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Evaluation of Ballistic Performance of Solid Propellants by Means of a Constant-Volume Bomb

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Summary: To obtain information quickly on the solid propellants under the laboratory-scale research, a method of the specific-impulse estimation by employing a ballistic bomb has been studied. Based on the maximum burning pressures of the liquid monopropellants is provided the covolume in a convenient form as a function of the loading density (Δ) alone with Noble-Abel equation of state, $p(v-\alpha)=nRT$. Thus, it becames possible to evaluate the impetus of propellant $\left(\frac{RT}{\overline{m}}\right)_{p\to 0}$ without rendering extrapolation $p\to 0$ from the plots of $p_{\max}v$ against the loading density, and the specific impulse can be derived. This method employing an approximation $\alpha=f(\Delta)$ leads to identical results with performance data obtained according to Griffin's procedure, and is supported also by the fact that the same α vs. Δ relation can be applied to all the propellants mainly composed of carbon, hydrogen, oxygen, chlorine and nitrogen. Namely, by applying $\alpha=f(\Delta)$ specified from a few selected propellants, the specific impulse is calculated for all the propellants of this type within experimental error throughout if some data of maximum burning pressures at high loading densities are obtained. Performance data of typical composite propellants are presented and compared to theoretical. With non-aluminized propellants measured values approach calculated, but there is a considerable discrepancy between these two values for aluminized propellants. The innappropriate assumption in the theoretical calculation and incomplete burning of aluminum particles seem to be the most likely cause of its discrepancy.

Symbols

A_i: i-th substance in explosion products
c_v: heat capacity at constant volume, Kcal/mole-°K
F: specific free energy, Kcal/g
f: fugacity, kg/cm^2
f_i: partial fugacity of i-th component, kg/cm^2
I_{sp}: specific impulse, sec
I_0: impetus of a given propellant, kg-cm/kg
I_0': apparent impetus of a given propellant, kg-cm/kg
K_p: pressure equilibrium constant
K: concentration equilibrium constant
$\overline{m}$: mean molecular weight of reaction product, g/mole

N_i: mole fraction of i-th component
n: number of moles per unit weight propellant, mole/g
p_c: pressure of rocket combustion chamber, kg/cm^2
p_i: partical pressure of i-th component, kg/cm^2
p_j: nozzle exit pressure, kg/cm^2
p_{max}: explosion pressure (maximum burning pressure), kg/cm^2
Q: heat of explosion, Kcal/mole
R: universal gas constant, l-atm/K°-mole
T_e: explosion temperature, K°
T_c: combustion temperature, K°
v: specific volume, cm^3/g
α: covolume, cm^3/g
Δ: loading density, g/cm^3
κ: specific heat ratio
θ_1, θ_2: parametric constants
ν_i: stoichiometric coefficient of substance A_i

1. Introduction

For the evaluation of the ballistic performance of solid propellants which have been developed in the laboratories, the measurement of combustion characteristics is needed. The actual approach to the availability demonstration should be achieved by a static firing test using a micorocket motor. However, as a matter of fact, it is laborious and expensive to carry out this examinations and there is no small sample quantity to confirm the available data. If it becomes possible to evaluate urgently the propellant investigators would find their own course promptly by checking for a propellant on the half-way of the development work. Griffin [1] developed a novel method for the evaluation of liquid monopropellants by means of a closed bomb of constant volume widely known as Vieille bomb for the determination of brisance or impetus of the explosives. Griffin proposed to relate the terms $\frac{RT_c}{\overline{m}}$ in the impulse equation to the impetus $\left(\frac{RT_e}{\overline{m}}\right)_{p\to 0}$ by an approximation that the total heat release is deemed equal in both cases. This assumption predicts that one may obtain the propellant performance by measuring the impetus. However, in order to derive $\left(\frac{RT_e}{\overline{m}}\right)_{p\to 0}$ with a sufficient accuracy it is required to measure repeatedly the maximum burning pressures (explosion pressures) varying in the loading density. Moreover, this method is likely to involve a considerable error inherent in the graphical extrapolation to the position corresponding to zero pressure.

This paper discusses on whether Griffin's method is applicable to solid propellants or not and describes a modified procedure to derive $\left(\frac{RT}{\overline{m}}\right)_{p\to 0}$ more easily with less sample amount.

