MEMORANDUM REPORT ARBRL-MR-03152

COMBUSTION STUDIES OF VERY HIGH BURNING RATE (VHBR) PROPELLANTS

Arpad A. Juhasz
Ingo W. May
William P. Aungst
Franz R. Lynn

FEBRUARY 1982

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: Memorandum Report ARBRL-MR-03152
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): Combustion Studies of Very High Burning Rate (VHBR) Propellants

5. TYPE OF REPORT & PERIOD COVERED: Memorandum Report

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): Arpad A. Juhasz, Ingo W. May, William P. Aungst, Franz R. Lynn

8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS
U.S. Army Ballistic Research Laboratory
ATTN: DRDAR-BLI
Aberdeen Proving Ground, MD 21005

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 1L162618AH80

11. CONTROLLING OFFICE NAME AND ADDRESS
U.S. Army Armament Research & Development Command
U.S. Army Ballistic Research Laboratory
ATTN: DRDAR-BL
Aberdeen Proving Ground, MD 21005

12. REPORT DATE: FEBRUARY 1982

13. NUMBER OF PAGES: 48

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) jmk

The burning and impetus characteristics of a family of very high burning rate (VHBR) boron-hydride-based propellants were determined using the closed chamber technique. A systematic examination of burning behavior vs chemical composition was made. The samples studied included bare, steel cased, and larger full bore cylindrical samples. Pressure time data were reduced to apparent linear burning rates using the conventional laminar burning assumptions made in closed chamber reductions. The results indicate that tailoring sample

burning rates between 1 and 500 m/s may be possible. On the other hand, unlike conventional propellants, VHBR propellant burning rates are thought to depend not only on sample formulation but also on porosity, physical integrity, sample diameter, and confinement. These results point to a possible burning-with-breakup mechanism for these materials.

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I. INTRODUCTION

Nonconventional propulsion concepts are being seriously considered in today's gun ballistics community to achieve muzzle velocities considerably in excess of current state-of-the-art gun systems. The higher muzzle velocities are highly desirable for increasing the effective range, improving target penetration, or increasing the hit probability of gun systems.

The use of conventional gun propellants with burning rates on the order of 0.2 m/s has, in the past, been a major factor preventing the successful exploitation of promising non-conventional propulsion concepts such as the traveling charge effect originated by Langweiler as "Impulse Antrieb"[1]. In fact, Langweiler's original calculations indicated that burning rates up to 500 m/s would be required for traveling charge propellants.

Explosives detonate at rates of 2000 m/s and higher. These reaction propagation rates are, unfortunately, too high for use in gun propulsion applications. What is needed, therefore, is a family of propellants which has propagation rates intermediate between deflagration and detonation, materials reacting between 1 and 1000 meters per second. Materials such as these could make feasible a variety of advanced propulsion concepts such as traveling charge,[2] consumable sabot[3] and FILMBAL[4]. Unfortunately, thermodynamic theory indicates only two stable reaction regimes to be possible, deflagration and a high order detonation[5]. This would seem to make the desired intermediate range inaccessible. In practice, however, intermediate rate reactions have been observed in some condensed explosives[5] and further,

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[1] *H. Langweiler, "A Proposal for Increasing the Performance of Weapons by the Correct Burning of Propellant, Impulse Propulsion," June 1939, British Intelligence Objective Sub-Committee, Group 2, Ft. Halstead Exploiting Center, 1247.*

[2] *D. C. Vest, "An Experimental Traveling Charge Gun," Ballistic Research Laboratories Report No. 773, October 1951.* (AD 801783)

[3] *J. S. Ward, U.S. Naval Weapons Center, China Lake, CA, "High Burning Rate Propellant Applications," briefing, USA ARRADCOM, Edgewood Area, Aberdeen Proving Ground, MD, 30 September 1976.*

[4] *J. L. Johndrow, "Development of the Film Ballistics (FILMBAL) Gun Propulsion Concept," Naval Surface Weapons Center, Dahlgren Laboratory Technical Report No. NSWC/DLTR-3820, April 1978.*

[5] *J. A. Brown and M. Collins, "Explosion Phenomena Intermediate Between Deflagration and Detonation," Esso Research and Engineering Co., Inc., October 1967, (AD662778).*

ignition compositions with apparently stable propagation rates between 15 and 330 meters per second have been reported in the patent literature[6]. In addition to this, a family of proprietary materials with propagation velocities up to 600 meters per second has been marketed commercially under the trade name "Hivelite" for ignition propagation cord and other ordnance applications[7-9]. The claims for the materials have included extensive tailoring capabilities for burning rate and impetus coupled with good thermal stability characteristics.

Limited experiments by several investigators appeared to substantiate some of these claims. M. Finger of the Lawrence Livermore Laboratory studied the burning of one Hivelite formulation under ambient pressure conditions[10]. The experimental technique involved the mounting of a barium titanate pressure transducer at the base of a cylindrical (12.7-mm dia.) sample, igniting the other end and determining the reaction front transit time as a function of sample length. The maximum sample length studied was 120-mm. The reaction propagation-burning-rate of the material appeared to have two components, an initial value of 230 meters per second over the first 20 millimeters and a final value of 1200 meters per second. The author cautioned, however, that the data could be construed as showing burning rate acceleration, a potentially undesirable effect.

As part of a study to evaluate the "FILMBAL" concept, Johndrow[11] reports strand burner data for several Hivelite formulations at 6.9 MPa and

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[6] *R. K. Armstrong, "Ignition Compositions Comprising Boron Containing Salts," U.S. Patent 3,126,305, E. J. DuPont de Nemours and Co., Wilmington, DE, March 24, 1964.*

[7] *Teledyne McCormick-Selph, Hivelite High Velocity Ignition Propagation Cord Product Information Bulletin, Hollister, CA, February 1973.*

[8] *Teledyne McCormick-Selph, Hivelite Briefing Book, Hollister, CA, (no date).*

[9] *C. Wright, "SCID and Ordnance Distribution Systems," Teledyne McCormick-Selph, Hollister, CA (no date).*

[10] *M. B. Finger and B. Hayes, "Hivelite Propellant Characterization," Lawrence Livermore Laboratory Report No. UCID-16748, March 14, 1975.*

[11] *J. L. Johndrow, "Development of the Film Ballistics (FILMBAL) Gun Propulsion Concept," Naval Surface Weapons Center, Dahlgren Laboratory Technical Report No. NSWC/DLTR-3820, p. 22 and Appendix 1, April 1978.*

13.8 MPa as well as high pressure burning rate data for two formulations up to 207 MPa. The experimental technique involved the use of optical sensors as opposed to the conventional fuse wire technique used in such studies. Burning rates for the formulations studied ranged from 0.76 to 7.0 m/s. The data clearly showed that in the case of one sample, burning rate decreased with pressure while in the case of the other, burning rate increased with pressure. The burning rate data showed some scatter suggesting sample-to-sample variability.

The promising developments in the preparation of materials with burning rates in the 1-1000 meter per second range prompted our re-examination of the traveling charge gun concept[12]. A variety of new, very high burning rate (VHBR) propellant formulations have resulted from these efforts[13,14,15]. This report documents the findings of combustion studies performed on samples prepared under BRL sponsored propellant formulation efforts at Teledyne McCormick-Selph and the Naval Weapons Center, China Lake.

A. Propellant Requirements for Traveling Charge

In the traveling charge concept, the propellant moves along with the projectile providing direct thrust as well as combustion products to maintain pressure behind the moving projectile. In the approaches pursued by BRL, one configuration involved the use of a cigarette type or end burning propellant grain. The charge would be made of parallel layers of successively higher burning rate propellants, the highest burning rate samples being consumed just prior to muzzle exit. The range of propellant burning rates required to achieve the target muzzle velocities was estimated to be from 0.4 to 400 meters per second. The propellant impetus requirements were stipulated to be equivalent to M30A1, approximately 1070 joules per gram.

Sample preparation efforts involved an initial screening of many combinations of fuel/oxidizer/binder materials and the fabrication of the most promising ones into test specimens for burning rate, impetus, and deflagration-to-detonation (DDT) characterization. (See references 13, 14, and 15 for details).

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[12] *I. W. May, A. F. Baran, P. G. Baer, and P. S. Gough, "The Traveling Charge Effect," Ballistic Research Laboratories Memorandum Report, BRL MR-03034, July, 1980.* (AD B052135)

[13] *R. M. Price, "Traveling Charge Propellant Studies (Progress for 1 October 1977 - 1 October 1978)," Naval Weapons Center Report No. NWCTM 3627, October 1978.*

[14] *R. M. Price, "Traveling Charge 40-mm Pellet Production 12 March 1979 - 1 November 1979," Naval Weapons Center Report No. NWCTM 4070, November 1979.*

[15] *C. Leveritt, "Ultra High Burning Rate Propellants for Traveling Charge Gun, Ballistic Research Laboratories Contractor Report, ARBRL-CR-00447, February, 1981.* (AD B057369L)

B. Chemistry of Very High Burning Rate Propellants

The VHBR propellants studied are generically related to the igniter/pyrotechnic compositions described by Armstrong[6]. The propellants consist of a fuel (a borate salt, of either decahydrodecaboric acid or dodecahydrododecaboric acid) and an oxidizer (inorganic or organic, NH_4NO_3, TAGN, etc.) held together by a binder. The ingredients are physically blended, pressed, and cured to give the finished propellant samples. Figure 1 details such a generic composition.

