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METAL-OXIDANT IGNITER MATERIALS

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ABSTRACT

An investigation of the physical and chemical factors affecting propellant ignition is being conducted with the ultimate objective of producing information useful in the design and development of ignition systems for solid-propellant rockets. This investigation has largely been concerned with a study of the materials used to ignite rocket motors, that is, black powder and metal-oxidant formulations. This paper presents the results of calculations made on five metal fuels with conventional oxidizers to determine, under adiabatic conditions, what maximum flame temperatures could be reached and what the physical states of the products might be. Results of experimental characterization studies covered in this paper include determinations of heats of explosion, gas volumes produced, and the effectiveness of various igniter compositions in igniting a propellant specimen in a laboratory ignitibility test. In addition, unusual ignitibility effectiveness of fuel-rich magnesium—potassium nitrate mixtures is discussed in terms of a secondary ignition effect of igniter combustion products, and the results of a limited investigation of factors affecting the combustion rate of elemental boron are given.

INTRODUCTION

The use of metal-oxidant materials to ignite solid-propellant rockets has become an accepted procedure where black powder or resin-oxidizer compositions are either inadequate to transfer ignition to a propellant grain satisfactorily or produce undesirable pressure peaks in the process. Because of the high heats of combustion of the metallic components and thermal stability of the oxides formed, metal-oxidant igniters develop high flame temperatures. In addition to the usual modes of heat transfer to the propellant afforded by black powder, namely, convection and radiation, the metal-fuel igniter may efficiently transfer heat by (1) condensation of vapors on the surface liberating the heats of vaporization and fusion, (2) impingement of solid particles on the surface, and (3) improved radiation due to high emissivity of the particles. By using these more powerful modes of heat transfer and by

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2. The attached technical paper, "Metal-Oxidant Igniter Materials," by Samuel Zeman, is included in the <u>2nd JANNAF Ignition Symposium, Volume I</u>, 1956, which is not available at this Command. It is suggested that a copy of the entire symposium be obtained from the Chemical Propulsion Information Agency, Johns Hopkins University, Applied Physics Laboratory, 8621 Georgia Avenue, Silver Spring, Maryland 20910.

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for F. W. JAMES
Director, Propulsion Directorate
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propriately varying the composition of the igniter, it is possible to ect much better control over the heat-transfer rate than is possible th black powder alone.

In this paper, estimates are given of the maximum flame mperatures that can be reached by various binary metal-oxidant xtures under adiabatic conditions, and the experimental performance aracteristics of many of these compositions in small-scale tests have been determined.

ADIABATIC FLAME TEMPERATURE CALCULATIONS

The maximum flame temperature of an igniter reaction serves artly to indicate the rate of heat transfer from the igniter products to the propellant, a factor of importance in determining propellant ignition effectiveness of various metal-oxidant mixtures. It is true that the attainment of high temperatures is a necessary function of igniters, but practical considerations in many cases limit the design of igniter compositions and configurations to temperature levels consistent with propellant and rocket system requirements. In such cases the attainment of maximum flame temperatures that might give rise to ssure peaks and shock transients is undesirable, and of greater portance is more efficient utilization of igniter combustion products transferring heat to the propellant surface. The evolution of metallic oxides having high latent heats of fusion and vaporization and high heat capacities at relatively high temperatures is in many cases more desirable in ignition than achievement of high flame temperatures. Nevertheless, it is of interest to know the limiting values of adiabatic flame temperatures produced by various metal-oxidant mixtures.

The chemical reactions chosen for the production of high temperatures must fulfill several simultaneous requirements:) the reaction must be rapid, (2) the reaction must produce a high othermic heat of reaction, (3) the products must have great thermal bility, and (4) the heat capacities of the products should be low. e requirements of rapid reaction and high exothermicity, although portant, are generally recognized, whereas the importance of ermal stability is frequently overlooked. The role played by ssociation of the reaction products in limiting attainment of very gh temperatures can be illustrated by the combustion of carbon in ygen. The theoretical temperature attainable in this case is about 0,000°C. Actually, however, owing to the dissociation of the reaction products, 2500°C represents about the maximum possible temperature attainable in this combustion. These same considerations apply in the combustion of metals and emphasize the importance of reaction product stability in producing high temperatures. Indeed, the high temperatures capable of being produced by the combustion of metals is due, for the most part, to the high thermal stability of certain metallic oxides.[1]

Whereas the adiabatic flame temperatures of propellants may be accurately calculated, similar calculations for inorganic explosives or pyrotechnics yield results that can only be accepted as approximations of the true values. This is because parameters such as heats of reaction, mechanism and extent of reaction, heat capacities at high temperatures of the products, the nature and energies involved in phase transitions, and dissociation of the various products are not accurately known.

The method used for calculating maximum flame temperatures of 15 igniter reactions in this paper is similar to that used by Levy[2] for several primer mixtures, but the calculations include corrections for dissociation of certain products because of the high temperatures involved. To carry out the required calculations, it was necessary to extrapolate the available specific-heat data to very high temperatures, to use data for analogous compounds in a few instances, and to make logical estimates of phase-transition heats and heat capacities in several cases.

The flame temperatures were first calculated assuming no dissociation of the products. The temperatures calculated by this method were all very high, and subsequent calculations were made including corrections for dissociation. The calculations are based on the igniter mixtures reacting instantaneously at 300°K according to the assumed mechanisms and the resulting products then being heated to the adiabatic flame temperature. To estimate the flame temperature, the heat contents of the products of reaction plus the heat absorbed in phase changes were set equal to the heat of reaction, namely

$$\Delta H_1 = \left[\int_{300}^{T_M} C_{p_s}\, dt + \Delta H_f + \int_{T_M}^{T_V} C_{p_l}\, dt + \Delta H_V + \int_{T_V}^{T_F} C_{p_g}\, dt + \Delta H_d \right]_A$$

$$+ \left[\qquad \right]_B + \left[\qquad \right]_C + \dots$$

where ΔH_1 = heat of reaction at 298°K

T_M = melting point of each product

T_V = boiling point of each product

T_F = flame temperature

C_{p_s}, C_{p_l}, C_{p_g} = molar heat capacities of each product in solid, liquid, and gaseous states, respectively

ΔH_f, ΔH_V, ΔH_d = heats of fusion, vaporization, and dissociation, respectively

A, B, C, etc. = individual reaction products

The reactions were assumed to proceed in the following manner, the extent of reaction being dependent on temperature and quantity of energy available:

$$KClO_4(s) \rightarrow KCl(s) \rightarrow KCl(l) \rightarrow KCl(g) \rightarrow K(g) + Cl(g)$$

$$Ba(NO_3)_2(s) \rightarrow BaO(s) \rightarrow BaO(l) \rightarrow BaO(g) \rightarrow Ba(g) + O(g)$$

$$KNO_3(s) \rightarrow K_2O(s) \rightarrow K(g) + O(g)$$

$$Mg(s) \rightarrow MgO(s) \rightarrow MgO(l) \rightarrow MgO(g)$$

$$Al(s) \rightarrow Al_2O_3(s) \rightarrow Al_2O_3(l) \rightarrow AlO(g) + O(g)$$

$$Ti(s) \rightarrow Ti_2O_3(s) \rightarrow Ti_2O_3(l) \rightarrow TiO(g) + TiO_2(g)$$

$$Zr(s) \rightarrow ZrO_2(s) \rightarrow ZrO_2(l) \rightarrow ZrO_2(g)$$

$$B(s) \rightarrow B_2O_3(s) \rightarrow B_2O_3(l) \rightarrow B_2O_3(g) \rightarrow BO(g) + O(g)$$

Table I gives the thermochemical constants for the metals, oxidizers, and their reaction products. It is seen from Table I that all the metallic oxides except B_2O_3 have relatively high heats of fusion at high temperatures, which contributes to their effectiveness as heat-transfer media in ignition systems. Heats of vaporization of the metallic oxides are very high, and in all cases except for boron, the maximum flame temperatures that can be attained are limited by the vaporization temperatures. Indications are that ZrO_2, MgO, and B_2O_3

survive the vaporization process as gaseous species, whereas Al_2O_3 and Ti_2O_3 dissociate on vaporization at high temperatures into simpler molecules or atoms.[8, 14-17] Table I indicates that the thermal stability of gaseous oxidizer decomposition products decreases in the order BaO, KCl, K_2O, with K_2O being almost nonexistent as a gas and BaO having the lowest tendency to dissociate.[8, 11, 12, 18]

Table II gives the heat-capacity data for the assumed products of igniter reactions; as can be seen, data for many of these simple compounds at low as well as high temperatures are not available in the literature. As with latent heats of phase changes, the heat capacities of the metallic oxides are high, particularly in the liquid states. It should be noted that B_2O_3, which has a heat of fusion of only 5.5 kcal/mole, may exist as a liquid from 723 to 2500°K, with an average heat capacity of 30.5 cal/mole/°K, and may transfer 54.9 kcal/mole as it cools from its boiling point to the fusion temperature.

The following sample calculation for the reaction between zirconium and potassium perchlorate will illustrate the methods employed in obtaining the results shown in Table III.

