

# Fundamental Studies on Combustion of Solid Propellants

## Part II. Burning Velocities of Multi-component Fuel

Masao Nagao\* and Tsutomu Hikita\*\*

### I. Introduction

In combustion of composite propellants, many sorts of the gas-phase reactions among pyrolysis products of fuel and oxidizer components occur. Both fuel and oxidizer gases consist of a number of components. In such a system, different phenomena will be expected to take place from those in systems which consist of a single component of fuel and oxidizer respectively.

Especially in an ammonium perchlorate oxidized propellant, ammonia is liberated into pyrolysis products, which produces nitrogen oxides during combustion. Consequently ammonia will affect burning velocities of hydrocarbon air systems.

McD. Cummings<sup>1)</sup> investigated perchloric acid flames with methane, ethane and so on. This seems the first report concerning burning velocities in a system of pyrolysis products of composite propellants. With regard to combustion in multi-component systems, J. W. Armitage and P. Gray<sup>2)</sup> reported an investigation dealing with ternary mixtures of ammonia with hydrogen, nitric oxide, nitrous oxide or oxygen. As to systems including hydrocarbons, many investigations have been reported of inflammability limits but those of burning velocities are very few except investigations regarding effects of a small amount of additives on burning velocities. In a study

by Simon<sup>3)</sup> on the effect of additives on a propane-air flame, carbon disulfide was used as one of the additives and it was found that, despite the burning velocity of carbon disulfide in saturated air being higher than that of propane in air, the addition of carbon disulfide to the propane flame reduced the burning velocity over the wide range of fuel/air ratio studied. This reduction continued progressively until forty percent of the fuel was carbon disulfide, when the investigation was terminated.

In this program, an investigation was conducted of burning velocities of combustible gases, the components of which were determined after pyrolysis study of polymeric binder of a composite propellant, which were determined after pyrolysis study of polymeric binder of a composite propellant, which was reported previously.<sup>4)</sup> This study may offer a better understanding of the mechanism not only of flame propagation but also of composite propellant combustion.

Of a number of method of measuring burning velocity, a tube method was employed. This method is very simple in operations of the apparatus. A difficult problem exists only in that calculation of flame front area is complex when hemispheric shapes of flames are not obtained. And although limitation exists that burning velocities are reduced in a tube by cooling effect of the tube wall, this method has been utilised by various investigators.<sup>5)-10)</sup>

### II. Experimental Apparatus and Procedure

Received. July 22, 1966

\* At present, Sakanoichi-Plant, Asahi Kasei Co. Ltd., Ohita.

\*\* Faculty of Engg., Univ. of Tokyo, Bunkyoiku, Tokyo.

A flame-speed measuring apparatus consisted of a Pyrex tube, 1,220 mm long, with an internal diameter of 26 mm open at the ignition end and closed at the other end. The apparatus assembles for the introduction of a fuel-air mixture are shown in Figure 1. Two tungsten electrodes, which were located in the tube at 30 mm from the open end, were used to ignite the mixture.

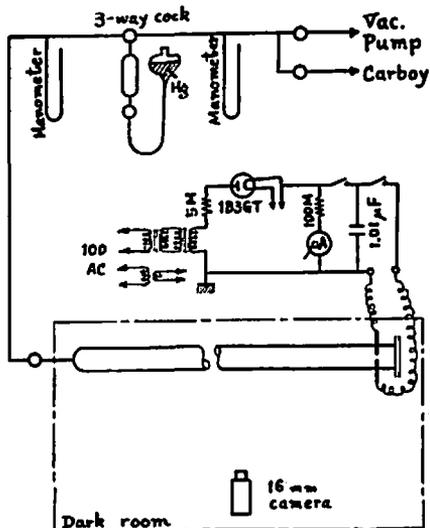


Fig. 1. Apparatus for Measuring Burning Velocity

As fuels, butadiene-1,3, ethylene and ammonia were selected for reasons described above.

