of solvated RMD polymer.

Experiments exploring the latter possibility was pursued by allowing the polymer and ethyl silicate to stand overnight in methylene chloride. Catalyst was added the following day. In this experiment the oven got out of hand and reached 180°C for an indefinite period, and part of the material liquified. A small amount of ethyl silicate was added to the liquid, and the temperature was lowered to 150°C. After heat treatment the product was quite brittle but melted below 120°C.

After 20 hr. a solution of the ingredients was heat-treated in the bomb at 150°C. The dish containing the material was on an incline in the oven so that a thin and thick layer were obtained. The thick layer melted between 323 and 344°C. The thin film melted between 368 and 394°C.

The factors leading to high-melting-point polymers were gradually being understood. Because we could extract 80% of the starting material from treated polymer, it was indicated that the evaporation phenomenon was of considerable importance.

The fact that thin-film material melted higher than the thick-film material demonstrated the importance of film thickness. It also resulted in an experiment in which the material was reacted in a pure, moist, flowing oxygen stream. The experiment showed that pure oxygen had no effect.

Throughout all the experiments the catalyst (tin octoate) was the only ingredient that had not been varied. It was decided to run a series of experiments in order to compare the efficacy of various tin catalyst compounds.

A solution of 5 grams of RMD polymer with the required amount of ethyl silicate was dissolved in 30 cc of dichloromethane and divided into six parts. One drop of the following catalysts or mixtures of catalysts was added: (1) Nuocure 28, (2) Thermolite, (3) T-9, (4) Nuocure 28 plus Thermolite mixture, (5) Nuocure 28 plus T-9 mixture, and (6) Nuocure T-9, and Thermolite mixture. After heat processing there was no appreciable difference in the melting points.

The final parameter was explored in a series of experiments in which the ethyl silicate was employed in three- to four-fold excess, compared to mixtures with no catalyst at all. Two grams of RMD polymer were dissolved in dichloromethane with three times the required amount of ethyl silicate. This solution was divided into two equal parts and one drop of Nuocure 28 catalyst was added to one dish; at the same time a similar mixture containing four times the requisite amount of ethyl silicate was halved and one drop of Nuocure 28 catalyst was added to the remaining half.

The results were quite surprising. The dishes containing no catalyst both melted above 400°C, whereas the catalyst containing samples melted at a lower temperature (324 to 345°C for the three-fold ethyl silicate experiment (13-1) and 354 to 390°C for the four-fold ethyl silicate experiment (13-3). The aforementioned material (13-1) was extracted with dichloromethane, yielding 59% of its weight. It then melted at 400°C. The material extracted melted below 100°C. The companion material to 13-1, which contained no catalyst, similarly extracted yielded only 14% of its weight. These and other data are summarized in Table 1.

From the above experiments it would seem that the catalyst has a deleterious effect not only on the melting point but also on the production of useful polymer.

B. Production of Propellant Polymer

The polymer was produced in 50-gram batches by using a three-fold excess of ethyl silicate and no catalyst in shallow aluminum pans. After dissolving 50 grams of RMD in 100 cc dichloromethane overnight, 8 cc (ethyl silicate was dissolved in the solution. The solution was poured into the pans and covered with aluminum foil. A piece of dry ice was placed on the foil to allow the dichloromethane to reflux for a time, so that all the ingredients reached 80°C. The foil was removed after 10 or 15 min. Then the normal heat processing took

Table 1

CROSS-LINKING STUDY

Run Number	Amount of $(EtO)_4$ x 5%	Catalyst	Melting Point °C	Remarks
C15555-8	2	Nuocure 28	323-344 388-394	Thick Film Thin Film
C15555-9	2	Nuocure 28 Benzolyl Peroxide	374-380	
C15555-10-1	1	Nuocure 28	364-378	
-10-2	1	T-9	373-385	
-10-3	1	Nuocure 28 + thermolite	362-372	
-10-4	1		364-369	
-10-5	1	Nuocure + T9	370-385	
-10-6	1	Nuocure + T9 + thermolite	368-378	
C15555-11-0	1	None	368-380	Done in flowing oxygen + moisture
-11-1	1	Nuocure	364-370	
-11-2	1	T9 + thermolite	370-380	
C15555-13-1	3	Nuocure 28	325-345	
-13-2	3	None	>400	
-13-3	4	Nuocure 28	354-385-90	
-13-4	4	None	>400	
-13-1a	3		>400	Extracted with CH_2Cl_2
-13-2a	3			

place, 48 hr at 80°C and 48 hr at 150°C. The product was broken up and extracted for 40 to 48 hr. The yield varied from 30 to 38 grams per batch.