Composition:

56.84% Zirconium
43.16% Potassium perchlorate

Reaction: in moles or gram atoms per 100 grams

$$0.6231\,Zr(s) + 0.3115\,KClO_4(s) \rightarrow 0.6231\,ZrO_2(s) + 0.3115\,KCl(s)$$

The heat of reaction, in kilocalories per 100 grams, is therefore

$$H\ \text{reaction} = H\ \text{products} - H\ \text{reactants}$$

$$\Delta H_1 = \overset{ZrO_2}{(0.6231)(258.4)} + \overset{KCl}{(0.3115)(104.3)} - \overset{KClO_4}{(0.3115)(112.71)} - \overset{Zr}{(0.6231)(0)}$$

$$\Delta H_1 = 158.39\ \text{kcal}/100\ \text{grams}$$

With the knowledge that 158.39 kcal is evolved from the reaction, a flame temperature is assumed and a determination is made of the heat required to raise the products to the assumed temperature. The energy required to heat the products to the assumed temperature may then be plotted graphically versus the assumed temperature. By graphically interpolating, the adiabatic flame temperature is found.

However, for the example given when a flame temperature is assumed of 4600°K, the approximate boiling point of ZrO_2, sufficient energy is found to be available from the reaction to vaporize only a portion of the ZrO_2. Moreover, a study of the literature indicates that KCl(g) dissociates at temperatures below 3000°K. A separate calculation is made to determine the extent of dissociation of KCl(g) into atoms at various temperatures. The product of heat of dissociation and fraction dissociated is then treated in the same manner as latent heats. The products of the overall reaction are then represented as absorbing heat through their various phase changes and by integration of the heat-capacity equations over the temperature range. The heat absorbed by dissociation of KCl at the flame temperature is added to the latent heats and the heat absorption due to heat capacities and again equated graphically to the heat of reaction, ΔH_1. If this equality is not obtained, a new temperature higher, or lower, is assumed, and the calculation is repeated until a heat balance is obtained. In the example given, the flame temperature is limited by the boiling point of ZrO_2, and after other assignments have been made, any excess energy available is shown to be absorbed in vaporizing the proportionate fraction of $ZrO_2(l)$.

The extent of dissociation of gases such as KCl at high temperatures was determined by solving for the equilibrium constant, K, from the relation

$$\log K = \frac{-\Delta F}{2.3RT}$$

The change in free energy, ΔF, for the dissociation reactions was determined from the derived equation

$$\Delta F = \Delta H_0 - \Delta C_p T 2.3 \log T + [6.7 \Delta C_p - \Delta S_{298}]T$$

for the reaction

where $\Delta H_0 = \Delta H_{298} - 298 \Delta C_p$

$\Delta H_{298} = \Delta H_{298}$ (products) $- \Delta H_{298}$ (reactants)

$\Delta C_p = C_p$ (products) $- C_p$ (reactants)

$\Delta S_{298} = S$ (products) $- S$ (reactants)

(C_p and S are heat capacity and entropy, respectively.)

Using the latent heats and other thermodynamic data from Table I and integration of the heat-capacity equations from Table II, the following equations represent the assignment of heats absorbed in raising the products to the limiting flame temperature, which is 4600°K:

$\Delta H_2 = ZrO_2(s) \rightarrow ZrO_2(l) = (0.6231)(20.8) =$ 12.96 kcal

$\Delta H_3 = KCl(s) \rightarrow KCl(l) = (0.3115)(6.1) =$ 1.90

$\Delta H_4 = KCl(l) \rightarrow KCl(g) = (0.3115)(38.8) =$ 12.09

(It is found by separate calculation that KCl(g) is 74% dissociated at 4600°K.)

$\Delta H_5 = KCl(g) \rightarrow K(g) + Cl(g) = (0.3115)(105)(0.74) =$ 24.20

The following heat-capacity equations show the product of moles, average heat capacity found by integrating equations in Table II, and temperature difference.

$C_1 = ZrO_2(s)(300° - 2988°) = (0.6231)(29.13)(2688)(10^{-3}) =$ 48.79

$C_2 = ZrO_2(l)(2988° - 4600°) = (0.6231)(35)(1612)(10^{-3}) =$ 35.16

$C_3 = KCl(s)(300° - 1043°) = (0.3115)(13.24)(743)(10^{-3}) =$ 3.06

$C_4 = KCl(l)(1043° - 1680°) = (0.3115)(16)(637)(10^{-3}) =$ 3.17

$C_5 = KCl(g)(1680° - 4600°) = (0.3115)(8.94)(2920)(10^{-3}) =$ 8.12

$$\sum_{2}^{5} \Delta H + \sum_{1}^{5} C = \quad 149.45 \text{ kcal}$$

$$\Delta H_1 - \left[\sum_{2}^{5} \Delta H + \sum_{1}^{5} C \right] = 158.39 - 149.45 = \Delta H_6$$

$\Delta H_6 =$ heat absorbed in vaporizing fraction of $ZrO_2(l) =$ 8.94 kcal

$$\frac{8.94}{(0.6231)(100)} = 14.34\% \; ZrO_2(l) \rightarrow ZrO_2(g)$$

158.39 kcal

Maximum adiabatic flame temperature limited by the boiling point of ZrO_2 is 4600°K.

Table III gives the calculated heats of reaction and maximum adiabatic flame temperatures for the compositions listed, and Table IV gives the theoretical reaction products existing at the maximum flame temperatures. Whereas most of the products of these metal-oxidant mixtures are shown to vaporize at the flame temperature, this is not the case with the zirconium mixtures. In Table IV, zirconium dioxide is shown to exist in the molten state at the calculated flame temperatures. The thermal stability and extremely high boiling point of ZrO_2 make possible the attainment of the highest calculated flame temperatures of the group by Zr-$KClO_4$ and Zr-$Ba(NO_3)_2$ mixtures.

All the mixtures of aluminum have heats of reaction high enough to bring the Al_2O_3 to its boiling point and to vaporize a portion of the oxide. The high heat of reaction of the Al-$KClO_4$ mixture leads to considerable dissociation of the products and the formation of a large quantity of condensible gases. In igniters, heavy confinement or extremely rapid reaction of this mixture leads to very high pressure peaks.

Heats of reaction of the magnesium mixtures are sufficient to raise the MgO to its boiling point and to vaporize a portion of it. The maximum flame temperatures of the magnesium mixtures, as with the aluminum and titanium mixtures, are determined by the boiling point of the metallic oxide product.

Because of the low boiling point of B_2O_3, the maximum flame temperatures of the boron mixtures are indicated to be somewhat below those of the other mixtures. The low boiling point of B_2O_3 also leads to the formation of large quantities of condensible gas at the flame temperature. It should be noted that the assumed mechanism for the reaction between boron and potassium nitrate is incorrect since heat-of-reaction measurements give higher than theoretical values at oxidizer loadings far below those used in these calculations. It has been postulated that the reaction of B-KNO_3 leads to the formation of KBO_2, potassium metaborate, as well as B_2O_3;[19] however, this was not considered in the calculations since thermochemical data on KBO_2 are not available.

As stated previously, the maximum flame temperatures that can be reached by the metal-oxidant compositions are in general limited to the temperature of vaporization of the metallic oxide. The quantity of condensible gases formed varies with each composition, but boron, magnesium, and aluminum fuels with $KClO_4$ or KNO_3 oxidizers have a greater tendency to vaporize the combustion products because of dissociation and high heats of reaction.

IGNITIBILITY TESTS

Initial consideration of an approach to study performance characteristics of experimental igniter materials indicated that studies of propellant ignitibility[20-23] were of sufficient interest to warrant a refinement of technique in order to evaluate igniter materials further for use in rocket igniters. To this end, equipment and techniques were developed to yield data showing the relative quantity of igniter material required to ignite a propellant sample and the action time of the igniter from photocell measurements of the luminous intensity as a function of time in a closed bomb.

Tests with black powder and JPN propellant indicated that ignition was achieved in as short a time as 25 msec, but since marginal quantities of igniter materials were being used, the ignition times varied from 25 msec up to several seconds. For experimental convenience, ignition of the propellant sample was recorded as having occurred when sufficient radiation was emitted for detection of its combustion by an infrared sensitive photocell within 1 sec after initiation of the igniter material. Fizz burning (nonluminous) of the propellant and hangfires of greater duration than 1 sec were classed as nonignitions.

APPARATUS AND PROCEDURE

The closed-bomb test chamber used in these experiments is shown in Fig. 1. It is fitted with five quartz observation ports for light transmission. The chamber has internal dimensions of 1 by 6 in. with a free volume of 61 cc. A small sample of propellant ($^1/_2$-inch OD by $^1/_8$-inch thick) is mounted in the receptacle approximately $3^3/_5$ in. above the base of the crucible containing igniter powder. Ignition of the powder is accomplished by passing current through a short length of wire embedded in the powder. Figure 2A shows a block diagram of the instrumentation used to follow the ignition process with photocells, and Fig. 2B is a block diagram of the apparatus. In effect the photocell nearest the igniter sample is used to observe the flash from the burning igniter powder, and the other photocells observe the light emission from the propellant when it begins to burn with a luminous flame. The output from the photocells is fed to a Dumont Type 322 cathode-ray oscillograph, a time base is provided by a Tektronix Type 180 Time Mark Generator, and the transient phenomena shown on the screen of the oscillograph are photographed with a Fairchild Oscillo-Record Camera.

For ignitibility tests, a small amount of powder is accurately weighed into the crucible and fired, the resultant ignition or nonignition of the propellant is determined either by observation or by examination of the film record. The statistical method used to determine the ignition probability is given by Churchman.[24] By this method, it is necessary to establish from past experience or intuitively an estimated range of charge weights required to obtain ignition every time or not at all. A predetermined number of tests, at least five, are made within this range with charge weights varying in equal increments until all the tests at a given charge weight level result in ignition and all tests at some lower charge weight result in nonignition of the propellant sample. Treatment of the data by the Churchman method results in a value for the charge weight required for 50 or 95% probability of ignition.