Gaseous mixtures of each fuel with air were made up in 20-liter carbonyls and were allowed to become completely homogeneous by standing 24 hours before samples were withdrawn. Besides, 8-liter flask with a circulation pump was designed after H. M. Papée et al,<sup>11)</sup> and utilized for mixing combustible gases. The combustion tube was evacuated to a pressure of at least 0.1 millimeter of mercury and the sample was introduced and brought up to atmospheric pressure. At least five minutes were allowed for the mixture to become quiescent, the stopper was carefully removed, and the mixture was ignited (1.01 micro-farad, 4.5 kV). Flame propagation was photograp-

hed by a framing camera (16 mm film, 64 frames per second), and a rotating drum camera. The film speed and exposure time of 16 mm moving camera were calibrated by photographing a luminous point swept at a known speed on an oscilloscope screen. For each fuel-air mixture three records were taken to obtain the values of flame velocity.

### III. Results

The mode of flame propagation consists of three regions, i.e., the initial phase, uniform movement out, See copy. Framing photographs and drum camera records of flame propagation in a tube are shown in Fig. 2. Propagation velocities of flames were measured

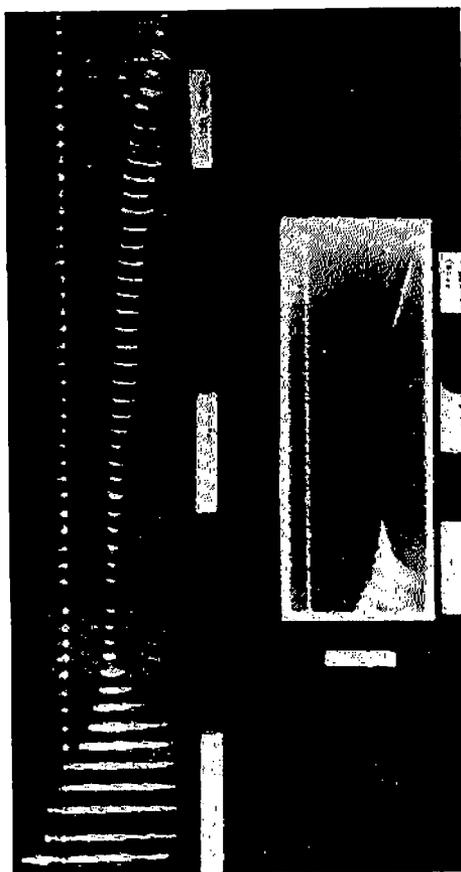


Fig. 2. High-speed Photographs (Left) and Rotating Drum-camera Record (Right) of Flame Propagation in a Tube (open at the ignition end and closed at the other end. Horizontal tube.) Mixture: 1.3-Butadiene (7.5%)-Air Initial Pressure: Atmospheric

from successive photographs. The burning velocity, or fundamental flame velocity, can be calculated from the following equation;

$$S_u = \frac{A_t}{A_f} V \quad (1)$$

where  $S_u$  is the burning velocity,  $A_t$  the cross area of the tube,  $A_f$  the flame front area, and  $V$  the propagation velocity of the flame. The area of flame surface is calculated

on the assumption based on the flame shape. Shapes of flames which propagate steadily in a tube, can be classified into two; a hemispheric and a tilted flame. For the latter, Coward and Hartwell<sup>12)</sup> proposed a semi-ellipsoid approximation. On this assumption the flame front area is approximately equal to that of a semi-ellipsoid, which is calculated by Equation (3). (See Table 1). The auth-

Table 1. Equations of Flame Front Areas

Approximation	Equation	
Hemisphere	$A_f = 2\pi r^2$	(2)
Semi-ellipsoid	$A_f = \pi b(a^2 - c^2)^{1/2} E(k, \phi) + \pi bc^2(a^2 - c^2)^{-1/2} F(k, \phi) + \pi c^2$	(3)
Paraboloid	$A_f = \frac{\pi}{6a^2} \left[ 4a^2(R-b)^2 + 1 \right]^{1/2} - 1 \left] + \frac{2}{a^2} \int_{\frac{(r-\beta)^2}{\xi}}^{\frac{(r+\beta)^2}{\xi}} \frac{\sqrt{4\xi^2 + 1} \cdot \xi \cdot \cos^{-1} \left[ \frac{1}{2\beta} \left( \frac{\beta^2 - r^2}{\xi} + \xi \right) \right]}{d\xi} \right]$	(4)