2. Determination of Thermochemical Relationship between Covolume of Noble-Abel Equation of State and Loading Density

2.1. Fundamental Equations

Generally, the ideal equation of state is utilized to calculate the theoretical specific impulse of rocket propellants. Properties of the burned gases on the ordinary combustion-pressure level of the actual rocket motor, seldom show a difference more than 5% from the ideal relation:

$$pv = nRT \tag{1}$$

However, at extremely high pressures, the above equation will deviate significantly from the relations for real gas. Explosion gases of solid or condensed explosives in a constant-volume bomb are recognized to involve a scatter as much as 30~50% from the ideal equation where the pressure itself is a measure of escaping tendency. In such a case Noble-Abel equation of state, which is one of the simplest equations susceptible for explosion gases, may be used:

$$p(v-\alpha) = nRT \tag{2}$$

where α represents the difference in the specific volumes of the gas in the ideal and the real conditions at a given pressure. α is called a covolume and a property of real gas given by a function of the loading density and temperature as follows:

$$\alpha = f(\Delta, T) \tag{3}$$

Although it is very difficult to express explicitly this function, for a given explosive or propellant, Eq. (3) can be simplified by the fact that its explosion temperature (burning temperature under the constant-volume condition) has weak dependency upon the reaction pressure. For example, the relations between theoretical explosion temperature (adiabatic burning temperature in the constant-volume bomb) and loading density of polysulfide~ammonium perchlorate propellant as shown in Fig. 1 support this prediction. Hence, the following relation will be derived:

$$\alpha \doteqdot f(\Delta) \tag{4}$$

On the other hand, the covolume may be defined as

$$\alpha = v_{\text{ideal}} - v_{\text{real}} = \frac{nRT}{p} - v_{\text{real}} \tag{5}$$

From Eq. (5), the following equation for the specific free energy is obtained in terms of α:

$$F_{\text{real}} = F_{\text{ideal}}^{p=1} + nRT \ln p - \int_0^p \alpha dp \tag{6}$$

By the definition of fugacity which indicates the activity of the real gas, the equation corresponding to Eq. (6) is

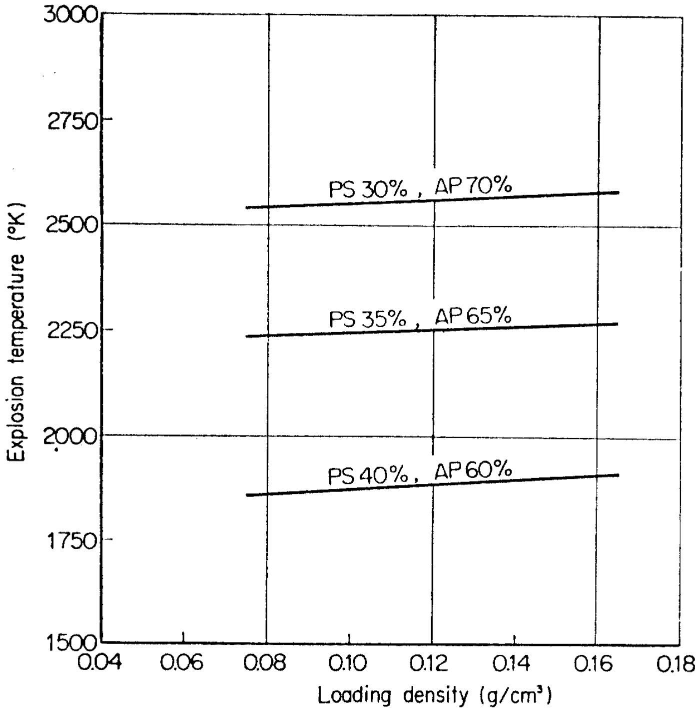

FIG. 1. Relation between explosion temperature and loading density for polysulfide~ammonium perchlorate propellant

$$F_{\text{real}} = F_{\text{ideal}}^{p=1} + nRT \ln f \tag{7}$$

Combining Eq. (6) with (7),

$$f = p \exp\left(-\frac{1}{nRT}\int_0^p \alpha dp\right) \tag{8}$$

Consider the following reaction in equilibrium in a closed bomb, with each component being in the gas phase:

$$n_1B_1 + n_2B_2 + n_3B_3 + \cdots\cdot = m_1A_1 + m_2A_2 + m_3A_3 + \cdots\cdot \tag{9}$$

where $A_1, A_2, A_3, \cdots\cdot, B_1, B_2, B_3, \cdots\cdot$ are symbols of product ingredients. $m_1, m_2, m_3\cdots\cdot, n_1, n_2, n_3, \cdots$ denote number of molecules, radicals, or atoms. The pressure equilibrium constant for this reaction is

$$K_p = \frac{(p_{A_1})^{m_1}(p_{A_2})^{m_2}(p_{A_3})^{m_3}\cdots\cdot}{(p_{B_1})^{n_1}(p_{B_2})^{n_2}(p_{B_3})^{n_3}\cdots\cdot} \tag{10}$$

For real gas the activities are equal to the fugacities, so that the equilibrium constant is expressed in terms of the partial fugacity as substitutes for the partial pressures as

$$K_p = \frac{(f_{A_1})^{m_1}(f_{A_2})^{m_2}(f_{A_3})^{m_3}\cdots\cdot}{(f_{B_1})^{n_1}(f_{B_2})^{n_2}(f_{B_3})^{n_3}\cdots\cdot} \tag{11}$$

where f_i is the partial fugacity defined by letting mole fraction of i-th component N_i as follows:

$$f_i = N_i f \tag{12}$$

Substituting Eq. (12) into Eq. (8),

$$(f_i/pN_i)^{\nu_i} = \exp\left(-\frac{\nu_i}{nRT}\int_0^p \alpha dp\right) \tag{13}$$

and the equilibrium constant may be written as

$$K_p = \prod_i f_i^{\nu_i} = \exp\left(\frac{-\Delta\nu}{nRT}\int_0^p \alpha dp\right)\prod_i (pN_i)^{\nu_i} \tag{14}$$

where

$$\Delta\nu = m_1 + m_2 + m_3 + \cdots \quad -n_1 - n_2 - n_3 - \cdots$$

Simplifying the above equation, the exponential term is written by the following definition:

$$y = -\frac{1}{nRT}\int_0^p \alpha dp = -\int_\infty^v \alpha d\left(\frac{1}{v-\alpha}\right) \tag{15}$$

then, it becomes

$$K_p a^{\Delta\nu} = \exp(\Delta\nu y)\prod_i (pN_i)^{\nu_i} = \exp(\Delta\nu y)\prod_i A_i^{\nu_i} \tag{16}$$

where

$$a = v - \alpha$$

Admittedly in such a constant-volume reaction the concentration equilibrium constants are available instead of pressure equilibrium. The relation between these two properties for the propellant amount of 100 grams is given as

$$K = \left(\frac{1.2181}{T}a\right)^{\Delta\nu} \times K_p \tag{17}$$

2.2. Numerical Calculation of Covolume

The chemical equilibrium equations for the reaction products composed of hydrogen, carbon, oxygen, chlorine and nitrogen, corresponding to Eq. (16) are given as follows:

$$(H_2)(O_2)^{1/2}/(H_2O) = a^{1/2}K_1 e^{y/2} \tag{18-1}$$

$$(H)/(H_2)^{1/2} = a^{1/2}K_2 e^{y/2} \tag{18-2}$$

$$(H_2)^{1/2}(OH)/(H_2O) = a^{1/2}K_3 e^{y/2} \tag{18-3}$$

$$(O)/(O_2)^{1/2} = a^{1/2}K_4 e^{y/2} \tag{18-4}$$

$$(N)/(N_2)^{1/2} = a^{1/2}K_5 e^{y/2} \tag{18-5}$$

$$(Cl)/)Cl_2)^{1/2} = a^{1/2}K_6 e^{y/2} \tag{18-6}$$

$$(CO)(H_2)/(H_2O)=aK_7e^y \text{ (carbon formation)} \tag{18-7}$$

$$(CO)(H_2)/(CH_4)(H_2O)=K_8 \tag{18-8}$$

$$(CO_2)(H_2)/(CO)(H_2O)=K_9 \tag{18-9}$$

$$(H_2)^{1/2}(Cl_2)^{1/2}/(HCl)=K_{10} \tag{18-10}$$

$$(N_2)^{1/2}(O_2)^{1/2}/(NO)=K_{11} \tag{18-11}$$

where $(Z_aY_b\cdots)$ is the number of atoms, moles, or radicals contained in the reaction products of the propellant of 100 grams. For the reaction process given by