The material recovered from the extraction was reprocessed in the same way. The yield of material was considerably less. From 100 grams of recovered polymer 26 grams of polymer melting above 400°C was obtained. This material was different from the original batches in that it was nonsticky and quite easy to grind. From 72 grams of twice recovered material 6 grams of polymeric material melting above 400°C was recovered.

The decline in attainment of polymers melting above 400°C from recovered RMD polymer leads to the conclusion that fractionation from high- to low-molecular-weight material is occurring. We have no firm evidence for our suspicion, but the 400°C polymer might be a combination of cross-linked clathrate polymer.

C. Fabrication of Propellant Grains

The propellant grains prepared on this program were made from a stoichiometric mixture of vanadium pentoxide and aluminum as the metal-metal oxide component. The RMD polymer content was 20% of this weight. A weighed amount of this granular mixture was poured into a cylindrical mold (1/2-in. or 1-1/8-in. diameter) and squeezed to the proper compaction pressure (20,800 psi). The mold was lubricated before each pressing operation with a silicone spray-mold release material. When the compaction pressure was reached, constant pressure was maintained for 1 min before the pressure was released. The compacted pellet was removed from the mold. Propellant grains totaling 2 lb were fabricated in this manner. The ingredients for preparing an additional 1-1/2 lb of propellant were furnished in unmixed granular form, as required under the terms of this contract.

The following materials were used in preparing the propellant grains:

Vanadium pentoxide - Matheson Coleman and Bell,
CB 1066 VX 38
99.5% powder, used as received.

Tungstic anhydride - Fisher Scientific Company
Catalog No. A-325
Tungstic anhydride -
purified, used as received.

Aluminum metal - Allied Chemical-Baker & Adams
aluminum metal dust, Code 1220
used as received.

Mold Release - "No Stick"
Ellen Products Company, Inc.
Stony Point, New York

D. Closed Bomb Measurements

The impetus of various metal-metal oxide mixtures with and without the polymer was measured in a closed bomb. The bomb design was patterned after one which had been devised on a program to develop improved closed bomb testing equipment.[1]

The equation of state of propellant gases contained in a closed vessel can be written[2]

$$P\ (V_0 + \frac{C}{\rho} + C\eta) = C\frac{R}{M}T \tag{1}$$

where

P is the partial pressure of the propellant gases

V is the initial volume available to the propellant gases at ignition

C is the mass of the propellant gases

ρ is the density of the solid propellant

η is the covolume of the propellant gases

R is the gas constant per mole

T is the gas temperature

M is the average molecular weight of the propellant gases.

The impetus (force constant) is defined as

$$F + \frac{R\ T_v}{M} \tag{2}$$

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[1] "Design of Closed Bomb Vessel and Recorder," Final Engineering Report, Sun 270-41, Sunflower Ordnance Works, Hercules Powder Company, March 31, 1961.

[2] Massey, J. M., Jr., "Measurement of Impetus Covolume and Burning Rate of Solid Propellants," NWL Report No. 1872, July 31, 1963.

where T_v is the temperature of the uncooled reaction products of the propellant, also known as the adiabatic constant-volume flame temperature. A simplified form of the above definition is

$$F = \frac{P\ (V - b)}{C} \qquad (3)$$

where V is the volume of the closed bomb

b is a covolume approximation obtained by division of the propellant weight by its density

C is the mass of the original propellant.

The data acquired by using the closed bomb are given in Table 2. The bomb was fitted with a three-way high-pressure valve to permit sampling of the combustion products. Graphite liners were used in the bomb to facilitate changes in the bomb volume and to protect the internal surfaces from the intense heat generated during combustion. The force constant obtained from these data are obviously quite low and require further elucidation.

It should be noted that calculation of impetus assumes thatthe propellant gases be uncooled at the time of measurement of maximum pressure. In Massey's evaluation[2] he was faced with the problem of either determining or negating the heat energy lost by the propellant gases, E_h.