Table 2. Calculation of  $A_f$  and  $S_u$

Run No.	(cm V/sec)	Approximation	$A_f$ (cm <sup>2</sup> )	$A_t/A_f$	(cm $S_u$ /sec)
EN-51 (Right)	77.0	Hemispheric	10.6	1/2	38.5
EN-53 (Left)	91.0	Parabolic	11.2	1/2.12	43.0
		Ellipsoidal	10.1	1/1.91	47.7

ors, on the other hand, presented a paraboloid approximation according to the shape of a flame photographed. By letting a formula of a paraboloid be

$$z = a(x^2 + y^2),$$

a flame front area is expressed by Equation (4).

An explanation Out, see copy (3) and derivation of Equation (4) are described in Appendix of this paper. The numerical integration of Eq. (4) is made possible by using Simpson's "a third power law". An example of calculation is illustrated in Table 2. and Figs 3. In a stoichiometric mixture of ethylene (1)-ammonia (0.4)-air, hemispheric flames were obtained in two measurements and in the third measurement [tilted flames were photographed. Burning velocities were calculated according to approximations



Fig. 3. Hemispheric and Tilted Flames in the Same Combustibles.

mentioned above and they were compared with each other (Table 2). The value obtained for the third by the paraboloid approximation gave a better agreement with those obtained for the first two on the hemispheric assumption, of errors could be regarded as the least of those which resulting from the three approximations. Against mixture composition are plotted burning velocities of ethylene air in Fig. 4,

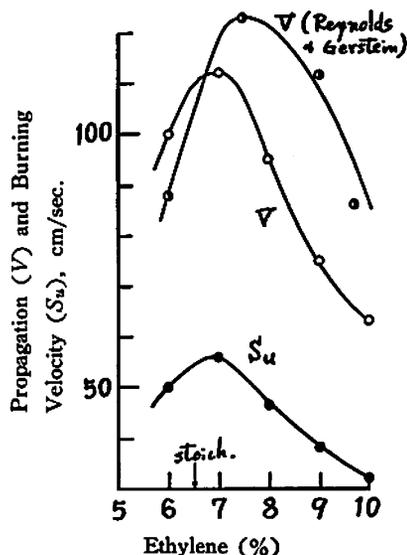


Fig. 4. Propagation and Burning Velocities of Flames in Ethylene-Air Mixtures.

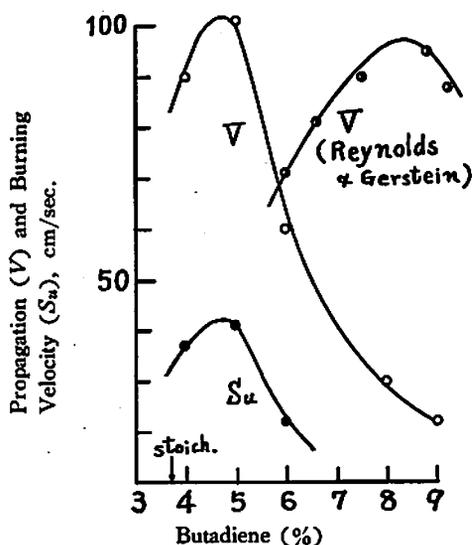


Fig. 5. Propagation and Burning velocities of Flames in Butadiene-Air Mixtures.

of butadiene-air in Fig. 5, of ethylene-butadiene-air in Fig. 6, of butadiene-ammonia-air and ethylene-ammonia-air in Fig. 7. The stoichiometric mixture of ammonia and air

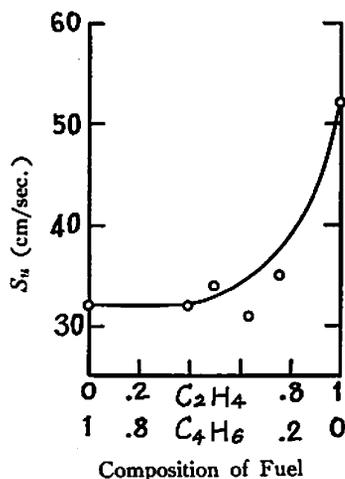


Fig. 6. Burning Velocities in stoichiometric Mixtures of Ethylene-Butadiene-Air.