$$Z_{a_0}Y_{b_0}\cdots \quad \rightarrow (Z_{a_1}Y_{b_1}\cdots)+(Z_{a_2}Y_{b_2}\cdots)+\cdots, \tag{19}$$

the conservation of mass is expressed as a set of the following equations:

$$\begin{aligned} a_0 &= a_1(Z_{a_1}Y_{b_1}\cdots)+a_2(Z_{a_2}Y_{b_2}\cdots)+\cdots \\ b_0 &= b_1(Z_{a_1}Y_{b_1}\cdots)+b_2(Z_{a_2}Y_{b_2}\cdots)+\cdots \\ &\vdots \end{aligned} \tag{20}$$

where a_0, b_0, $\cdots$ are the total number of atoms of the elements included in the propellant of 100 grams and a_1, a_2, $\cdots$ can take only positive integer or zero. Moreover, an energy balance equation is

$$T_e=Q/\overline{c_v}+T_0 \tag{21}$$

where T_e and T_0 are adiabatic explosion temperature and initial temperature respectively. Q represents the heat of explosion and $\overline{c_v}$ is the average heat capacity.

Eqs. (18) (20) (21) and (2) would make it possible to determine Δ based on p_{max} data and to give simultaneous solutions for the other properties. However, it is, of course, not easy to perform the calculation since exponential terms are included in Eq. (18). It is also required to provide accurate pressure data over the wide range of the loading density.

For the avoidance of a source of difficulty that might occur in the present computation, one may allow approximating y by combining the Δ vs. p_{max} relation of liquid monopropellants with those obtained by Cook [3] with respect to some explosives, now that is known the real significance of α. Herein, the approximation of α containing exponential terms of Δ was adopted. A trial-and-error method has been employed to solve the foregoing equations for the typical liquid monopropellants whose maximum burning-pressure data were given by Griffin.

Computation results conducted on OKITAK 5090 digital computer for an iterative process whose method is on the same principle as that developed by authors [2] for determining combustion temperature and product compositions are plotted in Fig. 2. The solid curve drawn through the authors' and Lunn's data [3] were utilized to estimate the covolume of all the propellants of interest. Fig. 2 indicates that weak dependency of α upon the explosion temperature is valid concerning the propellants

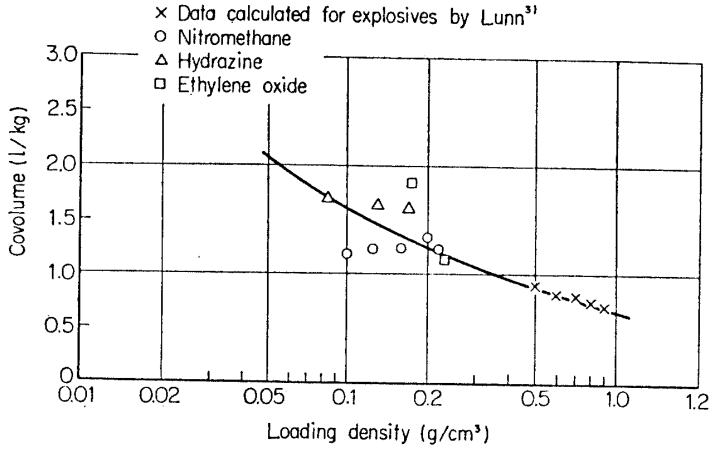

FIG. 2. Calculated relation between covolume and loading density, based on the maximum burning-pressure data of typical liquid mono-propellants and condensed explosives in ballistic bombs

of similar compositions. The postulation of being treated the covolume as a function of the loading density regardless its explosion temperature was already proposed by Cook [*3*], [*4*] for the high explosives. Expanding this concept to the heterogeneous propellants should be allowed without risk of oversimplification, although there still exists a problem with respect to metallized propellants.