Since no direct accurate method of determining E_h exists, he chose to grind his propellants into granules that would pass a 30-mesh sieve, thus reducing the burning time to less than

Table 2

CLOSED BOMB MEASUREMENTS

System	% Polymer	Weight of Pellet, g	% of Theoretical Density	b Covolume, in³	V Bomb Volume, in³	P_{max}, psig	Impetus, ft-lb/lb	$T_{P_{max}}$, msec	Pellet Compaction Pressure, psi	Polymer Form	Burning Rate, in/sec
[illegible] Al · WO$_3$	10	4.4[illegible]	47	0.04[illegible]	2.6246	[illegible]	2,900	500	15,300	Powder	1.0
		4.4[illegible]	47	0.048[illegible]	[illegible]	[illegible]	3,300	460	15,300	Powder	1.1
		[illegible]	47	[illegible]	[illegible]	145	5,300	[illegible]	15,300	Powder	0.7
		4.4[illegible]	40	0.048[illegible]	0.9500	[illegible]	1,500	200	36,800	Granular	2.5
		4.[illegible]	47	0.04[illegible]	[illegible]	173	5,200	175	36,800	Granular	2.9
[illegible] Al · WO$_3$	10	4.44	4	0.048[illegible]	2.6246	155	3,400	225	36,800	Granular	2.2
[illegible] Al · V$_2$O$_5$	20	[illegible]	60	0.06[illegible]	[illegible]	195	2,300	4500	36,800	Powder	0.11
		2.54	40	[illegible]	0.9500	204	2,400	2500	4,800	Powder	0.2[illegible]
		[illegible]	30	0.01778	[illegible]	75	1,500	2000	0	Powder	0.25
		[illegible]	55	0.062[illegible]	0.9500	181	2,200	2300	20,800	Granular	0.22
		[illegible]4	70	0.02466	0.9500	82	2,600	2200	68,800	Powder	0.23
		2.64	55	0.06345	2.6246	195	6,700	650	20,800	Granular	0.77
[illegible] Al · V$_2$O$_5$	20	2.64	55	0.0[illegible]	1.6246	177	8,300	900	20,800	Granular	0.56
[illegible] Al · V$_2$O$_5$	27.5	3.11	55	0.07407	0.9500	173	1,800	2200	20,800	Granular	0.27
M1[illegible]	-	0.4030		0.02635	2.6246	110	26,800	450	-	-	
M1[illegible]	-	0.4028		0.02635	2.6246	115	28,000	450	-	-	
Black powder	-	0.4964		0.01307	2.6246	200	40,700	50	-	-	
Black powder	-	0.4860		0.01306	2.6246	193	39,300	50	-	-	

10 msec. The measured pressure-time curve was then extrapolated from the pressures just behind P_{max} to give a pressure at zero time. The pressure was termed P'_{max}.

The characteristic reaction time of a metal-metal oxide system is intrinsically much longer than a typical gun system propellant. For example, an aluminum-tungstic oxide system containing 10% polymer (in a fine powder form) has a burning rate of 0.7 to 1.2 in./sec, depending upon the amount of compaction pressure used to form the pellet. The fastest rate is in a finely powdered form, all of which would pass a 100-mesh sieve. The burning rate of this system can be increased by selective granulation of the polymer. This is demonstrated by the fact that selectively screened particles of polymer, which would pass a 14-mesh but were retained on a 20-mesh screen, when used to comprise the 10% portion of the above propellant, demonstrated burning rates up to 2.9 in./sec, even when compacted into a pellet form.

The same effect is noted with the vanadium pentoxide-aluminum system. This system, however, has a much slower burning rate. The typical rates for a formulation consisting of 20% polymer in the vanadium pentoxide-aluminum matrix are 0.1 to 0.25 in./sec, depending upon the compaction pressure with the polymer in a finely ground state (pass 230-mesh sieve). This burning rate is accelerated to the range of 0.22 to 0.77

in. per sec, at a polymer percentage of 27.5, if the polymer is in the granular form within the pelletized metal-metal oxide systems.