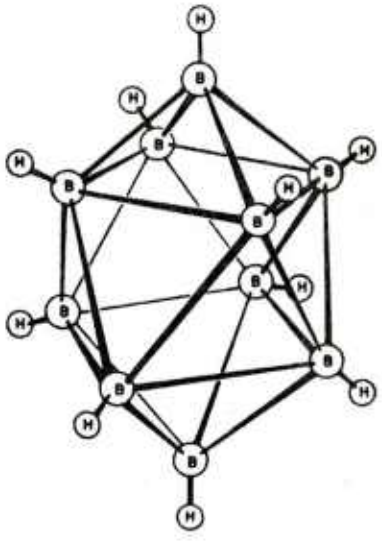
FUEL		OXIDIZER	BINDER
$2[N(CH_3)_4]+$			
	=	$[NH_4NO_3]$	[EPOXY]

Figure 1. Generic Composition of a VHBR Propellant

The precise chemical composition of the fuel constituents used in the samples under study is proprietary. Accordingly, a numeric code is used in this paper to describe these ingredients. Other constituents used are identified. The compositions of the samples studied are given in Table 1.

TABLE 1. VHBR PROPELLANT FORMULATIONS STUDIED

Sample Code*	Fuel - (%)		Oxidizer - (%)		Binder - (%)	
1086-1D	498	10.2	HMX	74.8	CTPB	15.0
1086-2C	466	17.1	AN	70.9	CTPB	12.0
1086-3	466	25.7	AN	59.1	NC/DNT/A4	15.2
1086-4B	466	10.6	TAGN	74.2	NC/DNT/A4	15.2
1086-5A	498	8.8	TAGN	76.0	NC/DNT/A4	15.2
1086-6B	466	27.0	AN	67.1	C4000	5.0
1086-7B	466	10.5	TAGN	84.5	C4000	5.0
1086-8A	498	8.6	TAGN	86.4	C4000	5.0
30-4A	465	16.2	HMX	43.9	EPOXY	15.0
			AN	4.9	PNC	20.0
29-51A	466	1.6	HMX	32.9	EPOXY	15.0
	465	14.6	AN	11.0	PNC	20.0
			KNO_3	4.9		
29-51A Mod 4	466	1.6	HMX	37.3	EPOXY	15.0
	465	14.6	AN	6.6	PNC	20.0
			KNO_3	4.9		
29-51A Mod 7	466	1.6	HMX	35.1	EPOXY	15.0
	465	15.5	AN	7.9	PNC	20.0
			KNO_3	4.9		

* All samples with designation 1086-XX were fabricated by Teledyne McCormick-Selph, others by Naval Weapons Center, China Lake.

Selected combustion products of a typical VHBR propellant are compared with those from M30A1 in Table 2. The calculations were performed using the "Blake" thermochemical code[16]. The principal differences appear to be in the distribution of the products H_2, N_2, and CO_2. The higher proportion of hydrogen in the equilibrium products from sample 4B accounts in large part for the high impetus/low molecular weight characteristics noted (Table 3). Other significant differences between the two propellants involve the formation of gaseous HBO_2, B_2O_3, and HBO at levels of 0.186, 0.0072, and 0.092 moles/kg as well as liquid B_2O_3 at 1.88 m/kg in the case of the VHBR propellant. These products are, of course, totally absent for the M30A1. In addition, significant amounts of solid boron nitride were predicted for several of the compositions.

The thermochemical properties, calculated at 0.2 g/cc loading density, of a number of samples prepared by Teledyne McCormick-Selph for burning rate evaluation are given in Table 3.

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[16] *E. Freedman, "Blake - A Thermodynamics Code Based on 'Tiger', Users Guide and Manual," USA ARRADCOM, Ballistic Research Laboratory Report, in preparation.*

TABLE 2. COMPARISON OF MAJOR COMBUSTION PRODUCTS OF VHBR 1086-4B WITH M30A1*

Species	M30A1 (moles/kg)	1086-4B (moles/kg)
H_2	5.42	24.03
N_2	11.77	16.17
CO	11.72	10.01
H_2O	10.49	1.89
CO_2	2.99	0.12
NH_3	0.023	0.40
HCN	0.007	0.33
CH_4	0.0005	1.36
B_2O_3 (Liquid)	----	1.88

* Calculated for a loading density of 0.2 g/cm^3

TABLE 3. COMPARISON OF SELECTED THERMOCHEMICAL PROPERTIES OF VHBR PROPELLANTS WITH M30A1

Propellant	Impetus (J/g)	Temperature (K)	Molecular Weight (gas only)	Covolume (cm^3/g)	Specific Heat Ratio
M30A1	1064.7	3000	23.430	1.044	1.2406
1086-2C	976.0	2170	14.454	1.246	1.2679
1086-3	1094.6	2538	13.085	1.221	1.2670
1086-4B	1090.4	2402	15.926	1.301	1.2719
1086-5A	1124.7	2647	17.500	1.198	1.2662
1086-6B	1094.1	2488	12.245	1.240	1.2650
1086-7B	1084.4	2329	15.534	1.328	1.2710
1086-8A	1119.1	2539	16.815	1.229	1.2692

The data are referenced to M30A1, a conventional high impetus, moderate flame temperature propellant. Theoretical impetus values for several of the compositions are greater than for M30A1. Since theoretical impetus is a good measure of a propellant's ability to do useful work, these formulations may provide more propulsive energy per unit weight than M30A1. The flame temperatures of all the compositions are lower than for M30A1, approximately in the range expected for single base formulations. The low flame temperature characteristics could be of interest from an erosion-reduction point of view. The molecular weight of the VHBR propellant combustion products is lower, because of the larger amounts of hydrogen predicted for these compositions. This may be a disadvantage from muzzle flash considerations. The covolumes of the VHBR propellants are somewhat higher than for M30A1, which might be an advantage

from an interior ballistic point of view. This advantage may be offset, however, by the slightly larger values of the specific heat ratio for these formulations[17]. Overall, on the basis of theoretical performance calculations, the candidates appear to be promising propellants.

II. EXPERIMENTAL

Experiments were performed at the Interior Ballistics Division, BRL. Two chambers, with volumes of 40.3 and 177.8 cm^3, respectively, were used depending on sample size. Bomb volume determinations were made by filling the chambers with iso-octane and computing the volume from the weight of isooctane used. Pressure measurements were made using Kistler 607C2, PCB 118A, and BRL Minihat pressure transducers. Redundant pressure measurements were taken of each firing. A cross-sectional view of the small volume chamber is given in Figure 2. The device is a modification of a 20-mm cartridge case simulator.

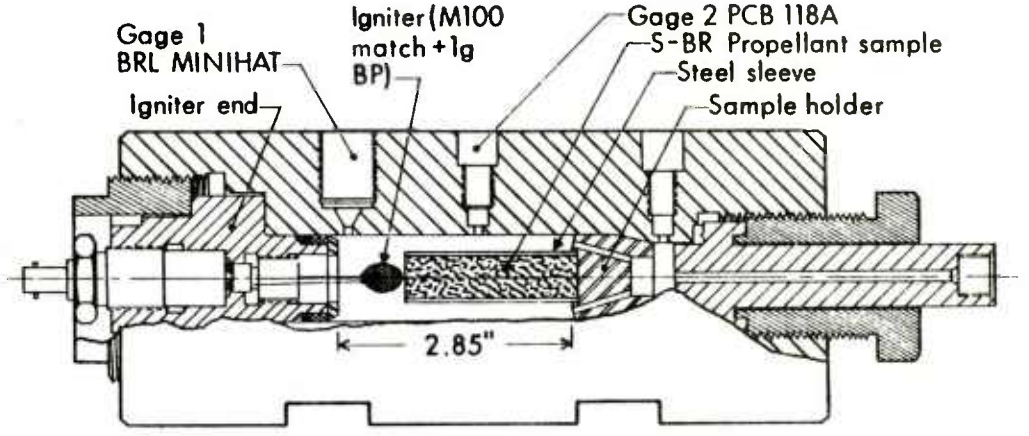

Figure 2. Small Firing Fixture (40.3 cm^3) with Sample and Igniter Configuration Indicated

The large volume chamber was designed for the study, a schematic is given in Figure 3. Data were recorded on wide band FM magnetic tape at 120 inches per second and subsequently digitized for analysis. Pressure gages used in the study were recalibrated frequently during the course of the firings. No significant degradation of response characteristics was observed. All experiments were performed at ambient temperature.