Heats of explosion were measured in a Parr Oxygen Bomb Calorimeter under 20 atm of helium. The results of some of the heat-of-explosion measurements are plotted in Fig. 3. The relative burning time of each igniter mixture was determined by burning 120-milligram samples in the window bomb with photoelectric instrumentation and measuring the duration of the flash as displayed on the screen of the oscillograph and photographed on 35-mm film.

A description of the materials used in the ignitibility tests is given in Table V. All the igniter mixtures were dry blended manually except those containing zirconium powder, which were mixed wet with benzene.

DISCUSSION OF RESULTS

Initially, propellant ignitibility tests in this program were performed with black powder and JPN propellant. It was found that the moisture content of black powder, within specification limits, and the use of air instead of nitrogen in the closed bomb played relatively minor roles in the overall ignition process. It was also found that the total energy and rate of burning of the igniter powder are significant factors in determining the effectiveness of the powder in igniting a double-base propellant under the conditions of this test. The effect of particle size on the ignitibility results was illustrated by comparing A-5 and A-3 black powder in the closed bomb. Considerably larger quantities of the slower burning A-3 black powder than of the A-5 were required for the same ignition probability. It was found that the effectiveness of black powder in igniting the test propellant could be increased by various additives, which either increased the heat of reaction of the mixture, reacted with the propellant decomposition products, or ejected molten materials that gave up their latent heats as they struck the propellant surface. An increase in effectiveness of 15 to 20% over A-5 black powder was obtained with mixtures of black powder and additives such as lead picrate and potassium dinitroacetonitrile. Since black powder is a relatively poor matrix for additives, emphasis was ected to pyrotechnic materials that evolve greater amounts of energy per unit weight and volume than does black powder.

This work to date has principally involved studies of five metal fuels: magnesium, aluminum, titanium, boron, and zirconium. The principal inorganic oxidizers used were potassium perchlorate, potassium nitrate, barium nitrate, and to some extent sodium nitrate. Magnesium received greatest attention in experimental investigations because it is believed to be representative of pyrotechnic fuels, many of its performance characteristics being typical for the group. Other metals and alloys were used in the investigations, but interest centered around the five metals. Heats of explosion, relative burning rates, ease of ignition, and gas volumes produced were measured experimentally for many of the compositions.

Figure 4A shows a representative intensity-time curve obtained from an ignition test of JPN with black powder, and Fig. 4B shows representative intensity-time curves from several igniter mixtures.

Table VI shows the results of tests with mixtures of magnesium and KNO_3, $KClO_4$, $NaNO_3$, and $Ba(NO_3)_2$ oxidizers. Initial tests performed with several compositions containing magnesium showed that the effectiveness of the powdered mixtures, as determined by the ignitibility tests, was highly dependent on the rate at which they evolved thermal energy. Therefore, an attempt was made to compare the relative effectiveness of these materials when their burning intervals (relative burning times) were more nearly the same. Factorial experiments were performed to determine the effect of particle size of fuel and oxidant in at least two mixture ratios on the burning time of the igniter mixtures. It was found that, when $KClO_4$ was used as the oxidant in the dry powdered mixtures, the shortest burning intervals (fastest burning) were obtained when the fuel was very fine and the perchlorate was coarse in comparison.

In the ignitibility tests, the fast-burning Mg-$KClO_4$ mixtures contained magnesium that would pass a 200-mesh screen and be retained on a 325-mesh screen and coarse perchlorate that would pass a 100-mesh screen and be retained on a 140-mesh screen. For nitrate oxidizers, as would normally be expected, the fastest burning mixtures were those containing finely divided fuel and oxidant. In the ignitibility tests, the magnesium used would pass a 200-mesh screen and be retained on a 325-mesh screen, and the oxidizers, KNO_3, $NaNO_3$, and $Ba(NO_3)_2$, were each sieved to pass a 200-mesh screen and be retained on a 325-mesh screen. Burning times measured for mixtures containing either perchlorate or nitrate oxidizers were thus placed on a comparable basis, as seen in Table VI. The reason for the difference in particle sizes required for rapid reaction of perchlorate versus nitrate oxidizers with magnesium fuel is apparently due in part to a bulk-density effect. It appears that the coating of magnesium powder on potassium perchlorate crystals results in faster burning than when Mg is coated with $KClO_4$ in dry powdered mixtures. Attempts were made to purify the oxidizers, but ignitibility tests and burning-time measurements indicated no significant performance difference between Reagent Grade and recrystallized oxidizers used in the igniter mixtures.

From the data shown in Table VI, it is difficult to draw strong conclusions concerning the effects of heat of explosion, total energy evolved from the igniters, relative burning times, relative rate of heat evolution, or gas volumes on the ignitibility effectiveness of these compositions. None of the compositions gave best performance for their individual group when the mixture ratios were designed to give the highest heats of explosion. Smaller quantities of igniter material were, however, required to ignite the double-base JPN test propellant as the Mg-KNO_3 and Mg-$NaNO_3$ compositions became more fuel rich, whereas the best performance from the Mg-$KClO_4$ and Mg-$Ba(NO_3)_2$ mixtures was obtained with the higher oxidizer containing compositions irrespective of heat of explosion. The best Mg-KNO_3 composition, igniter 57, has about 2.4 times the "igniting power" of A-5 black powder under the same conditions. Similarly, igniter 57 with a heat of explosion of about 1300 cal/g has almost twice the "igniting power" of igniter 51 (Mg and $KClO_4$), which has a heat of explosion of 2300 cal/g.

The effect of mixture ratio on the burning time is illustrated in Table VI. For mixtures of Mg and KNO_3, Mg and $Ba(NO_3)_2$, and Mg and $NaNO_3$ as the fuel content increases over the range tested, the relative burning time decreases indicating increasing reaction rate. For the Mg-$KClO_4$ compositions as the fuel content increases, the burning time increases indicating decreasing reaction rate.

The permanent gas volume produced is higher for the nitrate oxidizer mixtures, but since the reaction temperatures are higher for the Mg-$KClO_4$ mixtures, the maximum pressures developed in the closed bomb were higher for the Mg-$KClO_4$ mixtures. The data in

Tables VI and VII showing the measured gas volume produced by several of the mixtures indicates the significant influence of pressure in determining propellant ignitibility under the conditions of this test.

The indication that igniter mixtures containing KNO_3 as oxidizer are more efficient than the hotter mixtures containing $KClO_4$ oxidizer seemed unusual (in spite of the fact that $KClO_4$ contains 46.2% available oxygen and KNO_3 contains only 39.6% based on formation of KCl and K_2O combustion products). Additional investigations were made. It was found that, when Mg-KNO_3 mixtures were burned in the closed bomb in the absence of a propellant sample under helium or nitrogen, the residue from this combustion exploded when contacted by moist air or water. It was also observed that

1. Stoichiometric mixtures of Mg (38%) and KNO_3 (62%) based on formation of MgO and K_2O showed normal behavior in ignitibility tests and did not give products capable of secondary burning when exposed to moist air.

2. As the magnesium content of the binary mixtures was increased successively from 38 to 60%, the quantity of material capable of secondary burning increased.

3. When fuel-rich Mg-KNO_3 mixtures were burned in the presence of the test propellant in the closed-bomb ignitibility apparatus, the secondary burning effect was observable only in those cases where the propellant sample had not shown any tendency to ignite.

4. Since the products capable of secondary burning had spent themselves in every case where propellant ignition occurred, it appeared obvious that reaction occurred between the propellant combustion products and those of the igniter. It is believed that reaction of the igniter combustion products with the initial decomposition products of the propellant at or near the surface of the propellant either liberated sufficient energy to aid in ignition of the propellant or triggered further reaction of the propellant gases themselves.

5. If the secondary combustion reaction were due to "hot particles" or magnesium metal reacting with propellant gases, such effect would have been more pronounced with the hotter Mg-$KClO_4$ mixtures. This was not found.

6. If the secondary reaction were due to formation of Mg_3N_2 and subsequent reaction with propellant, this would have been noted in

the fuel-rich Mg-$KClO_4$ mixtures since the inert gas generally used in the closed bomb is nitrogen.

7. Several tests with Mg and $NaNO_3$ (fuel rich) indicated that a similar effect was produced by this reaction, but the effect was not so pronounced as with KNO_3.

It is postulated that the increased effectiveness of fuel-rich Mg-KNO_3 mixtures as igniters is due to the liberation of free potassium from the igniter combustion products. Because of extreme affinity for oxygen and high thermal stability of the oxide, magnesium in excess at high temperatures combines with the oxygen from dissociating K_2O liberating elemental potassium. Brewer[11, 12] has shown that K_2O as a gaseous species is virtually nonexistent and only Li_2O of the alkali metal oxides may exist as a stable gas. Since the stability of the alkali oxides increases in the order $Li > Na > K > Rb > Cs$, only potassium, rubidium, and cesium oxides would be readily reduced to their elemental form, whereas sodium oxide would be less likely to show this effect and lithium oxide would probably not show this effect at all.

Because such a large increase in ignition performance is shown by this reaction, it is clear that additional work should be done to determine if advantage can be taken of this type of reaction using metals that are more stable to corrosion than magnesium.