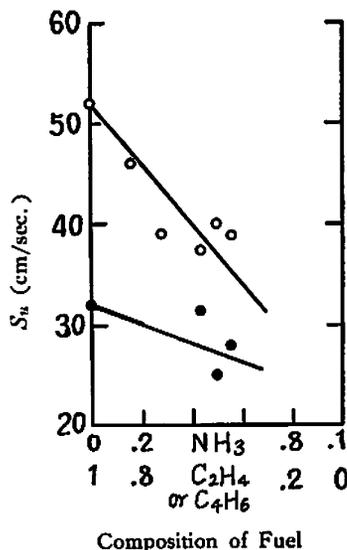


Fig. 7 Burning Velocities in Stoichiometric Mixtures of Ethylene-Ammonia-Air (—○—) and Butadiene-Ammonia-Air (—●—)

could not be ignited with the ignition device and energy employed here. And burning velocity of the mixture cannot be found in any literature although many investigations have been reported regarding combustion of

gases including ammonia. Effects of butadiene on burning velocities of ethylene-air, and of ammonia on those of ethylene-air and of butadiene-air were very remarkable. The burning velocity of the stoichiometric ethylene-air mixture was reduced to its seventy-three percent when twenty percent of ethylene was replaced by butadiene. However that of the stoichiometric mixture of butadiene-air was not almost changed even if forty percent of butadiene was replaced by ethylene. The effect of ammonia on burning velocities of ethylene-air is larger than that on those of butadiene-air. The extents of these effects are compared in terms of slopes of burning velocity versus fuel composition curves; the slope of the curve of ethylene-ammonia-air is minus 0.28 cm/sec. per percent of ammonia in fuel component, and that of butadiene-ammonia air minus 0.09 cm/sec. per percent of ammonia in fuel component.

#### IV. Discussion

In Figures 4 and 5, flame propagation velocities are plotted which were obtained by Reynolds and Gerstein<sup>6)</sup>. The difference is very large between our and their data. We plotted those values which were obtained in the "Uniform Movement" region by reading successive photographs. The data, however, of Reynolds and Gerstein were those which

were taken by using two photoelectric cells located at points 10 and 40 centimeters from the ignition spark gaps. (Other conditions, (i.e., a tube diameter, the initial pressure, a tube open at the ignition end and closed at the other end, etc.) were almost the same). Consequently their values correspond to mean values between those in the "Initial Phase" and those in the "Uniform Movement" or "Vibratory Burning" region. In fact, such mean values calculated from the authors' data are almost near to the values presented by Reynolds and Gerstein.

Burning velocities of ethylene-air and of butadiene-air are cited in Table 3 from literatures<sup>13-16)</sup>. The values obtained in this program are a little smaller than those obtained by burner and other methods. This resulted from the fact that part of energy of a flame was absorbed by the wall of the tube when a tube method was employed. A problem also exists in calculation of flame front areas. When hemispheric flames were obtained values of their surface areas are evaluated without difficulty.

When tilted flames were observed, however, the evaluation will easily introduce errors even by using the paraboloid approximation. Fortunately in our experiments, hemispheric flames were observed in most cases.