3. EXPERIMENTAL APPARATUS AND METHOD

A closed bomb in which composite solid propellants were burned is shown in Fig.3. The apparatus is suitable for the operation at pressures up to 3,000 kg/cm^2 It consists of heavy wall steel-cylinder of nearly 180 ml, installed a pressure transducer and a vent valve in one end and electrically-ignited pyrotechnique primer as an igniter in the opposite side. The transducer is a semi-conductor type of strain gauge mounted on the steel disc whose strain is transmitted by the piston rod. This pressure sensing element was satisfactorily available for measuring an ignition transient pressure. System calibration can be accomplished easily with static pressures. Illustrative calibration data representing electric resistance-stress relation of the strain gauge system is given in Fig. 4.

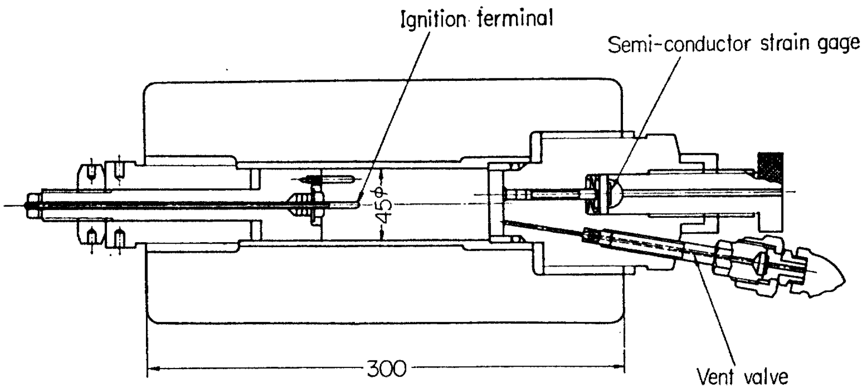

FIG. 3. Sectional view of ballistic bomb

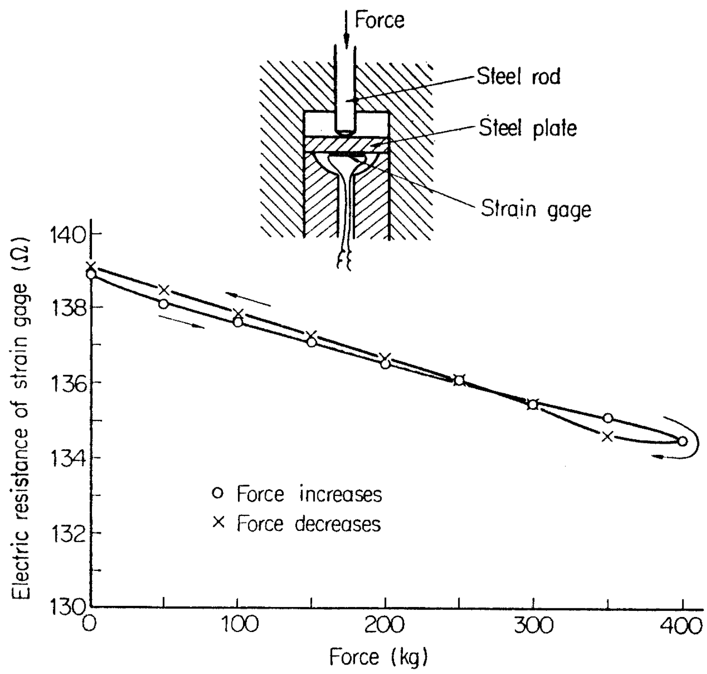

FIG. 4. Calibration curve of semi-conducter gauge reistance

The output of the bridge circuit of semi-conductor gauge is amplified and recorded by means of an electromagnetic oscillograph, synchroscope combined with camera and pen-writing recorder. A schematic diagram of the measurement system is shown in Fig. 5. Pressure-time history is put on record for the period of a few seconds from the instant of ignition. Test samples of solid propellants were of granular form. Aspect of the pressure-time curves until the maximum pressure has been reached, does not show significant discrepancy between the granular and the powder-state propellant.