Table VII shows the results obtained from ignitibility tests with various igniter mixtures; it is seen that the boron mixtures gave best performance based on the quantity of material required to ignite the test propellant. The B-$KClO_4$ mixtures were almost as effective in igniting the propellant sample as the best magnesium compositions. Burning-time measurements of compositions shown in Table VII, as well as many others not shown, indicate that for mixtures of B and KNO_3, B and $KClO_4$, Ti and $KClO_4$, Zr-Ni and $KClO_4$, and Ti and $Ba(NO_3)_2$ the reaction rate increases as the fuel content is increased past stoichiometric. Burning times measured for compositions containing Al and $KClO_4$ or Al and $Ba(NO_3)_2$ were found to be insensitive to small changes in composition.

Composition 118 in the B-KNO_3 series showed best performance with the highest measured heat of explosion and reaction rate for the group, whereas oxygen-rich composition 121 with the lowest heat of explosion and lowest reaction rate was next best. Of the B-$KClO_4$ igniters, oxygen-rich composition 125 with the lowest heat of explosion and lowest reaction rate was the most efficient in its group. Other mixtures in the B-$KClO_4$ series showed poorer performance as the reaction rate and heat of explosion increased.

The titanium mixtures were found to be the least efficient of those tested. Compositions 104 and 105 with $KClO_4$ oxidizer showed effectiveness only slightly better than black powder, whereas the Ti-$Ba(NO_3)_2$ mixture, composition 106, was found to be less effective than A-5 black powder under the test conditions. It is believed that this is due partly to the mode of burning of these mixtures. All the mixtures tested except the binary titanium-oxidant mixtures formed finely divided amorphous powders as combustion products, which were thoroughly coated on all interior parts of the bomb assembly. The titanium-oxidant mixtures, however, formed a molten mass of residue in the form of slag, which remained in or near the igniter container. The distribution of combustion products from the titanium mixtures in the ignitibility chamber was poor compared with that obtained from the magnesium or boron mixtures.

Compositions containing flake aluminum were difficult to ignite from a hot wire, but ignitibility test data obtained with igniters 85 and 86 showed performance comparable to that obtained with magnesium fuel. Atomized aluminum would not ignite at all from a glowing wire, but it was found that the addition of titanium metal powder to these mixtures resulted in easier ignition and measured heats of explosion approached the theoretical maximum. The formation of a molten glob of residue, as was found with titanium mixtures, was virtually eliminated in mixtures containing aluminum and titanium. Igniter T-1 containing atomized aluminum and titanium fuels, shown in Table VII, gave effective ignition of the propellant and showed a reaction time shorter than that measured for titanium or aluminum compositions individually. Considerable work has been done to exploit the advantages of this fuel combination, and performance was proved in many rocket-motor firings under the most adverse conditions.

Zirconium-nickel alloy (70/30) was found to be the slowest burning fuel tested. Igniter 95 showed only slightly greater ignition effectiveness than that obtained with the titanium mixtures or A-5 black powder.

Igniters containing zirconium metal powder in granular form could not be ignited from a hot wire, and consequently, no measurements were made with these mixtures. Pyrophoric zirconium powder has, however, been used extensively in investigations of fuels for squibs at this laboratory. This powder is manufactured by reduction of powdered ZrO_2 with excess calcium and is sensitive to ignition. Measurements of reaction time with stoichiometric Zr-$Ba(NO_3)_2$ mixtures (Zr approximately 6 μ with Fisher Sub-Sieve Sizer) indicate relative flash duration times less than one-half those of the fastest burning mixtures of boron or magnesium. Squibs containing zirconium fuel have been found to be extremely effective in initiating the most difficultly ignitible pyrotechnics under conditions of low confinement.

BORON-FUEL INVESTIGATION

The commercial preparation of amorphous boron is rather a crude process, and critical performance reproducibility of certain types of igniters containing boron may be difficult to obtain if careful controls are not exercised. In cooperation with the Redstone Division of the Thiokol Chemical Corporation, several parameters relating to the properties of boron for igniters were investigated. It was found at Thiokol that "rolled-tube"-type igniters prepared with certain lots of boron gave excellent performance in overall ignition times of rocket motors fired at low temperatures, whereas other lots gave marginal or extremely poor performance. Chemical analyses by "wet methods" failed to resolve the lot-to-lot performance variations observed. From Table VIII, it is seen that the total boron content of the various lots tested ranged from 65 to over 90%, and particle-size measurements by sub-sieve methods show minor differences.[25]

Attempts were made to characterize elemental boron using spectrographic analysis, X-ray diffraction, and electron microscopy techniques. In addition, it seemed appropriate to subject powdered samples of boron mixed with an oxidant to the closed-bomb combustion test in which the flash intensity is measured as a function of time. Approximately 22 samples of boron from separate lots were tested. The suppliers or manufacturers of the boron tested were Fisher Scientific Company, F. W. Berk & Co., Inc., American Potash & Chemical Corp., Cooper Metallurgical Associates, Arthur S. La Pine & Co., and Metalsalts Corporation.

No correlation with performance of the various samples could be made on the basis of electron microscopy or spectrographic analysis. Examination indicated that the impurities present corresponded to the composition of firebrick. Some correlation was possible, however, from X-ray diffraction patterns. Good correlation was obtained in comparing the results of closed-bomb combustion tests with actual performance of igniters fired in rocket motors at low temperatures.

Twenty-two samples of boron were intimately mixed with potassium perchlorate in the ratio

Boron	20.6%
$KClO_4$	79.4% (100% through 325 mesh)

Aliquot portions of each of the 22 mixtures (120 mg) were burned in the window bomb with photoelectric instrumentation to determine the relative flash intensities, the rate of rise of light intensity, and the flash duration. Marked differences in the intensity-time curves were obtained; in particular, it was found that many of the boron samples burned very rapidly, whereas others showed sluggish reaction. The representative intensity-time curves shown in Fig. 5 indicate the three distinct classifications that were obtained based on flash duration (relative reaction time). Of the 22 samples tested, six were found to react rapidly and give a time-intensity curve similar to that shown by curve A in Fig. 5, six samples gave curves similar to that represented by curve B, and 10 samples were found to be very slow burning giving curves similar to the one represented as C. Curve A has a characteristically high relative intensity, rapid rise rate, and short duration. Curve B has a high relative intensity, medium to rapid rise rate, and a duration of two to three times that of curve A. Curve C has a low relative intensity, low rise rate, and very long duration.

Actual rocket-motor firings at −50°F made by Thiokol indicated that igniters prepared from boron which exhibited rapid reaction in closed-bomb tests, Fig. 5, curve A, gave short, reproducible overall ignition delays, whereas the slow-burning samples of boron, Fig. 5, curve C, gave long ignition delays. It should be noted that the criteria for determining the suitability of the various lots of boron were based on tests in one type of motor with a particular igniter design. There are undoubtedly many igniter applications where the reaction rate of the boron used would either not be detected or would not significantly affect the ignition results.

Table VIII gives the average flash durations measured from five tests of each of the 22 mixtures, arranged in order of decreasing reaction rate. The best samples tested from the standpoint of reproducibility and combustion kinetics were those containing magnesium and sodium in a combined form (solid solution) with the boron called "Reactive Boron," manufactured by American Potash & Chemical Corp. The slowest burning samples were those containing very pure boron produced by electrolytic reduction. Crystalline boron produced by electrolysis, when mixed with $KClO_4$ and burned in the window bomb, showed a burning time of 233 msec as opposed to 17.7 msec for a sample containing "Reactive Boron." (Crystalline boron was reported to contain 99.2% B but only 92% was actually found.) This was somewhat surprising, but Professor Speiser[26] has recently stated that pure boron, probably crystalline, is an inert substance that is very difficult to ignite even under oxygen pressure and, after ignition by the addition of other fuels, shows very sluggish combustion.

Synthetic mixtures prepared by adding B_7O to fast-burning boron samples and finely divided magnesium to slow-burning samples gave results showing decreased reaction rates with addition of B_7O and increased reaction rates with addition of magnesium. This effect was also found by the Bureau of Mines[27, 28] in their solid ramjet research.

X-ray diffraction studies of elemental boron[29] showed that the slow-burning grades of boron were those that showed peaks for "d" values of 5.06A, a characteristic line of crystalline boron, and 4.71A. Many of the slow-burning boron samples, which are brown in color, were found to contain a high proportion of boron suboxides. X-ray diffraction patterns made with a control sample of B_7O indicated that the chief suboxide present in many of the borons was B_7O. It was also found that the slow-burning amorphous boron samples contained 10% or more B_7O, whereas the fast-burning samples showed negligible amounts of B_7O. The "d" values for B_7O are given in Table IX.

The outstanding factors found to affect combustion kinetics of boron adversely were (1) a high content of crystalline materials, particularly crystalline boron, and (2) a high content of lower oxides of boron, particularly B_7O.

CONCLUSIONS

1. Adiabatic flame temperature calculations show that zirconium-oxidant and aluminum-oxidant mixtures exhibit the highest flame temperatures of the mixtures studied. The maximum flame temperatures that can be reached by metal-oxidant compositions are, in general, limited to the vaporization temperature of the metallic oxide formed. When metal-oxidant compositions are burned at pressures above atmospheric, the increased boiling points of the products lead to corresponding increases in the flame temperatures and formation of larger quantities of condensible gases.

2. Data from closed-bomb ignitibility tests indicate that heats of explosion, flame temperatures, heats of condensation, reaction

products, and reaction rates are significant in determining the ignition effectiveness of various materials, but correlations based on simple analyses cannot be made. Metal-oxidant mixtures containing the fuels magnesium, boron, and aluminum gave good performance in small-scale ignitibility tests and have, in general, been found to give correspondingly desirable performance in rocket igniters. The ignitibility of aluminum compositions is greatly improved by addition of metals that react from their solid state, such as titanium or boron.