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[17] *P. G. Baer, "Practical Interior Ballistic Analysis of Guns," Progress in Astronautics and Aeronautics Volume 66, Interior Ballistics of Guns, American Institute of Aeronautics and Astronautics, 1979, p. 54.*

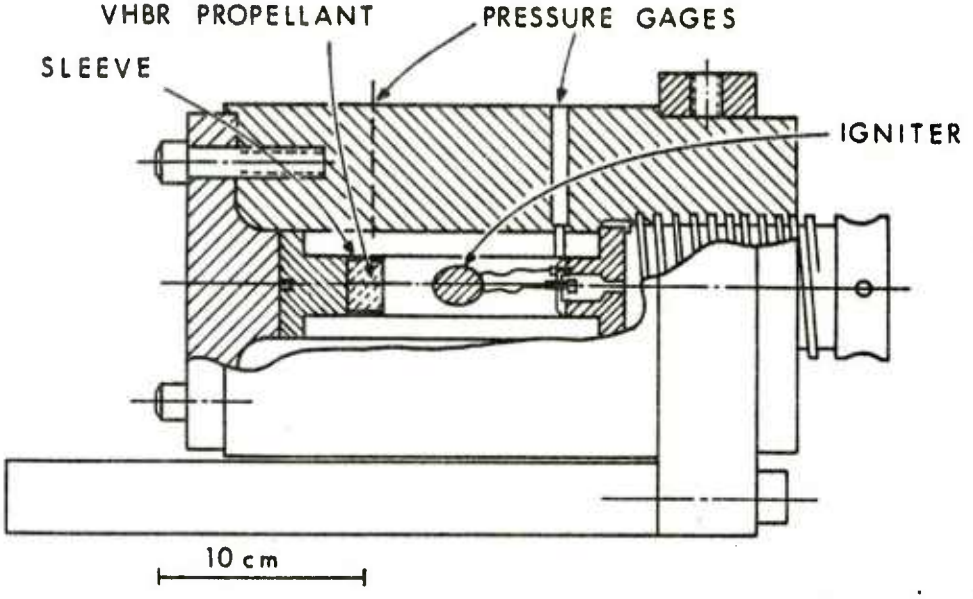

Figure 3. Large Firing Fixture (177.8 cm^3) with Sample and Igniter Configuration Indicated

The samples used in the study consisted of bare cylinders (12.7-mm diameter x 50.8-mm length), cylinders (12.7-mm diameter x 50.8-mm length) encased in steel sleeves 1.57 mm thick, and large cylindrical samples (36.6-mm diameter x 25.4-mm length). The large samples were bonded into steel sleeves (1.3-mm thickness) prior to firing. The large diameter sample with sleeve fit snugly into the bore of the vessel. All samples were end ignited to burn cigarette fashion, although in the case of the bare 12.7-mm sample firings no inhibitor was used on the sides of the sample. Steel cased 12.7-mm diameter samples were mounted in the chamber by epoxying them into the sample holder (see Figure 2). Bare samples were epoxied into thin (12.7-mm deep) aluminum cups which screwed into the sample holder. The 36.6-mm diameter samples were epoxied into the steel sleeves and the steel sleeves themselves were epoxied in place flush with the end of the chamber.

Considerable care was taken to keep samples sealed in moisture-proof packings until just before firing. Bare and steel cased small diameter samples were fired in duplicate with two pressure channels recorded for each event. Firings with the 36.6-mm diameter samples were done once on single increments in all cases except sample 1086-7B in which case duplicate firings were done. Two pressure channels were recorded for each firing. A summary of samples studied along with their respective densities is given in Table 4.

Solid residues were collected from the 36.6-mm sample firings. The residues were scraped from the walls of the chamber and stored in moisture-proof packings. Sample weights were determined on an analytical balance.

TABLE 4. VHBR PROPELLANTS AND DENSITIES

Sample Type	Small Confined		Small Unconfined		Large Diameter	
	Density (g/cm^3)	% Theoretical Density	Density (g/cm^3)	% Theoretical Density	Density (g/cm^3)	% Theoretical Density
1086-1D	1.585	92	1.480	86		
1086-26	1.340	90	1.280	86		
1086-3	1.238	83	1.367	91		
1086-4B	1.277	88	1.404	97		
1086-5A	1.280	85	1.305 1.486	86 98	1.486	98
1086-6B	1.240	84	1.254 1.297	85 88		
1086-7B	1.250	88	1.399	98	1.399	98
1086-8A	1.250	84	1.443	97	1.443	97
30-4A					1.313	89
29-51A					1.260	86
29-51A Mod 4					1.286	87
29-51A Mod 7					1.278	87

Analog records were digitized at different rates depending on the rise-time of the individual events. Digitization rates varied between 80 and 800 kilohertz. The data often contained large high-frequency signal components. The frequency content of the data was determined using Fast Fourier Transform Analysis techniques.

III. RESULTS

A. Confined Samples

The pressure vs time records from the firings frequently tended to be quite steep, with a significant high-frequency content. A typical raw data plot from the burning of a 12.7-mm diameter steel cased sample of VHBR 1086-4B is given in Figure 4. The total pressure rise takes place in a fraction of

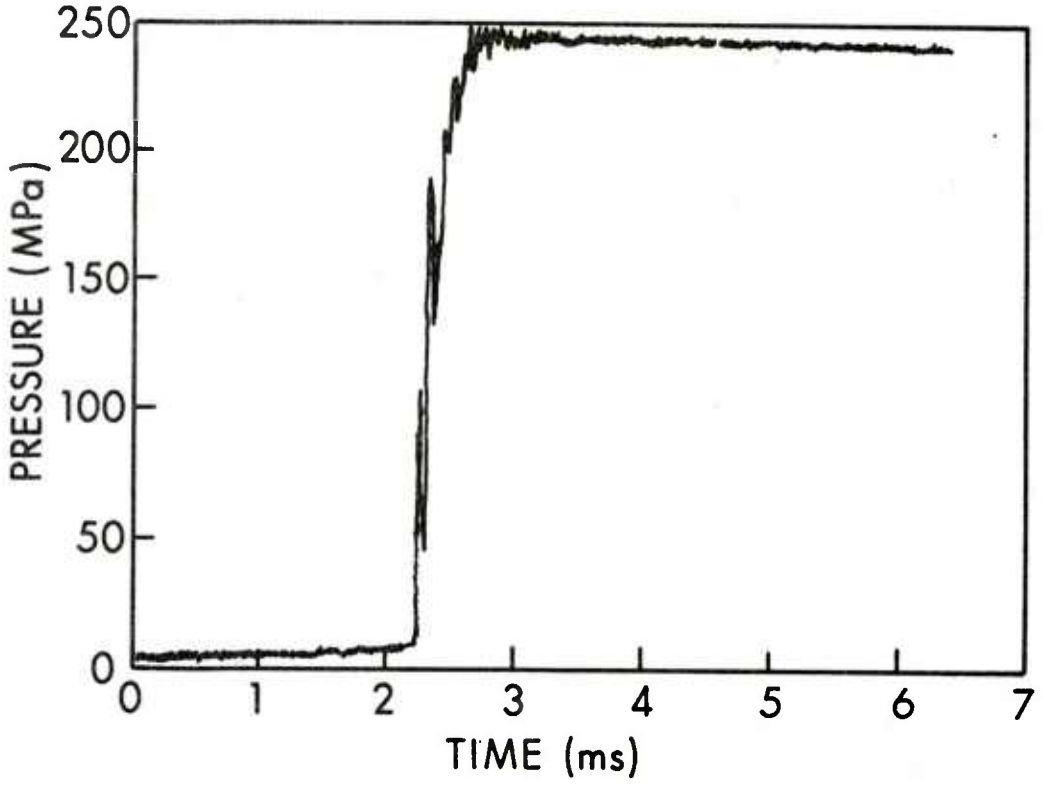

Figure 4. Pressure vs Time Plot from the Burning of a Confined Sample of VHBR 1086-4B

a millisecond. The rate of pressure rise is very high at first, then tapers off as the pressure maximum is approached. Since the sample was end ignited and inhibited on the outside by the steel cylinder, the web burned through during this time was 50 millimeters. Assuming a laminar burning mechanism, this corresponds to an overall average regression rate of 100 meters per second. The pressure maxima and action times (taken from 10 to 90 percent of

the maximum pressure attained) for the 12.7-mm diameter steel cased sample firings are given in Table 5. The sample action times ranged from 49.5 milliseconds for the slowest sample, 1086-1D, to 0.13 milliseconds for the fastest sample, 1086-5A. Maximum pressures ranged from 266.5 to 218.5 MPa. It was generally found that sample-to-sample reproducibility characteristics, though good overall, were better for the slower burning materials.

TABLE 5. ACTION TIMES AND PRESSURE MAXIMA OF CONFINED VHBR PROPELLANT FIRINGS

Sample	Loading Density (g/cm^3)	Action Time (ms)	Pressure Maxima (MPa)
1086-1D	.278	49.5 ± 0.5	266.5 ± 1.5
1086-2C	.235	19.0 ± 1.0	218.5 ± 0.5
1086-3*	.217	0.48 ± 0.07	240.0 ± 5.0
1086-4B	.224	0.31 ± 0.03	240.0 ± 4.0
1086-5A	.228	0.13 ± 0.03	234.0 ± 2.0
1086-6B	.220	1.10 ± 0.10	257.0 ± 3.0
1086-7B†	.222	0.2	245.0
1086-8A	.223	1.45 ± .05	249.0 ± 2.0

*Total four runs

† One firing (all other samples two firings each)

The high-frequency content of the data indicates considerable pressure oscillations in the chamber during firings. Comparison of the pressure-time outputs of gages located at different positions along the length of the chamber confirms the longitudinal unsteady pressure conditions in the chamber. Post-firing examination of the steel sleeves indicates the existence of radial pressure gradients in the chamber as well. The distortions of sample sleeves are illustrated in Figure 5. Generally, it was found that slow-burning samples caused little or no tube distortion while fast-burning samples caused considerable damage. Simple computations indicated that a pressure difference of 110 MPa would have to exist between the inside and outside of the tube in order for rupture to take place. The rate of burning of the faster samples, therefore, must have exceeded the rate at which product gases could be conducted away from inside the steel tube. An examination of the shape of the sample tubes indicates that a reaction front acceleration must have taken place. The tubes are weakly distorted at the ignition end but become increasingly distended in the direction of reaction propagation. The mass generation rate from the burning sample must have increasingly exceeded the ability of the system to conduct away the combustion products. It should be mentioned that the nature and extent of tube damage was quite reproducible from sample to sample for a given formulation. Significant amounts of solid combustion residues were noted for all the firings.