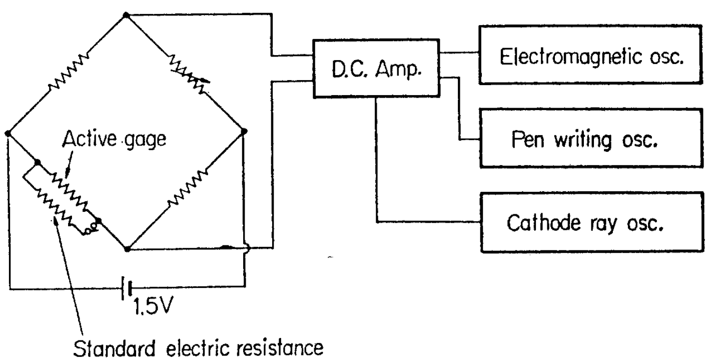

FIG. 5. Block diagram of measuring equipments

The semi-conductor gauge features to be capable of evaluating the explosion pressure and temperature based on the pressure decay curves, and the versatility of being permitted static calibration because there is no need to account for leakage of the electric change such as in the case of piezo-crystal gauge. On the other hand, disadvantage of this sensing element is to have high sensitivity to the ambient temperature. Accordingly, it must be avoided that these transducers are exposed to a severe environment. This requirement eliminates the most conventional design with respect to the strain gauge installation. In order to make the burning pressure data more accurate, it should be corrected for the reaction products of the igniter itself and heat loss during burning. However, as they are cancelled each other and generating gases from the primer of aluminum and potassium perchlorate particles combination are negligible compared to the free volume of the bomb, herein, no correction is conducted.

A typical record of the pressure-time history obtained on the electromagnetic oscillograph equipped with a galvanometer of the natural frequency of 2,000 cps is shown in Fig. 6. Prior to every firing, zero adjustment and pressure calibration by inserting the standard electric resistance in the position parallel with the active gauge have been made.

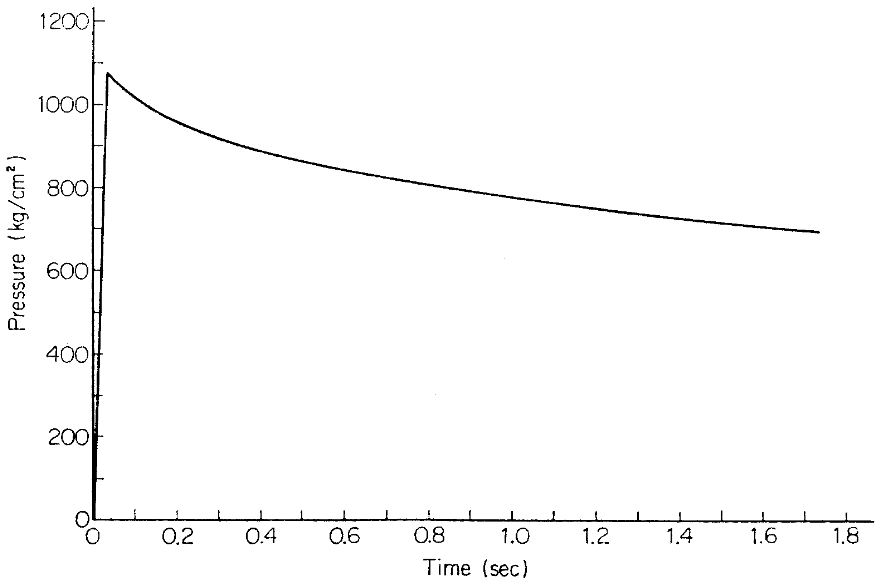

FIG. 6. Typical pressure-time history for composite solid propellant

The random scatter attributed to measurement uncertainties of pressure seems to be estimated as $\pm 3\%$ at 1,000 kg/cm^2 with an additional uncertainties $\pm 2\%$ due to non-uniform propellant properties. The percent standard deviation of 5 runs at nearly 1,000 kg/cm^2 has for the present system ranged $1 \sim 4\%$. If with the ballistic bomb method advanced instrumentation is taken in pressure measurement, the data scatter would be decreased to less than 2%. At the present time, an improvement in the pressure transducer and the overall recording are being undertaken. The use of Kistler quartz pressure transducer and transistorized change amplifier may provide more accurate measurement of dynamic pressure-oscillation at extremely high pressures.

After the firing test has been got through, burned gases are ejected through the venta valve out and reignited.