3. The content of crystalline materials and suboxides largely determine the reactivity of amorphous boron. Crystalline boron and amorphous boron containing a large proportion of suboxides show sluggish combustion, whereas boron with a very low suboxide content and dissolved "sensitizers" such as sodium or magnesium burns very rapidly.

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Table I
Thermochemical Constants

Table I
Thermochemical Constants

Species	Mol. Wt.	Heat of Formation, kcal/mole at 298°K	Melting Point, °K	Heat of Fusion, kcal/mole	Boiling Point, °K	Heat of Vaporization, kcal/mole	Vaporization Products	References
Zr	91.22	0	2125		> 3200			3, 5, 6
ZrO_2	123.22	258.4	3000	20.8	4573	92 to 117	$ZrO_2(g)$	3, 5, 8, 10
Al	26.97	0	933	2.6	2600	67.9		3, 5, 6
Al_2O_3	101.94	399	2318	26.0	3800	456 diss.	AlO(g) + O(g)	3, 5-9, 17
Mg	24.32	0	923	2.2	1393	31.5		3, 5, 6
MgO	40.32	145.7	2900	18.5	3350	80 to 100	MgO(g)	3, 5-8
Ti	47.90	0	2100		> 3300	112.7		3, 5, 6
TiO_2	79.90	214.1	2100	11.4	3000	63 to 77	TiO(g) + O(g)	3, 6, 10
Ti_2O_3	143.80	367	2400	≅16	3300	280 diss.	TiO(g) + O(g)	3, 5, 8, 14
B	10.82	0	2600		2800			3
B_2O_3	69.64	302	723	5.5	2520	77.6	$B_2O_3(g)$ > 2500°K diss.	3, 4, 5, 8, 15, 16
$KClO_4$	138.55	112.71						3, 9
KCl	74.55	104.3	1043	6.1	1680	38.8	KCl(g) > 2500°K diss.	3, 5, 7, 13, 18
KNO_3	101.1	118.78						3
K_2O	94.2	86.3			1750 sub.	189 diss.	K(g) + O(g)	3, 8, 11, 12, 13, 18
$Ba(NO_3)_2$	261.38	238.28						3
BaO	153.4	133.1	2190	12.5	2273	76.5	BaO(g) > 3000°K diss.	3, 5-8, 11, 18

Table II
Heat-capacity Data

Species	$C_p = a + b \times 10^{-3}T + c \times 10^5T^{-2}$ a	b	c	Temperature Range, °K	Avg C_p	Reference
$ZrO_2(s)$	11.62	10.64	−1.78	300 to 1673		7
$ZrO_2(l)$				3000	35	*
$Al_2O_3(s)$	27.43	3.06	−8.47	300 to 1800		4
$Al_2O_3(l)$				2300 to 3800	35	17
$MgO(s)$	10.18	1.74	−1.48	300 to 2100		4
$MgO(g)$	8.64	0.20	−0.75	300 to 3000		[illegible]
$TiO_2(s)$	17.97	0.28	−4.35	300 to 1800		4
$Ti_2O_3(\alpha)$	7.31	53.52		300 to 473		4
$Ti_2O_3(\beta)$	34.68	1.30	−10.20	473 to 1800		4
$Ti_2O_3(l)$				2400 to 3300	40	*
$B_2O_3(s)$	8.73	25.4	−1.31	300 to 723		4
$B_2O_3(l)$				723 to 1800	30.5	4
$B_2O_3(g)$					25	*
$KCl(s)$	9.89	5.2	0.77	300 to 1043		4
$KCl(l)$				1043 to 1200	16.0	4
$KCl(g)$	8.94		−0.24	300 to 2000		4
$K_2O(s)$				300 to 1200	18.8	*
$BaO(s)$	9.79	5.21		300 to 1000		4
$BaO(l)$					18	*
$BaO(g)$					10	*

*Estimated by Kopp's rule or by the "rough-and-ready" generalities discussed by Kelley.[4]

Table III
Calculated Heats of Reaction and Maximum Adiabatic Flame Temperatures of Stoichiometric Metal-Oxidant Igniter Mixtures

Composition	Ratio	Heat of Reaction (Calc.), cal/g	Maximum Adiabatic Flame Temp, °K
$Zr\text{-}KClO_4$	56.8/43.2	1584	4600
$Zr\text{-}Ba(NO_3)_2$	46.6/53.4	1105	4000
$Zr\text{-}KNO_3$	53.0/47.0	1149	3500
$Al\text{-}KClO_4$	34.2/65.8	2490	3800
$Al\text{-}Ba(NO_3)_2$	25.6/74.4	1594	3800
$Al\text{-}KNO_3$	30.8/69.2	1761	3800
$Mg\text{-}KClO_4$	41.2/58.8	2433	3350
$Mg\text{-}Ba(NO_3)_2$	31.8/68.2	1627	3350
$Mg\text{-}KNO_3$	37.5/62.4	1784	3350
$Ti\text{-}KClO_4$	48.0/52.0	1805	3300
$Ti\text{-}Ba(NO_3)_2$	37.9/62.1	1204	3300
$Ti\text{-}KNO_3$	44.2/55.8	1275	3300
$B\text{-}KClO_4$	17.2/82.8	2356	3340
$B\text{-}Ba(NO_3)_2$	12.1/87.9	1341	2520
$B\text{-}KNO_3$	15.2/84.8	1495	2520

Table IV

Theoretical Reaction Products in Moles at Maximum Flame Temperatur Produced by 100-gram Stoichiometric Mixtures of Metal-Oxidant Igniters

Products at Flame Temperature	Zr-KClO$_4$	Zr-KNO$_3$	Zr-Ba(NO$_3$)$_2$	Al-KClO$_4$	Al-KNO$_3$	Al-Ba(NO$_3$)$_2$	Mg-KClO$_4$	Mg-KNO$_3$	Mg-Ba(NO$_3$)$_2$	Ti-KClO$_4$	Ti-KNO$_3$	Ti-Ba(NO$_3$)$_2$	B-KClO$_4$	B-KNO$_3$	B-Ba(NO$_3$)$_2$
ZrO_2(l)	0.534	0.581	0.511												
ZrO_2(g)	0.009														
KCl(g)	0.081			0.328			0.370			0.334			0.514		
K(g)	0.230	0.465		0.147	0.604		0.054	0.618		0.041	0.552		0.083	0.838	
Cl(g)	0.230			0.147			0.054			0.041			0.083		
O_2(g)		0.079		0.205	0.030	0.078		0.128					0.092	0.209	
O(g)		0.074	0.043	0.410	0.075	0.194		0.054					0.046		
N_2(g)		0.232	0.204		0.342	0.285		0.309	0.261		0.276	0.237		0.419	0.336
BaO(g)			0.1[illegible]1			0.247			0.261			0.237			0.336
Ba(g)			0.043			0.038									
Al_2O_3(l)				0.359	0.521	0.371									
AlO(g)				0.546	0.100	0.208									
MgO(l)							0.378	1.174	0.752						
MgO(g)							1.316	0.370	0.553						
Ti_2O_3(l)										0.125	0.387	0.271			
TiO_2(g)										0.375	0.074	0.125			
TiO(g)										0.375	0.074	0.125			
B_2O_3(l)														0.275	
B_2O_3(g)													0.566	0.430	0.561
BO(g)													0.462		
Total moles	1.164	1.431	0.962	2.142	1.760	1.421	2.172	2.653	1.827	1.291	1.363	0.995	1.846	2.171	1.233
Total gas	0.630	0.85[illegible]	0.451	1.783	1.239	1.050	1.794	1.479	1.075	1.166	0.939	0.724	1.846	1.896	1.233
Permanent gas	0.000	0.232	0.204	0.000	0.342	0.285	0.000	0.309	0.261	0.000	0.276	0.237	0.000	0.419	0.336

Table V
Materials Used in Ignitibility Tests

Aluminum (atomized)	Reynolds type 120, 85% through 325 mesh, 99+% pure
Aluminum (flake)	Merck, 60% through 200 mesh, 40% through 325 mesh
Magnesium	(ground, dichromated) 100% through 200 mesh and retained on 325 mesh, 97.5% free magnesium
Titanium (degassed)	Metal hydrides, 100% through 325 mesh, 96.7% titanium
Boron (amorphous)	Fisher, total boron content 80%, less than 1μ average particle diameter (Fisher Sub-sieve Method)
Zirconium (granular)	Foote Mineral Company, 100 mesh × 10μ
Zirconium (powder)	Metal Hydrides, 100% through 200 mesh
Zirconium-Nickel Alloy powder	70/30 Metal Hydrides, 100% through 325 mesh
Potassium Perchlorate (Reagent Grade)	
Potassium Nitrate (Reagent Grade)	
Barium Nitrate (Reagent Grade)	
Sodium Nitrate (Reagent Grade)	

Nominal Composition of JPN Propellant,	Wt. %
Nitrocellulose (13.25% N)	51.40
Nitroglycerin	42.90
Diethyl phthalate	3.23
Ethyl centralite	1.00
Potassium sulfate	1.25
Carbon black	0.20
Candelilla wax	0.02

Table VI

Measurements with Magnesium-Oxidant Mixtures Using JPN Propellant in Ignitibility Tests