Table 3-1. Burning Velocities of Ethylene-Air Mixtures

Investigator	Pickering & Linnett <sup>13)</sup>	Strehlaw & Stuart <sup>13)</sup>	Conan & Linnett <sup>15)</sup>	Hoar & Linnett <sup>16)</sup>	
Method	Soap Bubl. (Schlirn.)	Improved Soap Bubl.	Burner (Schlirn.)	Burner (Shadow)	
Ethylene (%)	5	41.8		43.0	38.5
	6	56.6		55.6	52.1
	6.5	-	62.4	-	
	7	65.6	66.2	65.5	66.7
	7.5	-	68.6	67.8	68.8
	8	67.2	65.8	67.5	67.7
	9	55.1		56.9	58.7
	10	38.5		39.9	29.0

Table 3-2. Burning Velocities of 1,3-Butadiene

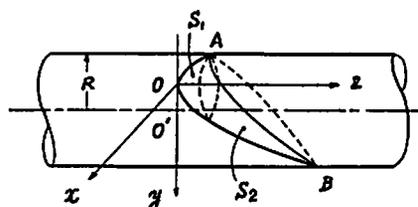
Investigator	Method	Composition of Mixture Gases	Burning Velocity cm/sec.
Fenn & calcote <sup>17)</sup>	?	Butadiene-Air (Stoich.)	49.6
Badin & Stuart <sup>18)</sup>	?	Butadiene-(He+O <sub>2</sub> ) (Stoich.)	145
Badin & Stuart <sup>18)</sup>	?	Butadiene-(N <sub>2</sub> +O <sub>2</sub> ) (Stoich.)	40

Many investigations have been reported of effects of additives on burning velocities of combustible gases of which fuel consists of a single component. Since hydrocarbons employed as additives would also act as a fuel component, it will be reasonable to regard fuels including additives as multi-component. Effect of an inhibitor as an additive, for example, is explained qualitatively in terms of its rapid reactions with reactive radicals such as oxygen, hydrogen, and hydroxyl. But these elementary reaction kinetics have not been developed enough to express over-all burning velocity. An attempt was made by van Tiggelen et al<sup>19)</sup> to estimate burning velocity from elementary reaction kinetics theoretically. On the other hand, burning velocity curves obtained for multi-component fuels in this research suggest us a probability that these curves will be explained in a manner analogous to kinetics of copolymerization or co-oxidation. Unfortunately, since elementary reactions remain to be worked out, further discussions are difficult at present. Nevertheless, this research gave a direction for further study in this field. And if the relationship between elementary reactions and over-all combustion were solved, the pressure dependence of burning velocities<sup>20)21)22)</sup> would necessarily be explained and this in turn would offer directions for formulations of solid rocket propellants.

### V. Appendix

#### Semi-ellipsoid approximation

According to Coward and Hartwell, the flame front area of a tilted flame was approx-



- O:  $x=0, y=0, z=0$
- O':  $x=0, y=b, z=0$
- A:  $x=0, y=-(R-b), z=a(R-b)^2$
- B:  $x=0, y=R+b, z=a(R+b)^2$

Fig. A-1. A Picture of a Tilted Flame

oximately equal to the area of a semi-ellipsoid, the axes of which were equal to (1) a line joining the points where the flame touched the top and bottom of the tube, (2) twice the perpendicular distance between that line and the point most remote from it on the photograph of the flame front, and (3) the diameter of the tube. The area of the half-surface of the ellipsoid was calculated by the following formula:

$$A_f = \pi b(a^2 - c^2)^{-1/2} E(k, \phi) + \pi b c^2 (a^2 - c^2)^{-1/2} F(k, \phi) + \pi c^2 \quad (3)$$

where  $a, b, c$  are the semi-axes,  $a > b > c$ ;  $k = c'/c$ ;  $\phi = \sin^{-1} e$ ;  $e$  and  $e'$  are the eccentricities of the ellipses in the plane of the axes  $a$  and  $c$ , and  $b$  and  $c$ , respectively. The values of  $E(k, \phi)$  and  $F(k, \phi)$ , the elliptic functions of the second and first kind respectively, are obtained from standard mathematical tables.