4. Experimental Results and Discussion

Measurements of burning pressure in a constant-volume bomb were made on both of aluminized and non-aluminized composite propellants. Polysulfide, polyurethane and polybutadiene elastomers as fuel binders were combined with ammonium perchlorate oxidizer. The oxidizer content was varied from 60 up to 80%. In Fig. 7, are shown the values of the maximum burning pressure against various loading densities for typical solid propellants. It is noticed that the following first-order approximation fits the data over the range of the loading density 0.08~0.2 g/cm³ suggesting that Noble-Abel equation is valid:

$$p=\frac{\theta_1 \Delta}{1-\theta_2 \Delta} \tag{22}$$

where θ_1 and θ_2 are parametric constants. Since Eq. (22) neglects effects of pressure and temperature on dissociation, the measurement result may be somewhat discrepant from this empirical equation. Nevertheless, the trend is quite clear.

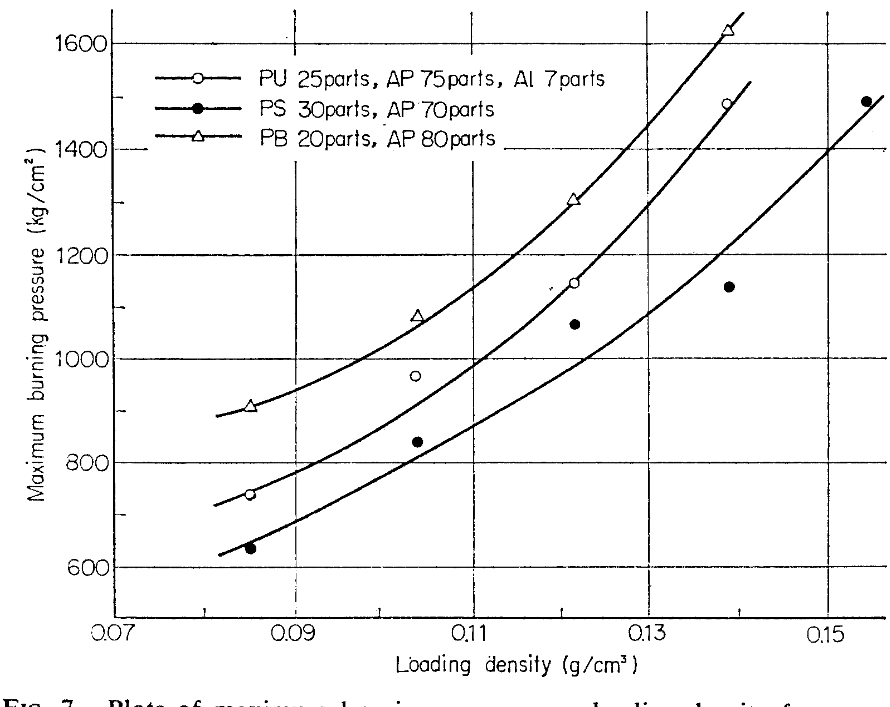

FIG. 7. Plots of maximum burning pressure vs. loading density for several composite solid propellants

When the solid propellant is burned in a constant-volume bomb, one must correlate the explosion temperature with the combustion temperature which is found in the specific impulse equation. The following relation proposed by Griffin facilitates an approximate estimate of the specific impulse:

$$T_e=\kappa T_c \tag{23}$$

On the other hand, by the definition of impetus it is expressed per unit mass of propellant as

$$I_0=\left(\frac{RT_e}{\overline{m}}\right)_{p\to 0} \tag{24}$$

The above equation implies that it requires the sufficient pressure data for obtaining a reliable impetus enough to perform the satisfactory graphical extrapolation $p\to 0$. Besides, of course, extrapolated values are greatly influenced by the end plots through which a line will be drawn out and relative heat loss during burning would be large in the case of the lower loading density, resulting in making underestimation for propellant performance. Therefore, there is a serious requirement for remedying "extrapolation difficulty".

Since the apparent impetus obtained from the firing test of the propellant in a closed bomb is written as the following:

$$I_0'=(RT_e/\overline{m})_{p\to 0}+\alpha p_{\max}=I_0+\alpha p_{\max} \tag{25}$$

Then, on the assumption described in Section 2, namely by utilizing the relation between the burning pressure and the loading density shown in Fig. 2 the impetus will be easily derived. If not permissible the prediction of the covolume based on one burning pressure datum only, $\left(\frac{RT_e}{\overline{m}}\right)_{p\to 0}$ is yielded with higher accuracy from the slope of the straight line given by some plots of I_0' vs. $p_{\max}$.