Igniter Number	Nominal Composition, wt % Mg	Nominal Composition, wt % Oxidizer	Measured Heat of Explosion, H, cal/g	Wt. Required for 50% Probability Ignition, w, mg	Total Heat Evolved, wH, cal	Relative Burning Time, t, msec	Relative Rate of Heat Evolution, r = w H/t, cal/msec	Measured Gas Volume at S. T. P., cc/g
58	65	35 KNO_3	1327	72.5	96.2	18.0	5.34	58.0
57	60	40 KNO_3	1315	66.5	87.5	19.6	4.46	58.0
55	55	45 KNO_3	1515	76.5	116.0	22.6	5.13	64.0
53	50	50 KNO_3	1658	88.5	146.7	26.4	5.55	65.3
56	45	55 KNO_3	1680	98.5	165.5	28.3	5.85	67.6
54	38	62 KNO_3	1674	108.5	181.6	40.5	4.47	63.0
52	50	50 $KClO_4$	2158	131.5	283.8	24.1	11.78	13.1
51	45	55 $KClO_4$	2300	115.5	265.6	22.4	11.85	15.6
49	40	60 $KClO_4$	2203	105.5	232.4	19.6	11.80	22.7
50	37	63 $KClO_4$	2050	98.5	202.0	17.8	11.35	44.9
84	60	40 $NaNO_3$	1742	73.5	128.0	17.0	7.52	
83	50	50 $NaNO_3$	1933	83.5	161.4	21.7	7.44	83
30	50	50 $Ba(NO_3)_2$	1516	100.5	152.3	14.5	10.50	15
61	45	55 $Ba(NO_3)_2$	1553	94.5	146.7	15.8	9.28	
60	40	60 $Ba(NO_3)_2$	1583	90.5	143.3	17.5	8.19	
37	32	68 $Ba(NO_3)_2$	1484	88.5	131.3	22.0	5.96	60
A-5	Black powder		711	160.2	113.9	34.0	3.35	224.0
A-3	Black powder		≅711	207.6	147.6	52.0	2.83	

Table VII
Propellant Ignitibility Tests with Various Igniter Mixtures

Igniter Number	Nominal Composition, wt % Fuel	Nominal Composition, wt % Oxidizer[a]	Measured Heat of Explosion, H, cal/g	Wt. Required for 50% Probability Ignition, w, mg	Total Heat Evolved, wH, cal	Relative Burning Time, t, msec	Relative Rate of Heat Evolution, r = w H/t, cal/msec	Measured Gas Volume at S.T.P., cc/g
118	30 B	70 KNO_3	1603	85.5	137.0	26.5	5.17	103
119	25 B	75 KNO_3	1410	96.5	136.1	33.0	4.12	
120	20 B	80 KNO_3	1280	90.5	115.8	39.4	2.94	89.0
121	15 B	85 KNO_3	1100	88.5	97.3	51.0	1.91	90.6
122	30 B	70 $KClO_4$	1323	114.5	151.5	28.2	5.37	40.8
123	25 B	75 $KClO_4$	1219	79.5	96.9	24.1	4.02	
124	20 B	80 $KClO_4$	1148	75.5	86.7	32.1	2.70	
125	15 B	85 $KClO_4$	1003	72.5	72.7	38.5	1.88	115
126	25 B	75 $Ba(NO_3)_2$	1330	106.5	141.6	41.7	3.39	
104	50 Ti	50 $KClO_4$	1740	154.5	268.8	57.4	4.68	67
105	55 Ti	45 $KClO_4$	1620	151.5	245.4	53.0	4.63	63
106	30 Ti	70 $Ba(NO_3)_2$		197.5		86.0		
86	30 Al†	70 $KClO_4$	2250	98.5	221.6	78.2	2.83	
85	35 Al†	65 $KClO_4$	2365	95.5	225.8	86.8	2.60	
T-1	22.2 Al‡ 14.3 Ti	63.5 $KClO_4$	2167	92.5	200.4	29.8	6.72	< 50
95	50 Zr-Ni	50 $KClO_4$	1209	141.5	171.1	120.0	1.42	

[a] Oxidizers 100% through 200-mesh and retained on 325-mesh screen.
† Flake.
‡ Atomized.

Table VIII
Measurements Made on Various Boron Samples

Sample Designation	Source	Particle* Size, µ	Total† Boron Content, %	Type Curve, Fig. 4	Flash Duration, ‡ msec
WS#4§	American Potash & Chemical Corp.	0.50	69.7	A	17.7
Fisher	Fisher Scientific Company	0.62	80.4	A	27.3
B-3	F. W. Berk & Co., Inc.	0.65	81.3	A	27.7
P-124, 125§	American Potash & Chemical Corp.	0.81	70.3	A	30.3
WS#2§	American Potash & Chemical Corp.	0.54	70.5	A	34
B-4	F. W. Berk & Co., Inc.	0.70	78.2	A	38
Trona	American Potash & Chemical Corp.	0.86	90.7	B	69
B-19	F. W. Berk & Co., Inc.	0.96	80.7	B	77
B-6	F. W. Berk & Co., Inc.	0.95	79.6	B	83
B-14	American Potash & Chemical Corp.	0.88	91.8	B	83
B-12	American Potash & Chemical Corp.	0.90	90.3	B	87
B-17	American Potash & Chemical Corp.	0.90	89.3	B	87
B-10	F. W. Berk & Co., Inc.	0.90	86.6	C	112
La Pine	Arthur S. La Pine & Co.		65.3	C	121
B-7	F. W. Berk & Co., Inc.	0.98	86.1	C	125
B-9	F. W. Berk & Co., Inc.	1.01	86.5	C	126
B-8	F. W. Berk & Co., Inc.	1.06	86.9	C	128
B-11	F. W. Berk & Co., Inc.	1.00	85.3	C	152
Metalsalts	Metalsalts Corporation	1.01	85.2	C	155
B-5	F. W. Berk & Co., Inc.	1.17	90.0	C	194
B-13	American Potash & Chemical Corp.	1.2	88.3	C	195
Cooper	Cooper Metallurgical Associates	1.9	92.0	C	233

*Fisher Sub-Sieve Analysis by Thiokol Chemical Corporation, Redstone Division.[25]

†By Na_2CO_3 fusion and titration with NaOH in presence of mannitol, measured by Thiokol Chemical Corporation, Redstone Division.[25]

‡ From initial detection of radiant intensity to a point which represents 10% of maximum intensity on the decay portion of intensity-time curve, when burned with $KClO_4$.

§"NAR" Grades of boron containing sodium and magnesium.

Table IX

Characteristic Lines of B_7O from X-ray Diffraction

Interplanar Spacing "d" Value, angstroms	Relative Intensity I*/I
4.17	52
3.77	16
2.60	100
2.30	62
2.19	9
1.87	7
1.70	7
1.65	7
1.47	15
1.44	17

*Intensity of line relative to strongest line = 100.