B. Unconfined Samples

The firing records of the bare samples evidenced longer action times, less reproducibility, and fewer high-frequency pressure oscillations than their steel cased counterparts. A pressure-time plot of the raw data from sample

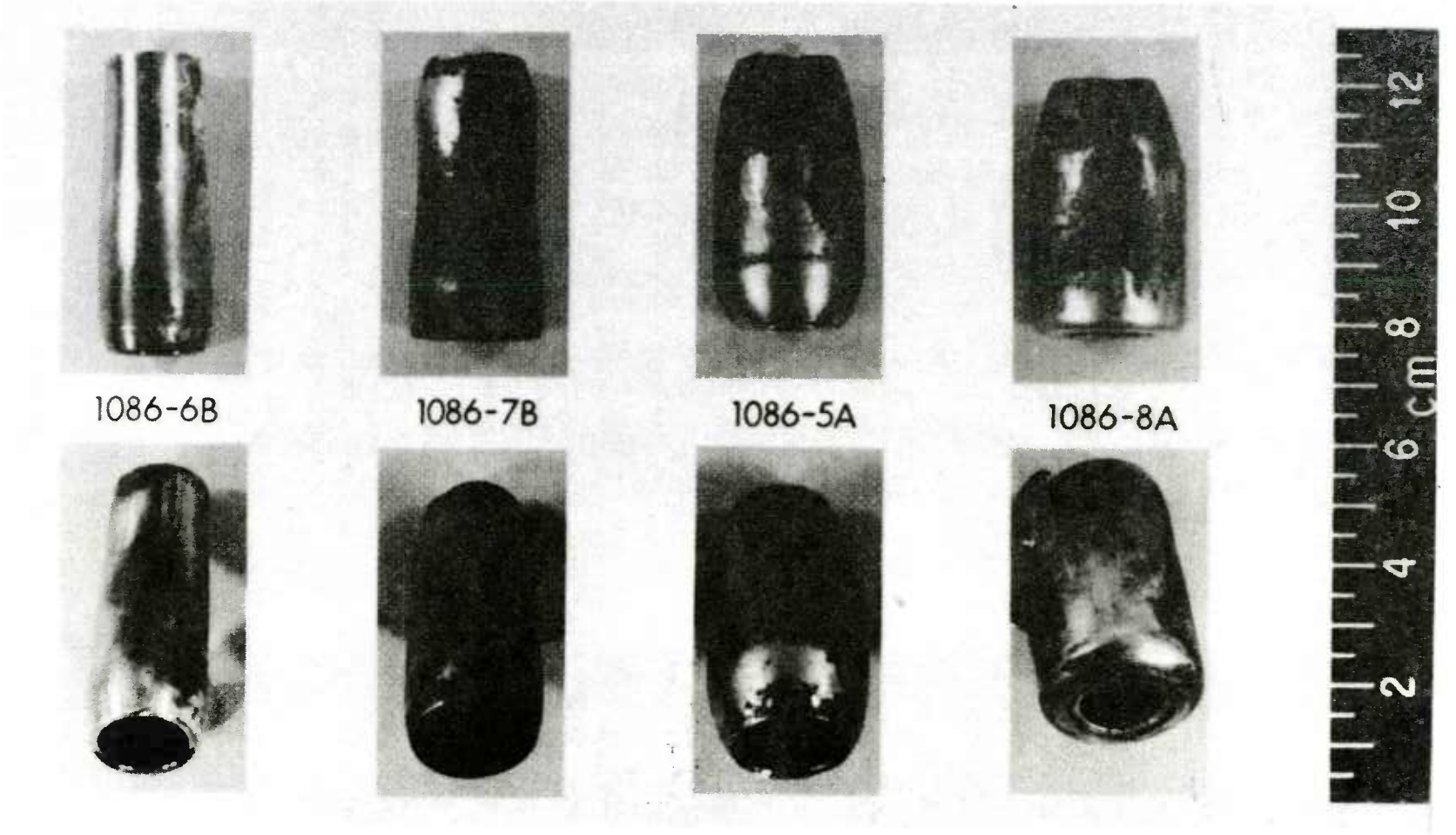

Figure 5. Steel Sleeves from Confined Samples After Combustion Tests

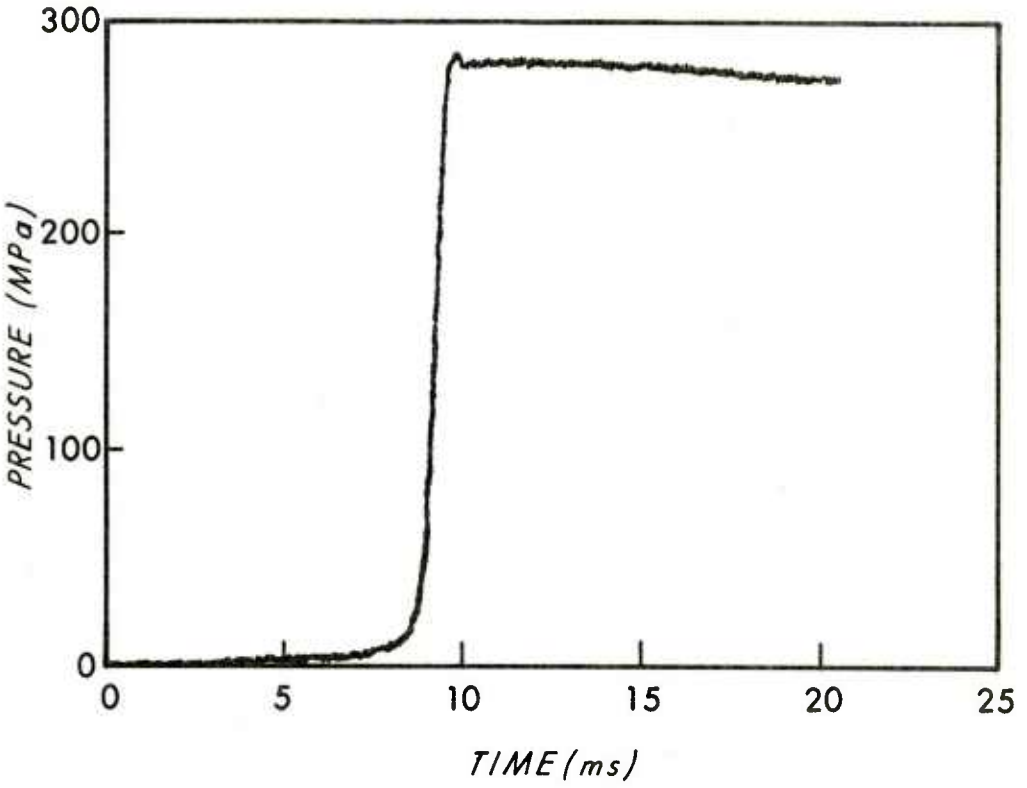

Figure 6. Pressure vs Time Plot from the Burning of an Unconfined Sample of VHBR 1086-4B

VHBR 1086-4B appears in Figure 6. The total pressure rise takes place in approximately two milliseconds. Compared with the cased sample, the rate of pressure rise is more gradual, achieves a reasonably constant level for most of the burning process, then drops off more quickly as the maximum pressure is achieved. The pressure time plot for the run is quite similar to normal closed chamber pressure time curves. The sample was end-ignited. If a laminar cigarette-type burning is assumed, the record would correspond to an average regression rate of 25 meters per second, a factor of four slower than its cased counterpart. Unfortunately, the densities of the cased and uncased samples were not the same (see Table 4). Variations in percent of theoretical maximum density (TMD) from 88 to 97 percent are significant. It is, therefore, impossible to ascribe the differences in burning characteristics solely to confinement effects. The variations could have been due to the differences in TMD above or to some synergistic effect of confinement and density. Pressure maxima and action times for the bare sample firings are given in Table 4. Comparing the action times of the bare samples with the steel-cased samples indicates a very strong tendency towards longer reaction times. The trend holds for all formulations except the 1086-5A. The low density bare samples of 1086-5A (1.305 g/cc density) have almost the same action time as the steel cased samples (1.280 g/cc). The higher density (1.486 g/cc) bare samples, on

the other hand, appear to be somewhat slower. This correlates with observations elsewhere[18] that VHBR propellant burning rates can be decreased by increasing sample density. The density effects observed for samples 5A and 6B in these firings, however, were not particularly strong. The relatively larger scatter in action times than in maximum pressures indicates that the combustion variability is most likely due to sample breakup during burning. Reduced local overpressure at the burning surface of the bare samples or flamespread effects may be among the mechanisms involved.