#### Paraboloid approximation

The authors regarded a tilted flame as a paraboloid enclosed in a tube with a parallel but detached center line (Figure A-1). Put coordinate axes as illustrated in the figure,

and let a formula of a paraboloid be

$$Z = a(x^2 + y^2)$$

Then, the flame front area can be expressed as a sum of  $S_1$  and  $S_2$  as follows;

$$A_f = \frac{\pi}{6a^2} \left[ 4a^2(R-b)^2 + 1 \right] - 1 \left[ \frac{(r+\beta)^2}{a^2} \int_{\frac{(r-\beta)^2}{a^2}}^{\frac{(r+\beta)^2}{a^2}} \sqrt{4\xi^2 + 1} \cdot \xi \cdot \cos^{-1} \left[ \frac{1}{2\beta} \left( \frac{\beta^2 - r^2}{\xi} + \xi \right) \right] d\xi \right] \quad (4)$$

where  $\beta$  is equal to  $ab$ ,  $r = aR$ , and  $\xi^2 = ax$ .

#### References:

- 1) Cummings, McD., 10th Symp. on Combustion, p. 1365 (1965)
- 2) Armitage, J. W., and P. Gray, Comb. and Flame, 9, p. 173 (1966)
- 3) Simon, D. M., Engine Report E. 69, (1951), Aero. Res. Labs. Dept. of Supply, Melbourne, Australis. The authors could not get the original paper and the information was obtained from "Selected Combustion Problems" (AGA-RD) p. 176 (1954)
- 4) Nagao, M., and T. Hikita, This journal, (1966)
- 5) Gerstein, M., O. Levine and E. L. Wong, J. Am. Chem. Soc., 73, p. 418 (1951)
- 6) Reynolds, T. W., and M. Gerstein, 3rd Symp. on Combustion, p. 790 (1951)
- 7) Mason, W., and R. V. Wheeler, J. Chem. Soc. (London), p. 1044 (1917)
- 8) Mason, W., and R. V. Wheeler, Ibid., p. 578 (1919)
- 9) Payman, W., and R. V. Wheeler, Ibid., p. 1251 (1923)
- 10) Chapman, W. R., and R. V. Wheeler, Ibid., p. 38 (1927)
- 11) Papée, H. M., A. Montefinale and T. W. Zawidzki, J. Sci. Instrum., 39, p. 394 (1962)
- 12) Coward, H. F., and F. J. Hartwell, J. Chem. Soc. (London), p. 2676 (1932)
- 13) Strehlow, R. A., and J. G. Stuart, 4th Symp. on Combustion p. 339 (1953)
- 14) Pickering, H. S., and J. W. Linnett, Trans. Trans. Faraday Soc., 47, p. 989 (1951) (1951)
- 15) Conan, H. R., and J. W. Linnett, Ibid., 47, p. 981 (1951)
- 16) Hoar, M. F., and J. W. Linnett, Ibid., 47, p. 176 (1951)
- 17) Fenn, J. B., and H. F. Calcote, 4th Symp. on Combustion, p. 231 (1953)
- 18) Badin, E. J., and J. G. Stuart and R. N. Pease, J. Chem. phys., 17, p. 314 (1949)
- 19) van Tiggelen, A., and J. Deckers, 6th Symp. on Combustion, p. 61 (1956)
- 20) Strauss, W. A., and R. Edse, 9th Symp. on Combustion, p. 377 (1959)
- 21) Simon, D. M., "Selected Combustion Problems" (AGARD), p. 59 (1953)
- 22) Lewis, B., Ibid., p. 177 (1954)

## 固体推進薬の燃焼に関する基礎的研究 (II)

### 多成分系燃料の燃焼速度

長尾雅男・疋田 強

混成系推進薬の気相における反応は燃料成分及び酸化剤成分の分解ガスの間で起る燃焼反応であり、燃料、酸化剤共に多成分からなる系の反応である。前者については著者らが前報で報告した通りであり、後者については既に多数の報文が提出されている。そこで (i) 一成分系燃料の燃焼速度 ( $S_u$ ) と多成分系燃料の  $S_u$  との比較 (ii) 炭化水素系燃料に  $NH_3$  (過安の分

解ガス成分) が含まれる場合の  $S_u$  の測定を行ない、(iii) 従来の燃料理論の限界を指摘し、(iv) 将来の研究方向に対して一提案を行なつた。

$S_u$  の測定には燃焼管法 (水平) を採用、火炎伝播速度 ( $v$ ) 及び火炎面々積 ( $A_f$ ) を高速度写真 (16mm フィルム, 64コマ/秒) で測定した。燃焼管断面積を  $A_t$  とすれば  $S_u = (A_t/A_f) \cdot v$  の算出に際し Coward

