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FLAME PROPAGATION PARAMETERS OF PYROTECHNIC DELAY AND IGNITION COMPOSITIONS

James E. Rose

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31 December 1971

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By

James E. Rose

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NAVAL ORDNANCE STATION
Indian Head, Maryland

B. W. FRESE, JR.
Captain, USNavy
Commanding Officer

JOE L. BROWNING
Technical Director

FOREWORD

The work reported herein was performed at the Patterson Pilot Plant under Naval Air Systems Command Task Assignment A350-5322/286B/IF17-546-501. This work was performed during the period July 1971 to September 1971 and is submitted with the reservation that it may be altered by future work.

The author wishes to acknowledge the helpful advice of Dr. Joseph H. McLain of Washington College concerning the propagation index parameters.

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Manager, CAD Branch

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ABSTRACT

Heat of explosion, ignition temperature, and McLain Propagation Index, P_I, defined as heat of explosion divided by ignition temperature, are correlated for various pyrotechnic delay and ignition compositions. A novel propagation index, described by heat of explosion, ignition temperature, burning rate, and density is proposed as a comparative screening criterion for pyrotechnic compositions.

INTRODUCTION AND BACKGROUND

To date, no suitable correlations of flame propagation characteristics of pyrotechnic compositions have been prepared. Now, in this report, the flame propagation parameters, heat of explosion, ignition temperature, and McLain Propagation Index, are correlated for various pyrotechnic delay and ignition compositions. The McLain Propagation Index is defined as heat of explosion divided by ignition temperature. It is measured in calories/gram-degrees centigrade (cal/g-°C), reminiscent of the entity known as heat capacity. The physical significance of the propagation index is that it is a comparative measure of ease of flame propagation in the pyrotechnic composition. The higher the propagation index, the better the flame propagation.

The propagation index was originally developed to describe the combustion of a delay composition. In the combustion of a delay composition, the flame front is believed to advance layer to layer, with each succeeding layer being ignited by the preceding burning layer. The ignition energy required by each succeeding layer is defined as activation energy. Energy available from the preceding layer for ignition is described by the heat of reaction, ΔH_R, or by the heat of explosion, HOE, in the case of an explosive or pyrotechnic composition. The ease which a flame propagates through a mass of pyrotechnic composition compressed in a tube is then directly proportional to the heat of explosion and inversely proportional to the activation energy.

According to the classic work of Henkin-McGill,[1] activation energy, E_a, varies directly with ignition temperature, T_i. This is logical to assume, since an easier propagating composition would have lower activation energy and lower ignition temperature as opposed to the higher activation energy and correspondingly higher ignition temperature of a more difficultly propagating composition. It was deduced, therefore, that ease of flame propagation may be empirically described by a propagation index, P_I, which varies directly with the heat of explosion and inversely with ignition temperature. In this manner, the propagation index came to be defined as

$$P_I = \frac{HOE}{T_i} \qquad (1)$$

[1] H. Henkin and R. McGill, Industrial and Engineering Chemistry 44 1391 (1952)

EXPERIMENTAL METHODS

Heat of Explosion Determinations

For most ignition compositions, heat of explosion determination is a matter of routine evaluation. However, for the delay compositions a modified procedure is followed. To prevent scattering of delay powder when ignited in the Parr calorimeter bomb, the composition is pelletized. Pellets are pressed at 30,000 psi in a 0.260-inch inner diameter aluminum test column, extracted with a ram, and dried in a vacuum desiccator for several days at room temperature to ensure complete dryness. Results are obtained using the standard procedures of the Parr adiabatic calorimeter, except that (1) a porcelain crucible is substituted for the stainless steel combustion cup, (2) 1-atmosphere initial pressure of helium gas is used, and (3) A1A ignition composition is used to ignite the delay compositions instead of the hot wire igniter. For most firings, the charge consists of about 5 grams of delay composition and about 0.1 gram of the A1A ignition composition. Appropriate corrections for heat evolved from the A1A igniter are made. Total error, considering the low heat output of some of the compositions being burned and error introduced in estimating the true temperature rise, could be as much as ±15 cal/g. In view of this and the special conditions under which the tests were conducted, results should be used for comparative information only.

Ignition Temperature Determination

Ignition temperatures are determined from the differential thermal analysis (DTA) plots using the method of tangents. This involves locating the exotherm which denotes ignition, constructing tangents to the peak and base line, and projecting the tangents intersection back to the base line for ignition temperature. Ignition temperature is then easily determined from a DTA calibration chart.