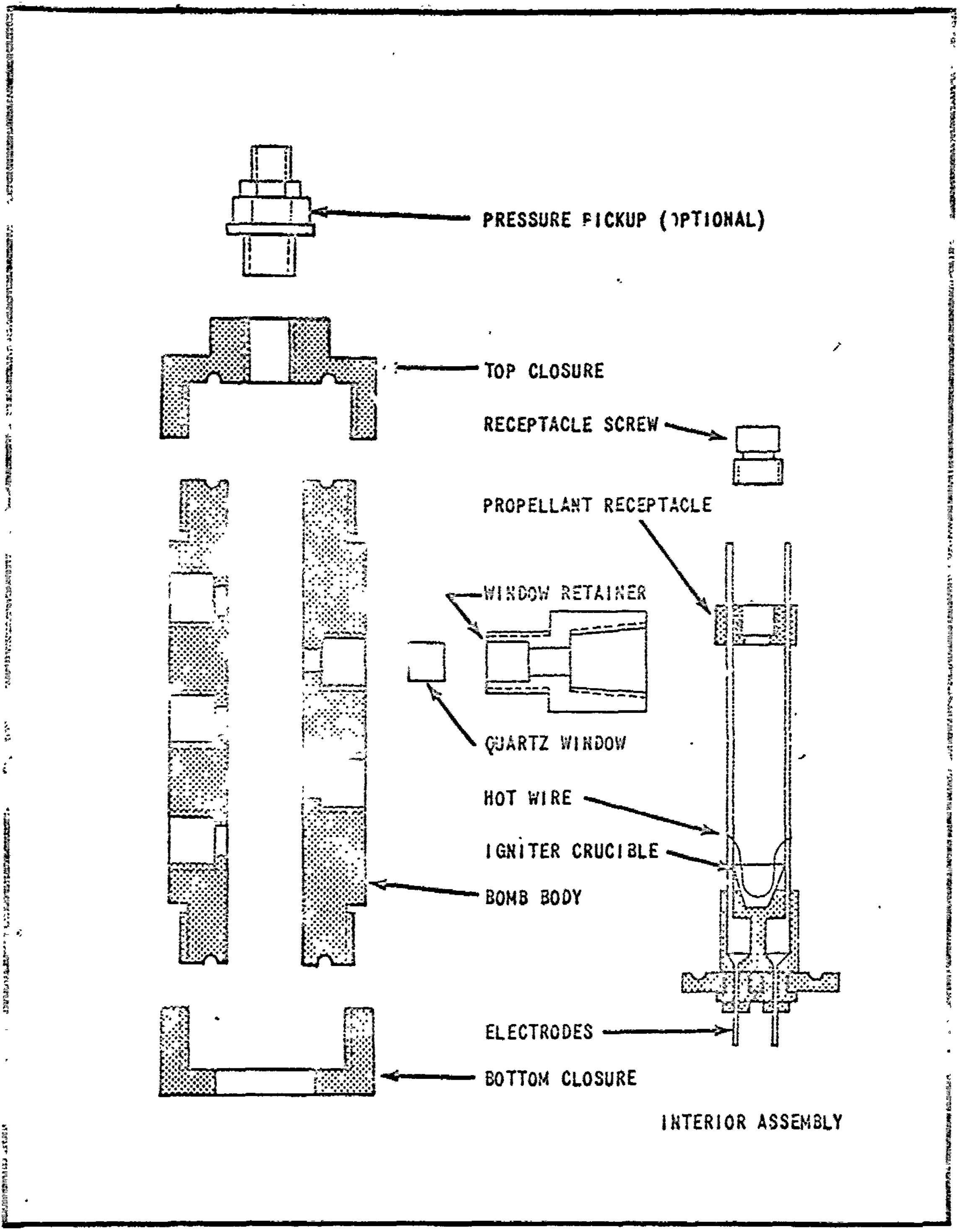

FIG. 1 WINDOW BOMB FOR IGNITION STUDIES

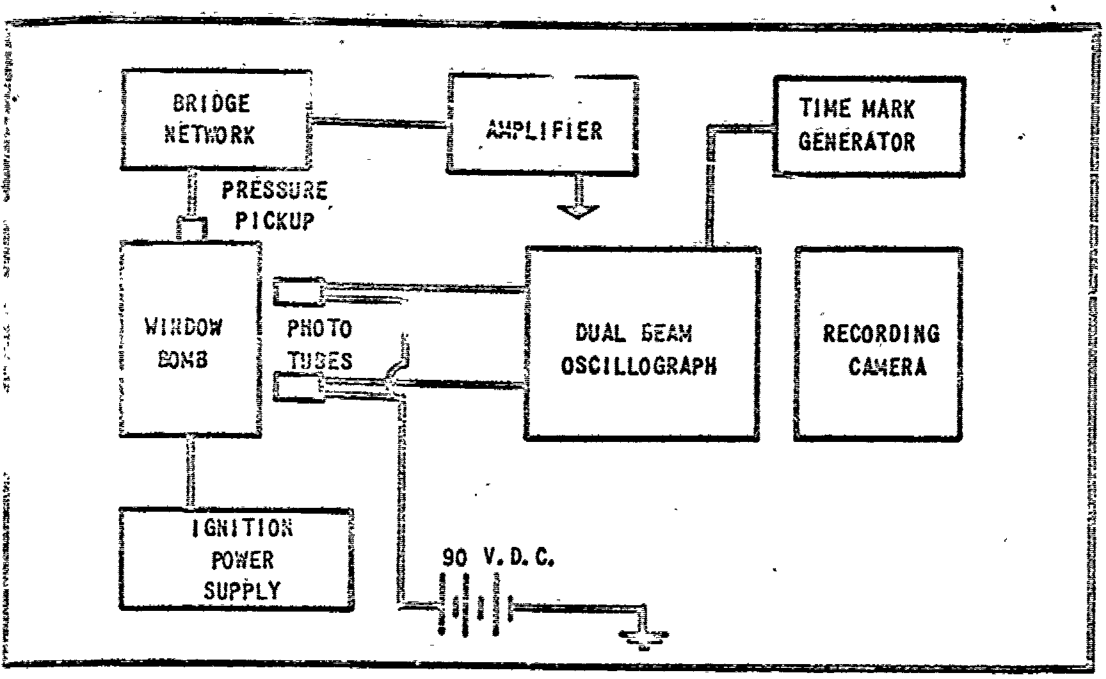

FIG. 2a BLOCK DIAGRAM OF INSTRUMENTATION FOR IGNITION STUDIES

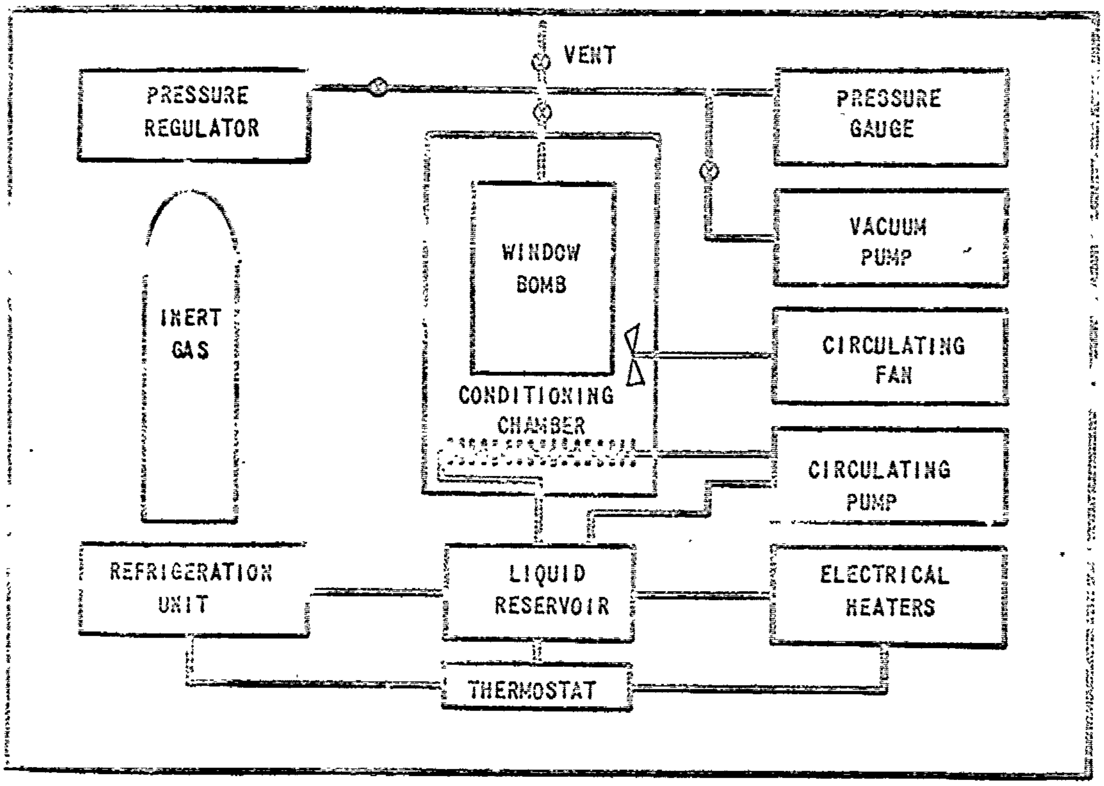

FIG. 2b BLOCK DIAGRAM OF APPARATUS FOR IGNITION STUDIES

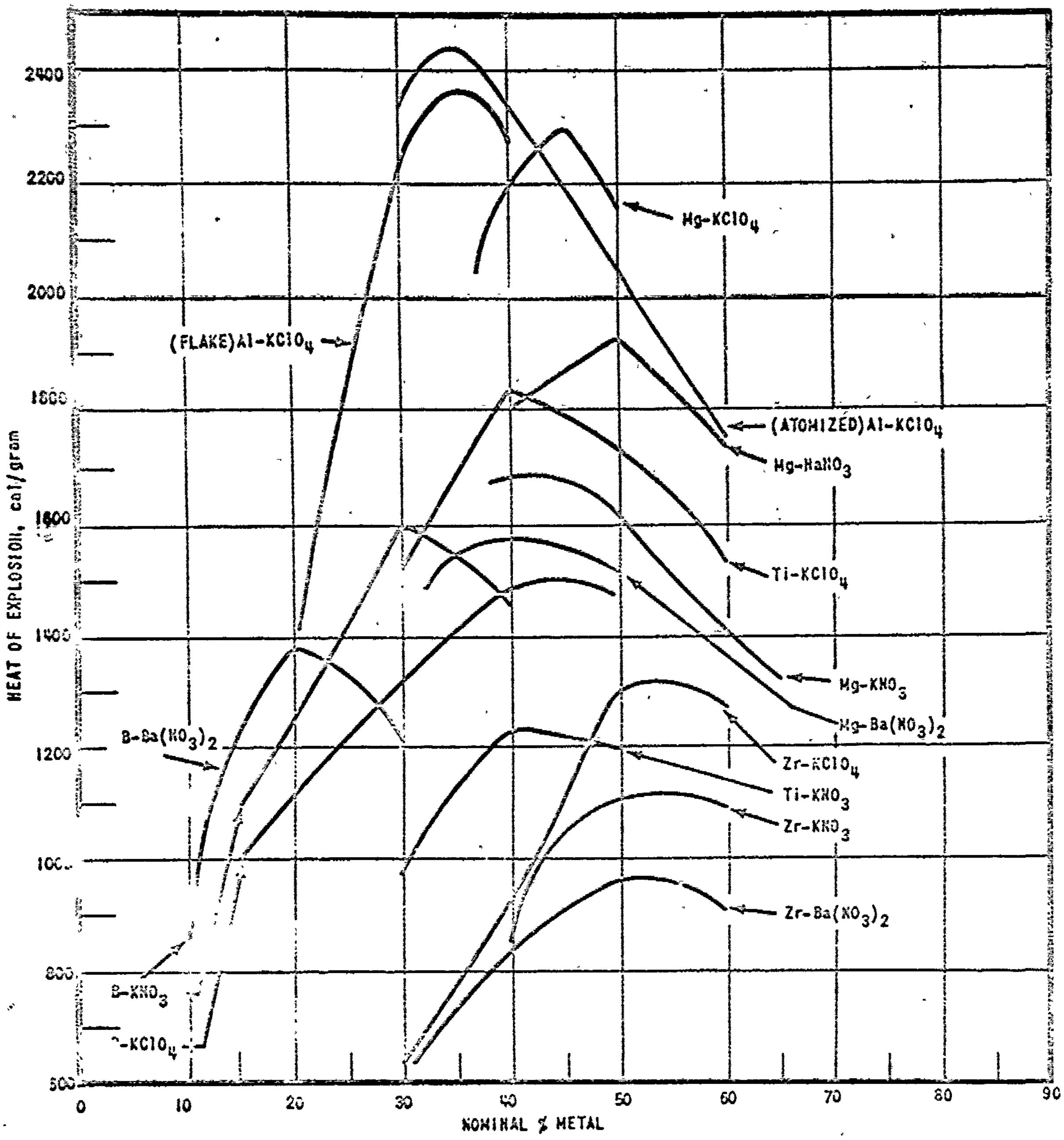

FIG. 3 MEASURED HEATS OF EXPLOSION OF METAL-OXIDANT MIXTURES

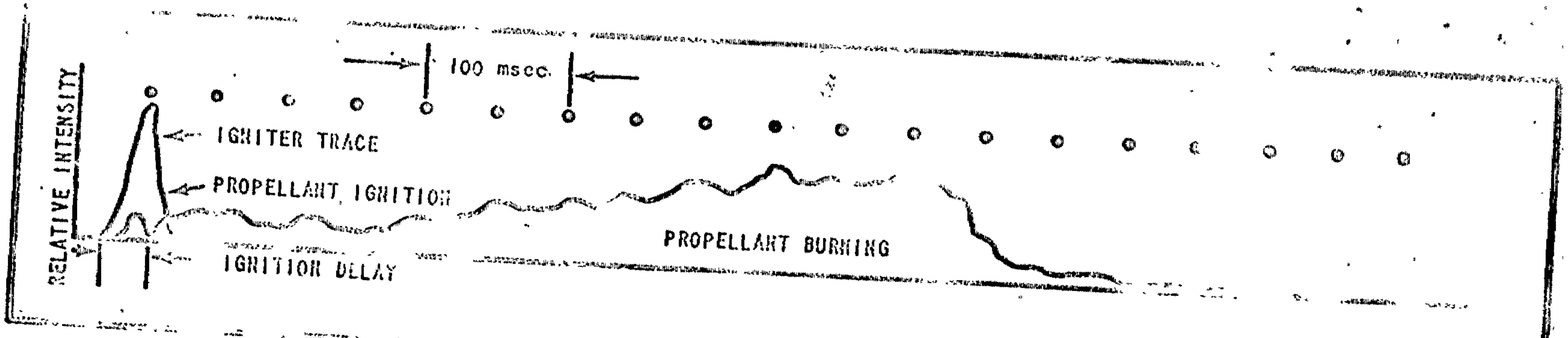