TABLE 6. ACTION TIMES AND PRESSURE MAXIMA OF UNCONFINED VHBR PROPELLANT FIRINGS

Sample	Loading Density (g/cm^3)	Action Time (ms)	Pressure Maxima (MPa)
1086-1D	.282	78.0 ± 3.50	245.5 ± 1.5
1086-2C	.244	32.5 ± 6.50	206.5 ± 2.5
1086-3	.239	0.56 ± 0.30	270.0 ± 3.0
1086-4B	.263	0.61 ± 0.09	281.0 ± 1.0
1086-5A[1]	.246	0.14 ± 0.06	283.5 ± 3.5
1086-5A[2]	.287	0.21 ± 0.05	315.0 ± 5.0
1086-6B[3]	.237	2.08 ± 0.83	245.0 ± 5.0
1086-6B[4]	.248	3.15 ± 0.25	248.5 ± 1.5
1086-7B	.264	11.15 ± 0.85	256.0 ± 1.0
1086-8A	.273	1.55 ± 0.00	290.0 ± 1.0

[1]Sample density 1.305 g/cc
[2]Sample density 1.486 g/cc
[3]Sample density 1.254 g/cc
[4]Sample density 1.297 g/cc

C. Large Diameter Samples

Based on the results of the firings with the confined and unconfined 12.7-mm diameter samples, a set of three formulations was chosen to cover the burning rate range required for the traveling charge study. The selected compositions were fabricated into cylinders 36.6 mm in diameter and 25.4 mm long. The samples were pressed to the same high densities as the bare 12.7 mm samples. Four other compositions, resulting from a formulation effort at the Naval Weapons Center[13,14], were made into samples having the same dimensions. It is important to note again that the large diameter samples were bonded into steel sleeves for the firings.

The samples were fired in the larger chamber as shown in Figure 3. Pressure-time records from these firings were generally contaminated by large

[18] *E. B. Fisher, "Closed Bomb Tests of Hivelite-Based VHBR Propellants," Ballistic Research Laboratory Contractor Report, ARBRL-CR-00449, March, 1981.* (AD B057344L)

pressure oscillations. The only exception was 1086-7B, which had a smooth, slow pressure rise. A pressure-time record for the firing of the 1086-8A sample is given in Figure 7. The oscillations on the record are typical of the high-frequency content encountered. The total pressure rise for this sample takes place over approximately 15 milliseconds. The majority of the pressure rise, however, occurs in a fraction of a millisecond. The record indicates that a slow-starting, but strongly accelerating reaction is taking place. The slow induction behavior was not observed for the other large diameter samples which burned with strong chamber oscillations. A summary of maximum pressures and action times for the large diameter sample firings is given in Table 7. Comparing the action times of the large diameter samples with the small diameter samples yields some interesting correlations. Sample 1086-5A appears to be consumed in the same time frame as both the smaller diameter samples, though the small diameter samples were twice as long. The average of the two 1086-7B samples (5.0 ± 0.5 ms) is just about half that of the bare small diameter 1086-7B samples (11.15 ± 0.85 ms). Since the large

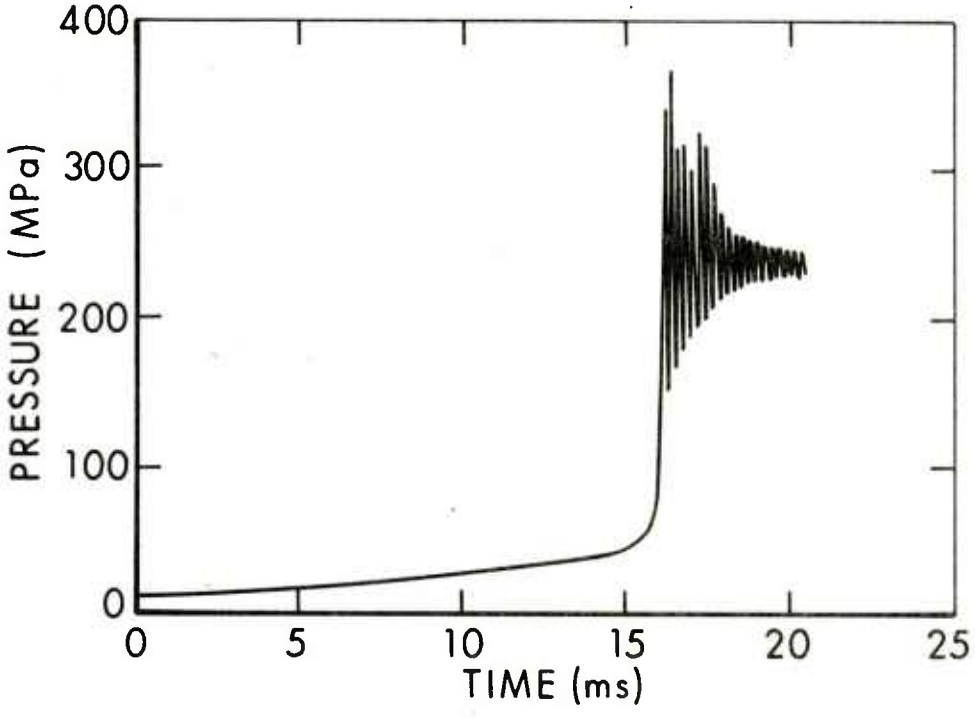

Figure 7. Pressure vs Time Plot from the Burning of Large Diameter VHBR 1086-8A

TABLE 7. ACTION TIMES AND PRESSURE MAXIMA OF LARGE DIAMETER VHBR PROPELLANT FIRINGS

Sample	Loading Density (g/cm^3)	Action Time (ms)	Pressure Maxima (MPa)
1086-5A	.223	0.23	240
1086-7B (lot 4)	.210	4.50	255
1086-7B (lot 5)	.193	5.50	255
1086-8A	.217	0.50*	260
29.51A	.198	0.22	228
29.51A Mod 4	.197	0.20	236
29.51A Mod 7	.194	0.75	218
30-4A	.195	0.45	206

* See text below

diameter samples are exactly half the length of the small diameter samples, the material appears to burn at the same rate in the two configurations. It should be noted, however, that the steel cased small diameter 1086-7B samples burned in 0.2 milliseconds, much faster than the others. There must be some significant difference in the mechanism of burning to cause this effect. The 1086-8A composition appears to have burned with a very long action time of 8.6 ms. This is deceptive, however, because the majority ($\sim$ 75 percent) of the sample burned very rapidly, in less than 0.5 milliseconds. This result is more like the steel cased sample than the bare sample.

Although no small diameter samples of the 29-51A or 30-4A formulations were burned at BRL during these studies, some closed chamber data were available from NWC on the burning of the same diameter samples. A comparison of the data derived from the raw data on pages 44 and 45 of Reference 14 with the experimental results obtained in this study indicates reasonable agreement in burn times for compositions 30-4A, 29-51A, and 29-51A Mod 4, even though the NWC samples were burned at lower loading densities and, therefore, attained lower maximum pressures.

IV. DISCUSSION

A. Data Filtering

The action times summarized previously can be used to compute gross mean regression rates for the samples. The values so obtained may be useful for comparison purposes, though they do not describe possible burning rate pressure dependence. For detailed interior ballistic modeling it is important to know the change of the propellant burning rate with pressure. Established methods exist for reducing closed chamber pressure-time data to propellant burning rates as a function of pressure[19]. The application of such methods to the VHBR closed chamber data requires a prior filtering of the data to strip

[19] *A. A. Juhasz and C. F. Price, "The Closed Bomb Technique for Burning Rate Measurement at High Pressure," Progress in Astronautics and Aeronautics Volume 63, Experimental Diagnostics in Combustion of Solids, American Institute of Aeronautics and Astronautics, 1978.*

the high frequency oscillations from the basic waveform describing the pressure rise event. The technique used in the study was Fast Fourier Transform Analysis[20]. The method allows the determination of the frequency content of the data by examining its power spectral density. Filters can then be designed to eliminate the unwanted frequency components. A program was written to use up to 127 filter coefficients with 512, 1024, or 2048 data points describing the pressure event. In most cases a high pass filter was used to isolate the high frequency components which were subsequently subtracted from the raw data to yield the desired waveform. A report on the applications of these methods to a variety of ballistic data is currently in preparation[21]. Identification of unwanted frequencies was made on the basis of matching with computed arrival times of oscillations in the chamber. The arrival times of the pressure fronts at the gage locations were computed using longitudinal chamber dimensions and the covolume equation of state for the speed of sound in the propellant combustion products. Agreement between calculated and measured frequencies was good. Superimposed plots of the raw and smoothed data for a 12.7-mm diameter sample of 1086-4B fired in the steel sleeve are shown in Figure 8. The important feature of the plot is the essential superimposability of the filtered data on the center of mass of the raw data plot. This subjective superimposability criterion was used as a check to insure that the filtering process did not unduly distort the pressure rise characteristics of the curve over the region of interest. It is believed that the filtered data faithfully describe the mean chamber pressure in the small chamber and a majority of the events recorded in the large chamber as well. Figure 9 shows the superimposed raw and filtered pressure time data for sample 29-51A, Mod 7 fired in the large chamber.