All compositions are used in the powder form for the DTA. It has been found that the DTA results of most ignition compositions are smoother and more easily evaluated at heating rates of 20° to 25° C/min. Sample size varies from 50 milligrams for the delay compositions to 30 to 40 milligrams for the ignition compositions.

DISCUSSION

Results

Correlations of the various pyrotechnic composition propagation parameters are presented in Table I. The propagation indices obtained seem to bear out the theory previously discussed. For slow burning compositions with low heat output such as delays, the propagation index lies in the range of 0.5 to 0.7 cal/g-°C. For faster burning, hotter compositions, such as boron potassium nitrate, the propagation index is between 0.8 and 2.8 cal/g-°C. A propagation index as high as 6.8 cal/g-°C was obtained for the explosive composition FA-878.

Table I

FLAME PROPAGATION PARAMETERS

Composition	% Ingredient	Heat of explosion (cal/g)	Ignition temperature (°C)	Heating rate (°C/min)	Propagation index (cal/g-°C)
Manganese delay, 9 sec/in.	35.8 Manganese 41.2 Lead chromate 23.0 Barium chromate	267	438	10	0.61
Manganese delay, 4 sec/in.	41 Manganese 49 Lead chromate 10 Barium chromate	254	421	10	0.60
Tungsten delays	30 Tungsten 50-60 Barium chromate 5-15 Potassium perchlorate 5 Superfloss[1]	260-330	460-480	30	0.55-0.70
A 1A	65 Zirconium 25 Ferric oxide 10 Superfloss	480	580	10	0.83
$BKNO_3$	23.7 Boron 70.7 Potassium nitrate 5.6 Laminac[2]	1600	565	25	2.8
A 1A/$BKNO_3$	80 A 1A 20 $BKNO_3$	610	410	25	1.5
TBK igniter	26 Titanium 64 Barium chromate 10 Potassium perchlorate	740	520	10	1.4
Hard igniter A	30 Zirconium 60 Barium chromate 10 Superfloss	433	433	20	1.0
Hard igniter B	58.5 Zirconium 31.5 Barium chromate 10.0 Superfloss	427	410	20	1.0
Soft igniter	16.4 Zirconium 73.6 Barium chromate 10.0 Superfloss	333	407	20	0.82
Titanium/ferric oxide	53 Titanium 47 Ferric oxide	560	676	20	0.83
FA-878	20 Barium nitrate 20 Lead dioxide 20 Pentaerythritol tetranitrate 40 Zirconium	1050	154.3 (explosion)	1	6.8

[1] Trade name of Johns-Manville Products Corp., New York, N.Y.
[2] Trade name for polyester resin, American Cyanamide Co., Wayne, N.J.

Of all the parameters, ignition temperature is the most difficult to define accurately, since it depends on the heating rate of the DTA apparatus. As the heating rate is increased for various compositions, the apparent ignition temperature also increases. As an example, the ignition temperatures for an A1A ignition composition (65% zirconium, 25% red ferric oxide, 10% diatomaceous earth) are given in Table II. The slower heating rates give not only lower ignition temperatures but also higher times to ignition. This is to be expected, however, as Henkin-McGill predicted that ignition temperature is related to time to ignition, t, by:

Table II

EFFECTS OF HEATING RATE ON IGNITION TEMPERATURE OF A1A COMPOSITION

Time to ignition (min)	Heating rate (°C/min)	Ignition temperature (°C)
55.5	10	580
37.6	20	776
33.0	25	850

$$\ln t = \frac{E_a}{RT^1} + \text{constant}. \qquad (2)$$

When the data in Table II are plotted on log-inverse temperature coordinates, a nearly straight line results as shown in Figure 1. This is in fair agreement with the Henkin-McGill equation (2). The activation energy determined from the plot is somewhat low compared to those of most chemical reactions which require 20 to 50 kilocalories/mole for activation. However, when one considers the high metal content and concomitant high thermal conductivity of the A1A composition, the reason for the low activation energy becomes obvious—the high thermal conductivity is linked with the ease of ignition of the composition.