Thus, specific impulse of solid propellants can be obtained by replacing Eqs. (23) and (24) into specific impulse equation as follows:

$$I_{sp}=\frac{1}{g}\sqrt{\frac{2gI_0}{\kappa-1}\{1-(p_j/p_c)^{\frac{\kappa-1}{\kappa}}\}} \tag{26}$$

For instance, if a specific heat ratio of 1.25 and an operating chamber pressure of 70 atm. are given, Eq. (26) becomes

$$I_{sp}=(7.462)(10^{-2})\sqrt{I_0} \tag{27}$$

Where I_0 is given by the unit of kg-cm/kg. In table 1 are summarized the illustrative specific impulse data calculated according to the method described in this section, which yield the results in considerable agreement with the theoretical performances, regarding non-aluminized propellants. Whereas with the aluminized propellants there is a large discrepancy between theory and experiment probably due to optimistic values of theoretical impulse as a result of poor information on the nature and thermodynamic properties of aluminium burning. The deviation of gas containing gaseous metal and condensed oxides from Noble-Abel equation must be also taken into consideration. However, performance data obtained by means of the test firings of midget motors are fairly reconciled with those of aluminized propellants calculated according to the present procedure. Thus, in spite of rough simplification, the feasibility of deriving the performance on both solid and liquid propellants by employing measurement results of the maximum burning pressure in a constant-volume bomb was ascertained, by a comparison of the calculated specific impulse with theoretical values for liquid monopropellants summarized in Table 2.

TABLE 1. A comparison of theoretical specific impulse of some composite solid propellants with values obtained by the modified ballistic bomb method

Propellant (parts by weight)			Specific impulse (sec)* p_c=70 ata	
Fuel binder	Oxidizer	Metal particles	Experimental	Theoretical
PB, 20 parts	AP, 80 parts	—	232	234
PB, 22	AP, 87	—	225	226
PU, 23.5	AP, 76.5	Al, 7	225	256
PU, 25	AP, 75	Al, 7	221	253
PS, 30	AP, 70	—	204	221
PS, 35	AP, 65	—	215	217
PS, 40	AP, 60	—	197	203

PB : Polybutadiene, PU : Polyurethane and PS : Polysulfide
* Values calculated from averaged p_{max} data at loading density 0.156

TABLE 2. A comparison of the specific impulse of some liquid monopropellants provided by the present method with Griffin's data

Propellant	Loading density (g/cm³)	Specific impulse (sec) p_c=315 Psia		
		Present method	Griffin's method	Theoretical value
Nitromethane	0.20 0.17 0.125	213 203 216	219	220
Hydrazine	0.17 0.125	181 184	188	188~190
Ethylene oxide	0.23 0.18	129 136	142	159~162*

* If ethylene oxide decomposes according a reaction, $C_2H_4O \rightarrow CO + 2H_2 + C$ (carbon in equilibrium with gas), the specific impulse becomes 128 sec.

5. CONCLUDING REMARKS

The validity of expressing the covolume of Noble-Abel equation of state as a function of the loading density alone has been confirmed from the maximum burning pressure data given by Griffin. For non-metallized propellants, it is possible to use a form of this function induced from semi-empirical thermodynamic calculation. This postulation has been applied to several composite solid propellants and on simple procedure will yield the specific impulse which approaches theoretical value. Although calculated performances for aluminized propellants show considerable difference from theoretical, these are rather reasonable in view of the data of motor firings. Behaviour of the burned gas of aluminized propellants in such a closed bomb is an interesting problem, but it seems likely that there is no remarkable escaping tendency from Noble-Abel equation of state.

This constant-volume method is available for ranking the solid propellants. However, it is recommended that measurement of burning pressure, in practice, is conducted at higher loading densities as far as possible, because lowering the loading density would apparently increase the heat loss percentages. If proper care on the experimental procedure and the improvement on the measuring system are taken, this would give a key for the preliminary judgement as to whether a propellant under the development is accepted or rejected, and would promise the available information that might serve as a criterion.

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