In the case of samples 29-51A, 29-51 Mod 4, and 1086-5A, fired in the large chamber, the rise times of the events were very close to the rise times of the chamber oscillations. In these cases the available filter combinations were not sufficient to provide similar high-quality separation of the chamber oscillations from the pressure rise data. An example of the raw and filtered data for sample 29-51A appears in Figure 10. It is evident that the filtered data has a lower slope than the initial oscillation. Just how meaningful this slope is to describing the pressure rise event is not clear. The filtered curves obtained for these firings simply represent the best match obtainable with the available tools. Certainly, any burning rate data extracted, for these samples, from the filtered data would have to be treated with caution. The burning rates obtained are likely to be lower than the "real" burning rates.

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[20] *C. K. Yuen and D. Fraser, Digital Spectral Analysis, Fearton Pitman Publishing Limited, Belmont, CA, 1979.*

[21] *J. Walbert, "Application of Digital Filters and the Fourier Transform to the Analysis of Ballistic Data, USA ARRADCOM, Ballistic Research Laboratory Report, in preparation.*

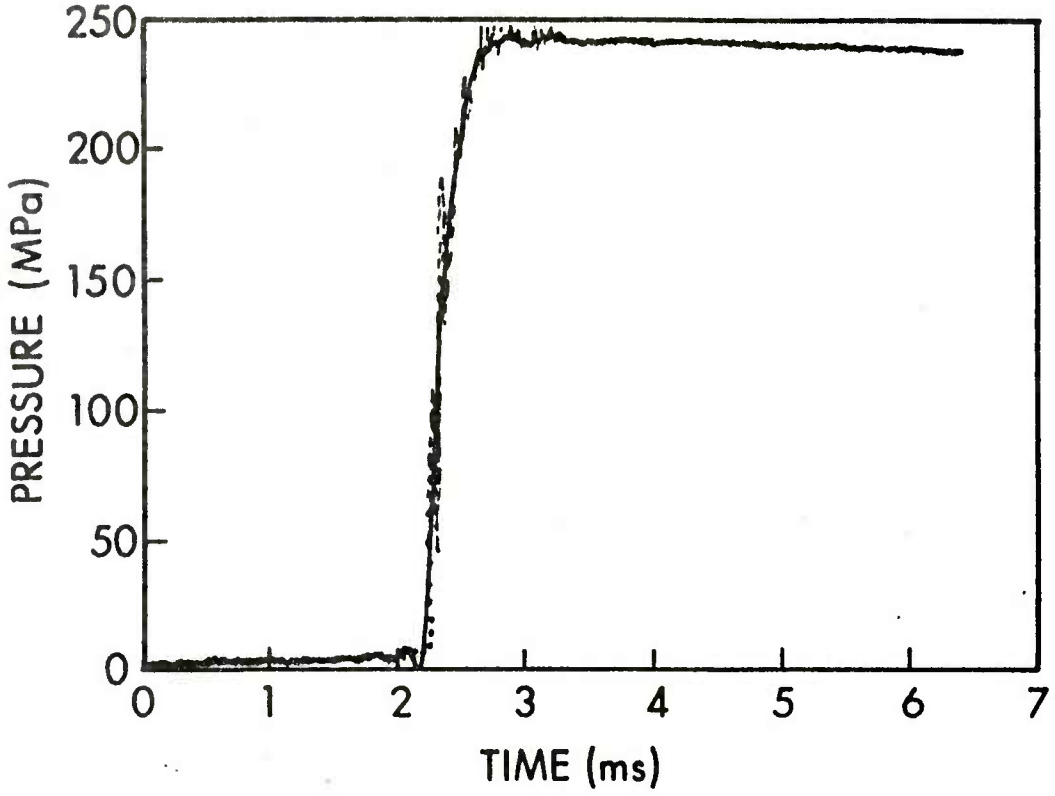

Figure 8. Raw and Filtered Data for the Burning of a Confined Sample of VHBR 1086-4B

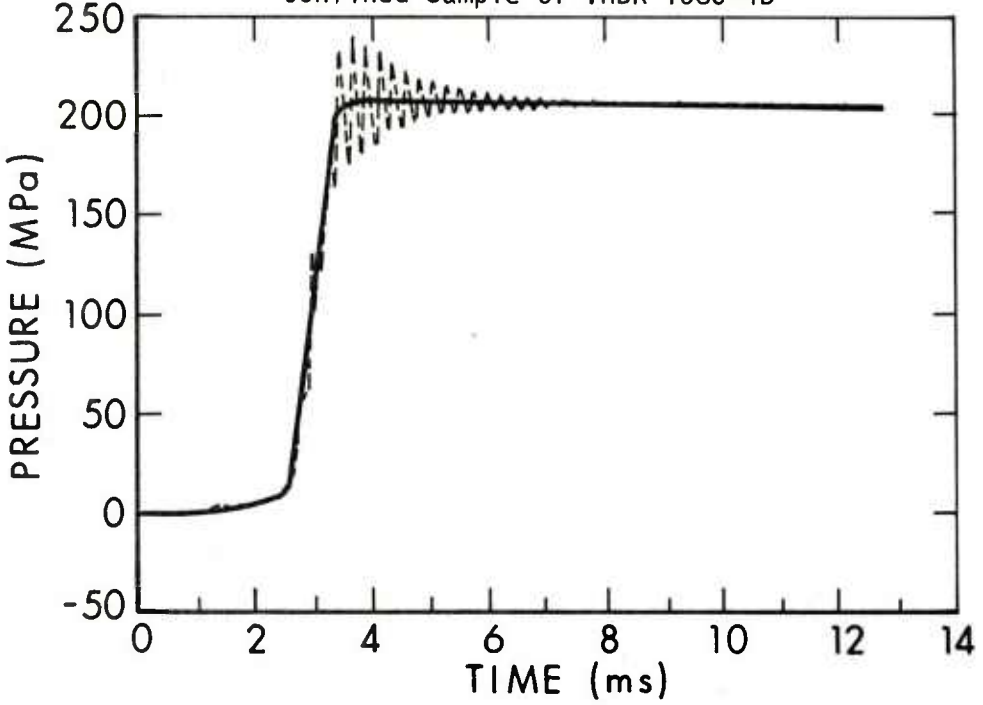

Figure 9. Raw and Filtered Data for the Burning of a Large Sample of VHBR 29-51A, Mod 7

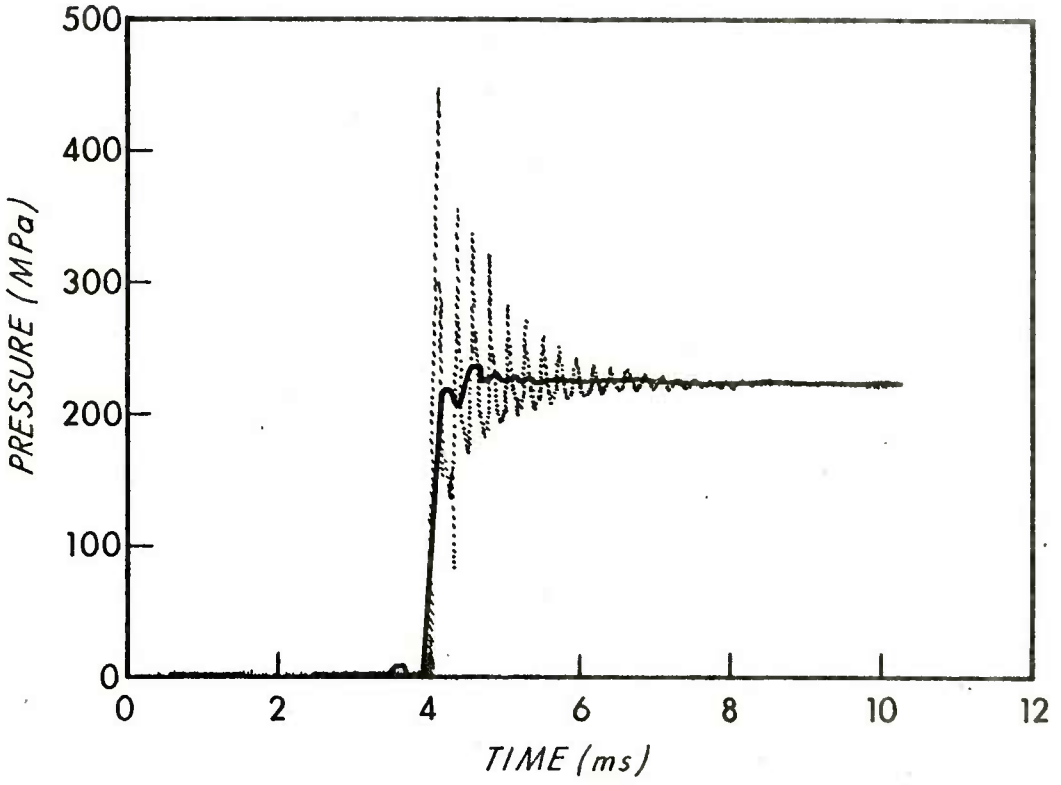

Figure 10. Raw and Filtered Data for the Burning of a Large Sample of VHBR 29-51A

It is quite apparent that in the presence of substantial pressure waves, the extraction of meaningful burning rates is a difficult, if not impossible, task. Since the burning propellant surface responds to the instantaneous pressure in a not yet completely understood transient fashion, the attempt to extract a mean chamber pressure and derive a steady state burning rate from its slope is fraught with theoretical as well as technical difficulties.