The above examples show that obtaining burning rates of less than 10 msec is not feasible with either of the metal-metal oxide systems under discussion. Thus the negation of E_h from consideration is also not feasible. An attempt to approximate the effect of E_h was made by burning M-17 propellant in the closed bomb at a prolonged burning time. This was accomplished by using a 1/2-in. diameter wafer of seven perf, M-17, weighing 0.4 grams. The composition of the M-17 propellant, from specification MIL-P-688A, is:

Nitrocellulose	22.00%
Nitrogen	13.15
Nitroglycerin	21.50
Nitroguanidine	54.70
Ethyl Centralite	1.50
Graphite (glaze added)	0.10
Cryolite	0.30
Ethyl Alcohol (residual)	0.30

The following are the calculated thermochemical values.

Isochloric flame temperature, °K	3,017
Force, ft-lb/lb	364,000
Heat of explosion, cal/gm	962

Covolume, in.^{3}/lb	29.50
Specific gravity	1.67

When the impetus (force) was calculated from the data obtained from burning the wafer form M-17, an average of 27,400 ft-lb/lb was obtained. This figure is only 7.5% of the reported impetus. Duplicate results were obtained with less than 5% maximum deviation.

If we then assume that a calibration factor of 7.5% can be applied to a propellant burning over a relatively long period of time (0.45 sec in the case of M-17) and apply this factor to the vanadium pentoxide system containing 20% granular polymer, we obtain

$$\frac{6{,}700 \text{ ft-lb/lb}}{0.075} = 89{,}400 \text{ ft-lb/lb}$$

It should be noted:

(a) the burning time of the vanadium pentoxide system was 0.65 sec, as compared with M-17's 0.45 sec.

(b) The products, as well as the mechanism of combustion of the two compared systems, are very different.

Using the same reasoning with the 10% polymer in the tungstic oxide system:

$$\frac{3{,}300 \text{ ft-lb/lb}}{0.075} = 44{,}000 \text{ ft-lb/lb.}$$

Extrapolating this information to a 27.5% polymeric material would yield an impetus of 123,000 ft-lb/lb.

III. METAL-METAL FLUORIDE STUDIES

A. Experimental Work

The main objective of this part of the program was the determination of the amount of water required to ignite a boron-silver fluoride mixture, so that the maximum amount of boron trifluoride gas would be produced. The complicating factor is that when BF_3 is produced, it is hydrolyzed by any water remaining in the vicinity of the reaction. When a drop of water was placed on a small sample of $B-AgF_2$ in air, the sample always ignited. Further experiments of this type have shown that ignition occurs with distilled water or sea water, and flow experiments have shown that ignition can be accomplished by passing water vapor over the samples. Thermal ignition can be carried out by heating samples open to the atmosphere, but much higher temperatures are required if the samples are heated in vacuo. Other experiments have shown that ignition can even occur under water.

Most of the ignition studies were conducted in a closed vessel. A measured amount of water was added to a sample in an evacuated chamber. The gases formed could be measured and analyzed if desired. The results of most of these experiments are shown in Table 3.

In an earlier series of experiments a Pyrex vessel was used to observe the reaction. In nearly all cases, when water

Table 3

ADDITION OF WATER TO BORON-SILVER FLUORIDE MIXTURES IN CLOSED VESSEL

Run No.	Sample Weight, g	H_2O Added, cc	Volume of Gas (STP), cc	Gas Per Gram of Sample, cc	H_2O Per Gram of Sample, cc
1	0.85	0.92	8.6	1.0	1.1
2	0.40	0.28	0.5	1.2	0.7
3	0.80	0.40	6.1	7.6	0.5
4	0.80	0.56	4.9	6.1	0.7
5	0.70	0.85	2.4	3.4	1.2
6	0.70	0.93	2.4	3.4	1.3
7	0.70	1.00	2.4	3.4	1.4
8	1.05	0.88	11.0	10.5	0.8
9	1.10	0.55	12.3	11.2	0.5
10	1.35	0.45	16.0	11.8	0.3
11	2.10	0.57	19.6	9.3	0.3
12	2.40	0.32	8.6	3.6	0.1
13	2.80	0.63	22.1	7.9	0.2
14	2.25	0.77	28.3	12.6	0.3

Note: If only oxygen is found,
$AgF_2 + 1/2\ H_2O \longrightarrow HF + AgF + 1/4\ O_2$;
38 cc per gram of sample, 100% hydrolysis.