FIG. 4a REPRESENTATIVE INTENSITY-TIME CURVE SHOWING IGNITION OF SHEET JPN PROPELLANT BEFORE IGNITER BURNOUT

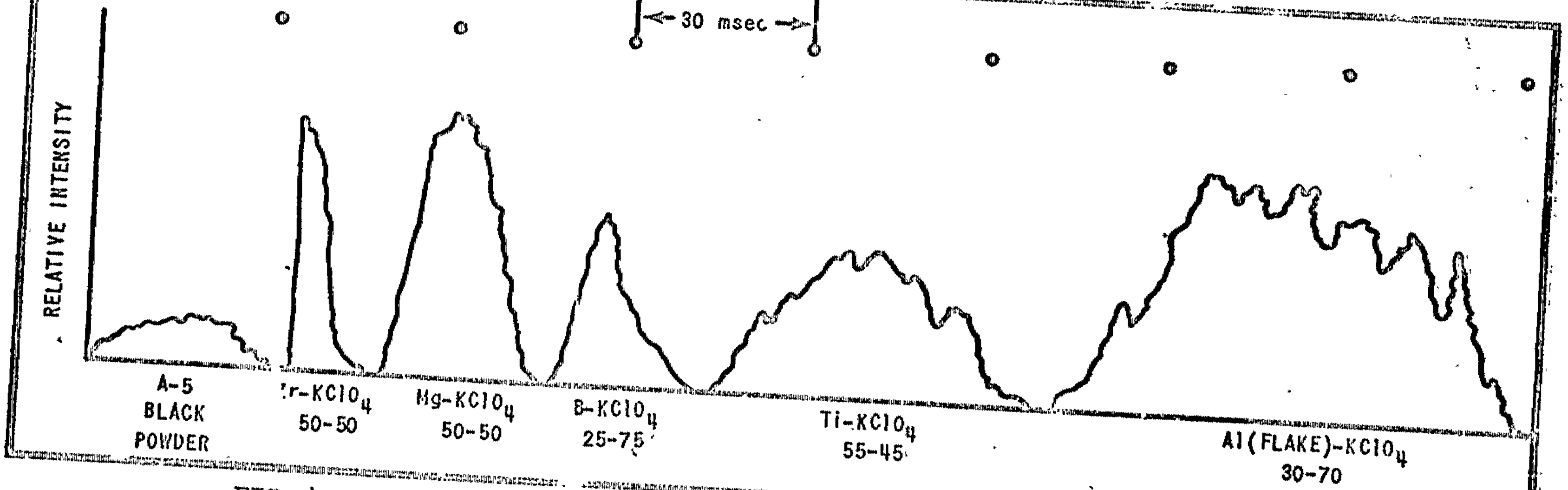

FIG. 4b REPRESENTATIVE INTENSITY-TIME TRACES OF SEVERAL IGNITER MIXTURES FROM CLOSED-BOMB TESTS

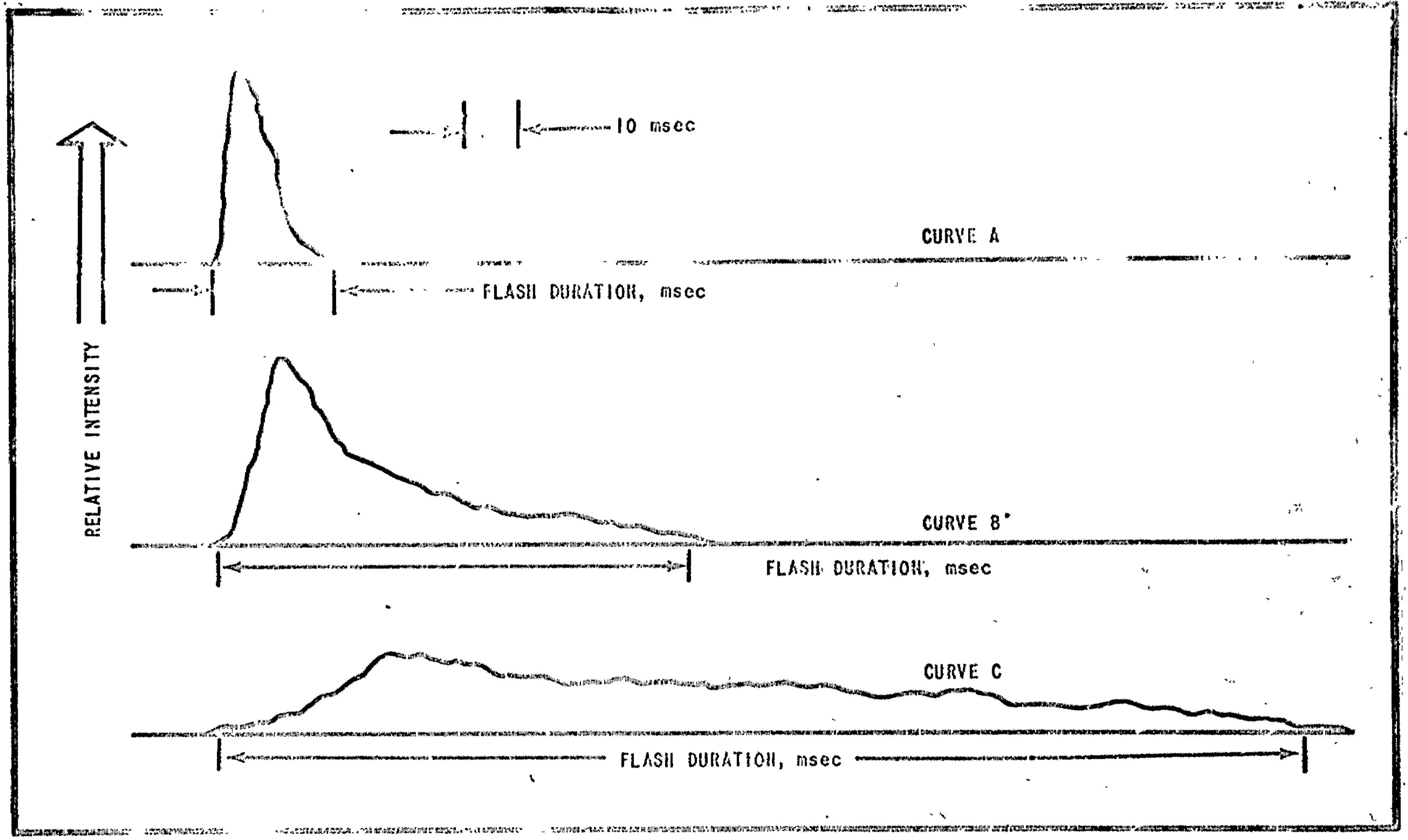

FIG. 5 TYPICAL CURVES OF INTENSITY vs. TIME OBTAINED WITH BORON-POTASSIUM PERCHLORATE MIXTURES USING VARIOUS LOTS OF BORON