B. Burning Rate Analysis

The simplest estimates of the VHBR propellant burning rates can be derived from the sample lengths and the action times as already previously mentioned. Since similar peak pressures were measured, such approximate average burning rates are useful and instructive from a qualitative ranking standpoint. They are summarized in Table 8.

From these results a case can be made that porosity is a factor in determining apparent burning rates. Both 5A and 6B unconfined samples show a substantial burning rate reduction as the densities increase.

Confinement effects can be argued from the data of the bare and steel-sleeved 6B results. An apparent doubling of the average burning rate due to confinement is postulated. Somewhat more clearcut evidence of confinement effects has been noted by Fisher[18]. It is difficult, however, to unravel combined effects of both changes in density and confinement. The fastest burning formulation, 5A, seems to show few effects that can be ascribed to confinement. This is clouded, however, by the increasing lack of precision at the very high burning rates. The data for 4B, 7B, and 8A are consistent, at least qualitatively, with combined confinement and porosity arguments. On the other hand, samples 1D and 2C, the slowest burning samples, appear to indicate that confinement effects overshadow density.

Of greater concern at this point is an explanation for the very low burning rates exhibited by 1D and 2C when compared with the other VHBR. Since these two samples were the only ones with a rubber type binder (CTPB), it is tempting to speculate that the mechanical properties of these samples play a role if grain breakup and progressive deconsolidation are an important part of the combustion mechanism. Recent high-strain-rate impact tests by Wires[22], appear to substantiate that the fast burning VHBR formulations tend to be more brittle.

For interior ballistic modeling purposes, it is essential to extract the pressure dependence of the burning rates for the VHBR propellants. This was accomplished using normal closed bomb burning rate analysis procedures. Reduction of the firing data to apparent linear burning rates was done using a simplified program containing a number of assumptions. Among these were constant heat loss rate, fixed gas composition throughout the burn, igniter burned prior to propellant ignition, equal heat capacities of igniter and propellant combustion products. The method was checked against both the BRL CBRED and the NOSIH closed chamber programs[23,24] and found to vary on the average of less than one percent from the NOSIH results and less than two percent from the CBRED results over the 5 to 95 percent of maximum pressure range. One final assumption made concerning the burning of the VHBR samples was that they burned in a cigarette fashion, with a constant surface area. This assumption, we realize, is perhaps, a difficult one to support.

Though the simplified theory used for data analysis gives essentially the same answers as standard reduction methods, some cautions must be raised concerning the use of closed chamber burning-rate reduction schemes for the VHBR propellant samples. All closed chamber burning-rate reductions assume the

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[22] *R. A. Wires, USA ARRADCOM, Ballistic Research Laboratory, personal communication.*

[23] *C. Price and A. Juhasz, "A Versatile User-Oriented Closed Bomb Data Reduction Program (CBRED)," USA ARRADCOM, Ballistic Research Laboratory Report ARBRL Report 2018, September 1977 (ADA049465).*

[24] *F. W. Robbins and A. W. Horst, "Numerical Simulation of Closed Bomb Performance Based on BLAKE Code Thermodynamic Data," Naval Ordnance Station, Indian Head Report No. 76-259, November 1976.*

TABLE 8. APPROXIMATE AVERAGE BURNING RATES FOR VHBR PROPELLANTS*

Sample Type	Unconfined		Confined		Large Diameter	
	% TMD	Burning Rate (m/s)	% TMD	Burning Rate (m/s)	% TMD	Burning Rate (m/s)
1086-1D	86	0.64	92	1.01		
1086-2C	86	1.54	90	2.63		
1086-3	91	89	83	104		
1086-4B	97	82	88	161		
1086-5A	86	357	85	385		
	98	238			98	109†
1086-6B	85	24	84	45		
	88	16				
1086-7B	98	4.5	88	250	98	5
1086-8A	97	32	84	192	97	50
29-51A					86	114†
29-51A Mod 4					87	125†
29-51A Mod 7					87	33
30-4A					89	55

* Average burning rate defined as sample length/action time
† Burning rates probably higher than listed value

existence of a space-mean pressure. Such an assumption may be quite inadequate to describe an event which, for an equillibrium pressure rise of 240 MPa, has superimposed on it peak-to-peak oscillations as large as 360 MPa as seen in Figure 10. If the constant pressure assumption is made, we ignore the fact that the propellant was burning at local pressures either above or below the assumed space-mean value at any given instant. The larger the oscillations, the more severe this error becomes. A second assumption made in closed chamber burning rate reduction is that we know the surface area of the propellant which is burning at any given instant. This is generally based on our knowledge of initial sample geometry and an assumption of laminar burning combined with freedom from sample breakup. Under the conditions of rapid reactions and high-amplitude pressure oscillations, however, freedom from breakup may be a questionable assumption for samples with relatively poor mechanical properties. Several of the VHBR propellants have been found to have poor mechanical properties compared with conventional propellants[22]. The laminar burning assumption may also be weak due to the high porosities of the VHBR propellant materials ranging from 83 to 98 percent of the theoretical maximum density versus 99.9 percent for conventional propellants. Materials having high porosities may actually burn via some form of distributed, convectively driven reaction zone.

Having looked at the possible shortcomings of the analytical methodology used, the path is cleared for a realistic examination of the burning rate information obtained. Table 9 summarizes burning rate and burning rate variability data at 50,100 and 150 MPa for the confined 12.7-mm diameter VHBR

TABLE 9. APPARENT BURNING RATES OF CONFINED VHBR SAMPLES

Sample	Burning Rate (m/s)		
	50 MPa	100 MPa	150 MPa
1086-1D	0.596 ± 0.005	1.117 ± 0.003	1.37 ± 0.04
1086-2C	2.200 ± 0.300	3.010 ± 0.020	2.72 ± 0.08
1086-3	242.0 ± 4.000	256.0 ± 7.000	181 ± 11
1086-4B	230.0 ± 20	235.0 ± 11	153 ± 15
1086-5A	451.0 ± 113	505.0 ± 137	442 ± 140
1086-6B	214.0 ± 3	231.0 ± 1	169 ± 3
1086-7B	304.0 ± 8	249.0 ± 1	318 ± 15
1086-8A	247.0 ± 19	2720 ± 15	220 ± 11

samples. In most cases, reproducibility is nowhere near as good as for conventional propellants, where run-to-run reproducibilities in the mid-range of the experimental pressures are frequently 1 percent or better. Nevertheless, in most cases it is not really bad. The most drastic variation occurred for the fastest burning sample, 5A, where a total variation of 200 meters per second is superimposed on an average value of 450 m/s at 50 MPa. The causes of the variability might be due to intrinsic sample differences, data manipulation techniques or both.

Figure 11 compares computed linear burning rates from two firings of formulation 1086-4B in the 12.7-mm diameter steel cased configuration. The curves superimpose quite well. Whatever the burning mechanism may be, the samples functioned reproducibly. This was true for most of the 12.7-mm steel cased samples tested.

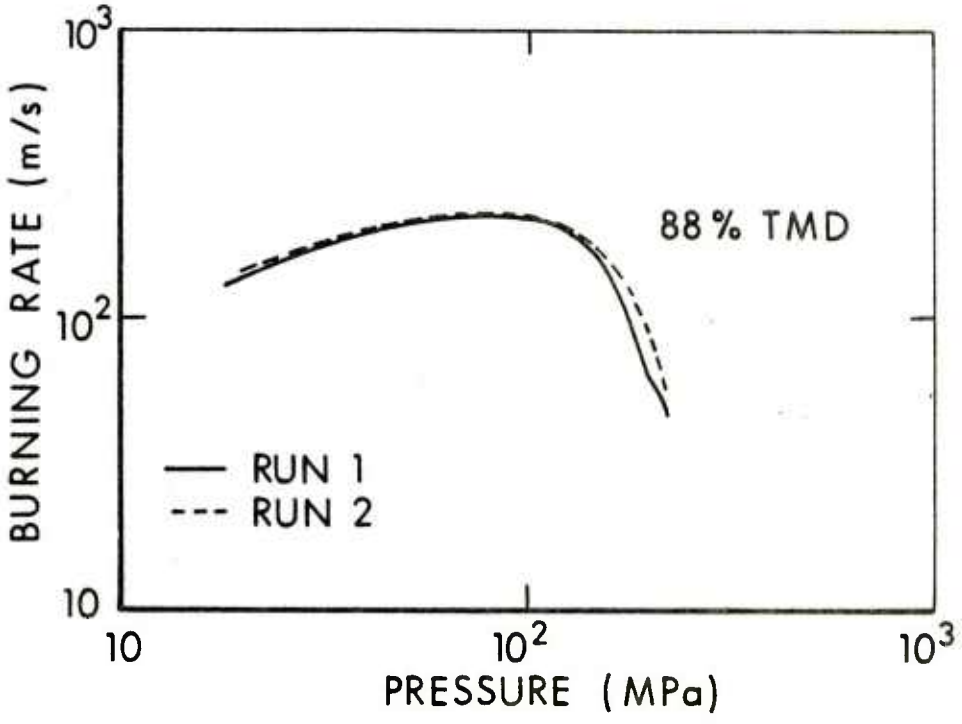

Figure 11. Apparent Burning Rate for Confined VHBR 1086-4B

A composite plot of the burning rate data computed for these firings appears in Figure 12. For purposes of reference, burning rate data for M30A1 propellant have been included. The burning rate range from sample 1086-1D to sample 1086-5A covers four orders of magnitude. This is, indeed, spectacular compared with the limited burning rate range of M30A1, a typical conventional propellant. Samples 1D and 2C burn 10 times faster than M30A1 at 100 MPa. Samples 5A and 7B burn some 10,000 times faster. Interestingly, the burning rate curves, especially those of the higher burning rate materials, appear to be rather flat. Pressure does not seem to affect burning rate below 100 MPa. Surprisingly, there doesn't seem to be a buildup phase in the burning rate plots of the fastest burning samples as there is with M30A1 and samples 1D and 2C. An examination of the foot of the pressure-time traces for the highest burning rate materials failed to reveal any smooth ignition-to-combustion transition effects. Apparently, for these samples, burning begins with a bang!