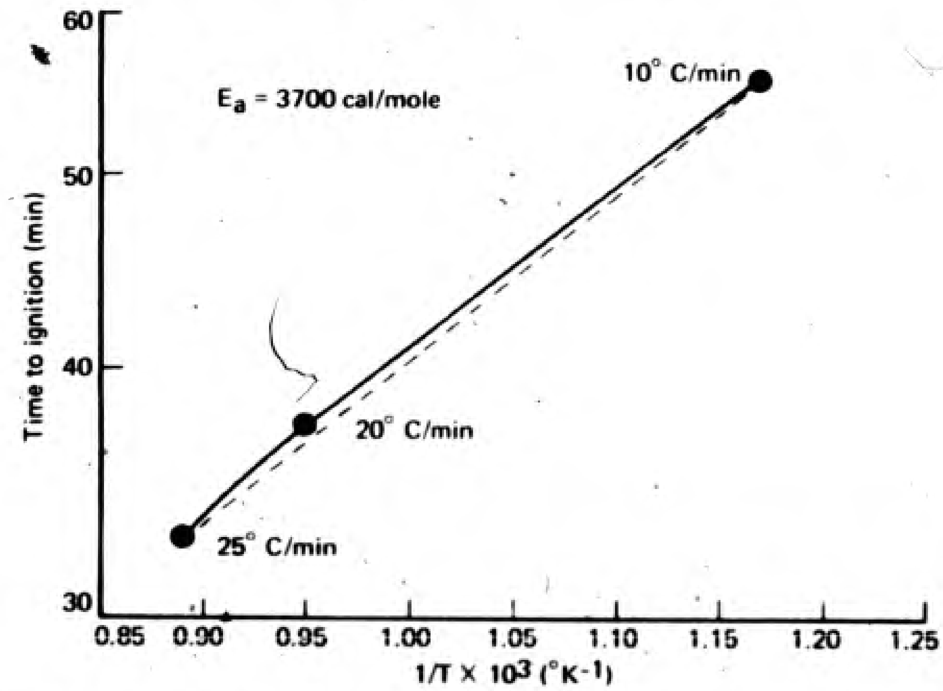

FIGURE 1. ACTIVATION ENERGY PLOT FOR A1A IGNITION COMPOSITION

[1] R = Universal gas constant and T = temperature in °K.

Additional Suggested Screening Criteria

To better define flame propagation in a pyrotechnic composition which has been compressed into a hollow tube, we need to consider the variables burning rate, BR, and pressed density, d. Ease of propagation should vary directly with pressed density, since the higher the density the better interparticle contact and flame transfer should be. Propagation should vary directly with burning rate, since a fast burning composition would transfer heat faster through itself and have less conductive heat loss to the surroundings than would a slower burning composition. When these variables are incorporated into equation (1), we have

$$P_I = \frac{HOE}{T_i} d(BR) \qquad (3)$$

with the units, cal/°C-sec-cm^2, dimensionally equivalent to the heat transfer coefficient. All parameters are to be measured in the same state. For example, if BR is determined for compressed material, then T_i and other parameters should also be determined for compressed material.

Application

The parameters described herein may be used as comparative screening criteria for pyrotechnic delay and ignition compositions which are used in aircraft personnel escape systems, aircraft stores separation, ship-to-ship or ship-to-shore ammunition, and Navy missile systems. The parameter, heat of explosion, has been used as a comparative acceptability screening criterion for many pyrotechnic ignition compositions. Successful and consistent internal ballistic performance of these systems is related to the successful and consistent performance of the delay and ignition compositions used in the components of these systems. It is recommended that sufficient data such as described herein continue to be accumulated so that comparative criteria for these compositions can be established.

CONCLUSIONS

Differential thermal analysis is adequate for determining ignition temperatures of pyrotechnic compositions if sample weight and heating rate are defined. The same heating rate should be used when comparing similar compositions.

The McLain Propagation Index is a useful comparative tool in describing performance characteristics of pyrotechnic compositions. The Rose-McLain Propagation Index (equation (3)), defined by heat of explosion, ignition temperature, pressed density, and burning rate of the composition, may also be a useful comparative tool in describing acceptability criteria of pyrotechnic compositions.

RECOMMENDATIONS

It is recommended that the McLain Propagation Index be used as a comparative reference screening criterion for the acceptability of a pyrotechnic composition. Data on ignition temperatures, burning rates, pressed densities, and heats of explosion of pyrotechnic compositions should be accumulated so that a solid basis for comparative screening criteria can be established.

Government and private industrial manufacturers of pyrotechnic compositions used in ordnance should consider the McLain Propagation Index and the Rose-McLain Propagation Index as comparative screening criteria for pyrotechnic compositions. Data on the pressed densities, burning rates, heats of explosion, and ignition temperatures should be collected and exchanged among manufacturers.

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