& Hartwell の回転楕円体面近似に対し、著者らは回転放物面近似を提出した。

可燃混合気体は前報に基きエチレン-空気 (I), ブタジエン-空気 (II), エチレン-ブタジエン-空気 (III), エチレン-アンモニア-空気 (IV), ブタジエン-アンモニア-空気 (V) を選び, (I), (II) についてはそれらの  $\nu$  を Reynolds & Gerstein の  $\nu$  と比較した。彼らの測定は光電管によるもので  $\nu$  の測定値は火災伝播の初期及び定常領域の平均値に相当し, 著者らが写真撮影により定常領域のみについて測定した  $\nu$  の値と大巾に異なっている。(I), (II) について測定された  $S_u$  はパーナー法等による  $S_u$  よりも低い値となっているが, これは火災のエネルギーが管壁に吸収されるため、燃焼管法自体に由来するものであ

る。燃料が二成分でも (III) と (IV) 及び (V) とでは  $S_u$  の変わり方が異なる。これらの場合、共酸化又は共重合に類似の速度論的考察が適用できると考えられ、種々の  $S_u$  ~ 燃料組成曲線が得られるのはそれぞれの系における各素反応の速度比によるものである。類似の実験結果はプロパン-二硫化炭素-空気系の  $S_u$  についても報告されている (Simon)。これらの実験結果は気体燃焼速度に関する従来の理論では説明できない。燃焼速度の圧力依存性が従来の理論で表わされないのもこの点に起因している。従つて今後は燃焼に含まれる素反応の機構と速度論の研究、及び素反応の速度と  $S_u$  との関係式の確立がなされねばならない。そうすれば  $S_u$  の圧力依存性及び添加剤の効果等が明白になるであろう。

訂 正

火薬類の熱安定度 (訂正)

27巻 105 頁の報文に就き、一部誤りがありますので訂正いたします (篠原昌史)。

頁 行	誤	正
105 右17	$\tau = A \exp \left[ -\frac{E}{RT} \right]$	$\tau = A \exp \left[ \frac{E}{RT} \right]$
105 右23回	—	本号に記す
106 左 2	$\log \tau = A' - \frac{E}{RT}$	$\log \tau = A' + \frac{E}{RT}$
106 左 7	22.1	22.6

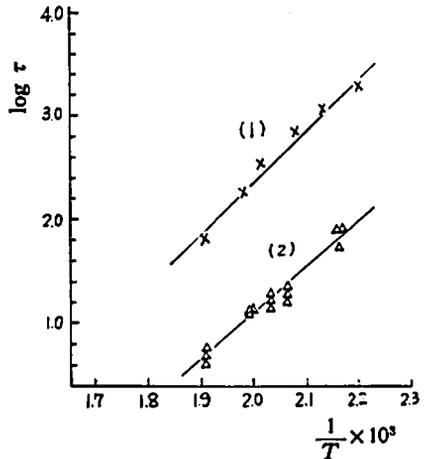


Fig. 1  $\log \tau$  v. s.  $\frac{1}{T}$  for smokeless powder  
(1) The method described in Vol. 27, p. 105  
(2) Krupp's method

Some Experiments on the Sensitivity of Initial Explosives (訂正)

27巻第2冊73頁の報文中誤りを次の如く訂正いたします (沢田維男)。

頁 行	誤	正
73 左 2	arried out	Carried out
" 右 Fig. 1	縦軸に	Detonation Velocity (m/sec) 入れる
75 左 mean value Hの項下から8	234	222
76 左 下から4	The between	The relations between
79 右 上から14	( $\Delta=0.577$ )	( $\Delta=0.557$ )
" 右 上から16	dry state, generaitive than	dry state generally more sensitive than
80 table 4 最右下から3	11.23	11.25
" " 下から1	59.6	9.98
85 右 下から10	oney by water	only by water