If only BF_3 is found,
$2/3\ B + AgF_2 \longrightarrow 2/3\ BF_3 + Ag$;
95 cc per gram of sample.

Gas is not hydrolyzed by adding excess H_2O; metal container is etched after reaction.

was added, ignition occurred, as evidenced by flashing and burning. In one case the reaction was vigorous enough to shatter the vessel.

In all the later experiments a stainless steel vessel was used. The main reaction that occurs when H_2O just touches B-AgF_2 is the hydrolysis of AgF_2:

$$AgF_2(S) + 1/2\ H_2O(L) \longrightarrow AgF(S) + HF(g)\ 1/4\ O_2(g) \qquad (4)$$

According to Equation4, 38 cc of oxygen should be produced for each gram of AgF_2 under standard conditions. It is believed that the heat produced by hydrolysis causes the boron to reduce AgF_2 and AgF to metallic silver. If all the boron present reacts to form BF_3 gas, 95 cc of BF_3 per gram of mixture should be produced under standard conditions. Note that only 0.06 cc of H_2 per gram of AgF_2 is required for complete hydrolysis.

Table 3 shows that in the case of run 14, when 0.3 cc of H_2O per gram was used, the maximum amount of gas per gram of sample was 12.6 cc. In all cases, more than 0.06 cc of H_2O per gram of mixture was used. In this series of experiments the gas produced was not hydrolyzed by the addition of water after the reaction was complete.

This fact and a material balance analysis lead to the conclusion that the gas formed was oxygen. Examination of the corrosion inside the vessel showed the presence of HF also. When the sample size was more than 2.0 grams, the reaction vessel was warm to the touch after the reaction was initiated. After the reaction was complete and the vessel was opened, no water could be observed, and a black deposit was present over the entire inside surface of the vessel.

B. Results

An analysis of the data in Table 3 allows us to draw several conclusions. First, in all cases the AgF_2 present was not completely hydrolyzed, even though sufficient water was added. Second, the fact that metallic silver was formed shows that ignition occurred. Third, this fact forces the conclusion that BF_3 gas was formed before all the water reacted, and the BF_3 gas was hydrolyzed to produce boron oxides and HF.

The most reasonable explanation of this situation is that AgF_2 and BF_3 compete to react with the available water. This competition is possible if some of the water vaporizes and is available in the vapor to react with the BF_3 gas. Thus, if BF_3 takes away the water required for hydrolysis, AgF_2 is not completely hydrolyzed.

In order to reduce the hydrolysis of BF_3, the sample size should be increased, and the vaporization of water should be stopped. This could be accomplished by using a larger reaction vessel with an atmosphere of cover gas or air. After the reaction is completed, the gas could be analyzed for BF_3 and oxygen with a mass spectrometer.

IV. CONCLUSIONS

The program reached a successful conclusion with the attainment of propellant grains capable of withstanding an 800°F environment for 1 hr and performing as required from computed impetus values. Conventional closed bomb evaluation of these typical slow-burning, high-temperature propellants was not applicable to these systems. This is due to the fact that the calculation of impetus assumes that the propellant gases are uncooled at the time of measurement of maximum pressure. By grinding a conventional propellant into small granules, the burn time is reduced to a value below 10 msec. The result is that the amount of heat lost to the propellant surroundings is minimized and not considered in the computation.

The characteristic reaction time of the metal-metal oxide-polymer propellant is, however, intrinsically much longer than a conventional propellant, and the heat energy lost by the propellant gases cannot be neglected. Faced with this fact, we burned a gun propellant of known impetus in a closed bomb at a prolonged rate. Calculation of impetus from these data resulted in a value of only 7.5% of the known impetus. These results again demonstrate the need for a more sophisticated method for evaluating these slow-burning propellants. Experiments have shown that the propellant contains enough gas at the reaction temperature to furnish an impetus of 100,000 ft-lb/lb.

The results of the B-AgF_2 study have shown the feasibility of optimizing the system and have further elucidated the reaction mechanism. Investigation has shown that in all cases the AgF_2 was not completely hydrolyzed, even though sufficient water was added. The fact that metallic silver was formed indicated that ignition occurred. These facts indicate that BF_3 was formed before all of the water reacted and BF_3 was hydrolyzed to produce boron oxides and HF.