The reproducibility characteristics of these formulations, coupled with the range in burning rates, are extremely encouraging. They indicate that the objective of tailoring formulations for specific burning rate levels may be

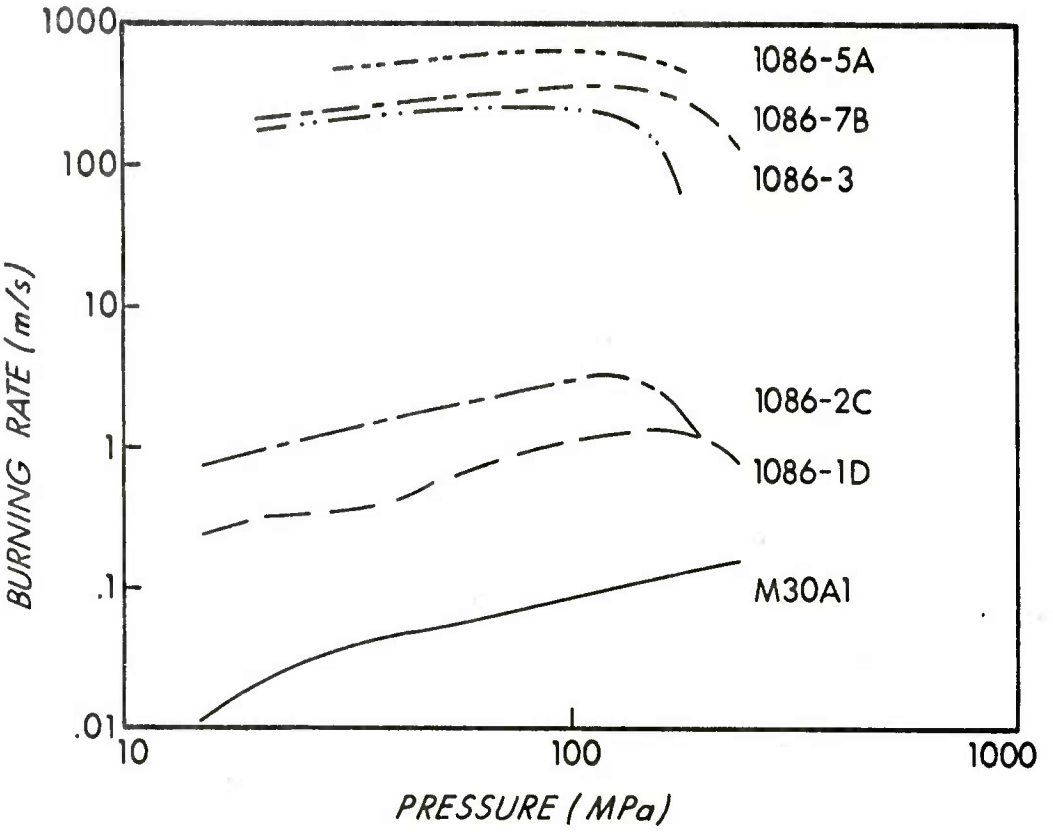

Figure 12. Apparent Closed Chamber Burning Rates for Confined VHBR Propellants and M30A1

attainable. Further, the information is indicative of the types of chemistry which may be used to attain the desired burning rate levels. The oxidizer in formulation 1D was HMX, the binder, a carboxy-terminated polybutadiene (CTPB). The oxidizer in 2C was ammonium nitrate, the binder also CTPB. It is possible that the CTPB binder, producing a physically stronger and tougher sample specimen, is responsible for the much reduced burning rates. If physical breakup or progressive deconsolidation is indeed the mechanism, then such a conclusion is logical and consistent. Formulations 4B through 8A used triaminoguanidinium (TAG) nitrate as the oxidizer and either nitrocellulose or carbowax as the binder. The fastest burning behavior was obtained with fuel 498, oxidizer TAGN, and NC binder (Lot 5A).

The initial encouragement caused by the burning characteristics of the confined, steel-cased samples was greatly tempered by the results of the unconfined bare sample firings. These samples burned with considerably less round-to-round reproducibility, as is evident in Table 10. Only samples 1D, 2C, 7B, and 8A functioned at all reproducibly. And even these samples failed to match the burning rates of the corresponding steel-cased configurations. Formulations 7B and 8A, particularly, burned far slower at 50 MPa than they did in the steel-cased configuration. The rest of the samples functioned quite irreproducibly. Even so, in most cases the extreme values of the burning rates for a given composition in the two configurations were still far apart (e.g. sample 3, minimum value at 50 MPa for steel cased configuration, 238 m/s;

TABLE 10. APPARENT BURNING RATES OF UNCONFINED SAMPLES

Sample	TMD(%)	Burning Rates (m/s) 50 MPa	100 MPa	150 MPa
1086-1D	86	0.36 ± 0.03	0.82 ± 0.03	1.12 ± 0.07
1086-2C	86	1.50 ± 0.20	2.00 ± 0.20	1.80 ± 0.20
1086-3	91	96 ± 40	145 ± 61	144 ± 71
1086-4B	97	47 ± 8	101 ± 14	101 ± 3
1086-5A	86	368 ± 176	455 ± 195	463 ± 195
1086-5A	98	256 ± 116	315 ± 133	332 ± 113
1086-6B	85	39 ± 26	57 ± 23	39 ± 15
1086-6B	88	22 ± 5	18.6 ± 0.6	17 ± 1
1086-7B	98	2.3 ± 0.1	4.22 ± 0.08	9.4 ± 0.9
1086-8A	97	11.6 ± 0.1	26.0 ± 0.4	102 ± 2

maximum value at 50 MPa for bare sample, 136 m/s.) The slower-burning, unconfined formulations did burn reproducibly, as in the case of sample 8A, Figure 13. The burning rate plot for sample 8A is unusual in that it shows

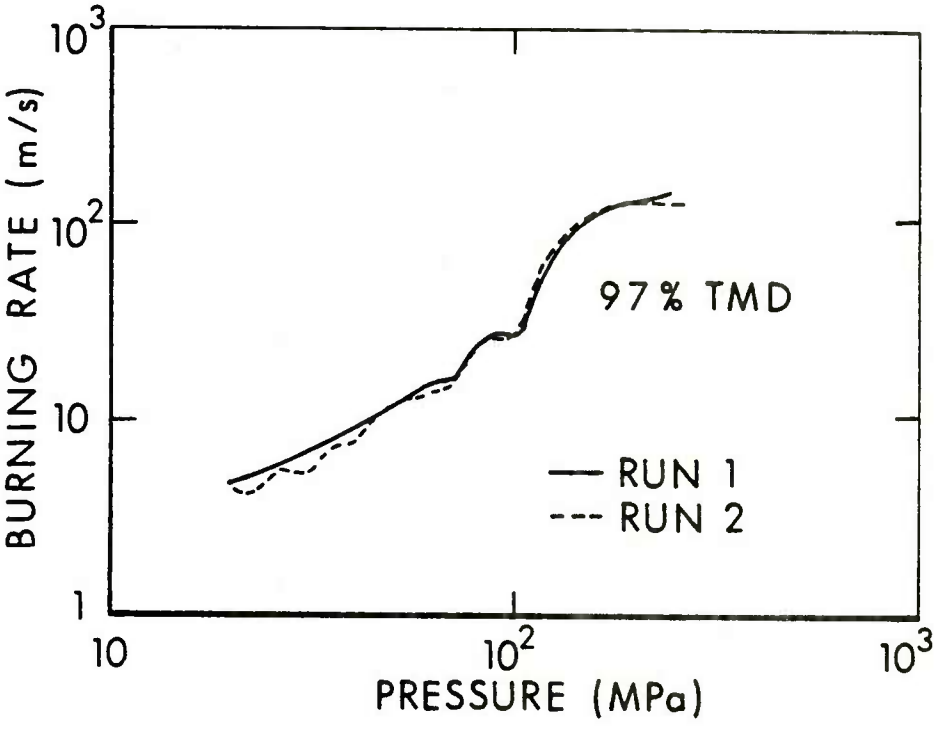

Figure 13. Reproducibility of Apparent Burning Rate of Unconfined VHBR 1086-8A

an increase of burning rate with pressure. For most of the VHBR samples fired, the burning rates fell off at higher pressures. Superimposed plots of the burning rates of formulation 8A in the confined and bare configuration are given in Figure 14. The percent TMD values for the cased and bare samples,

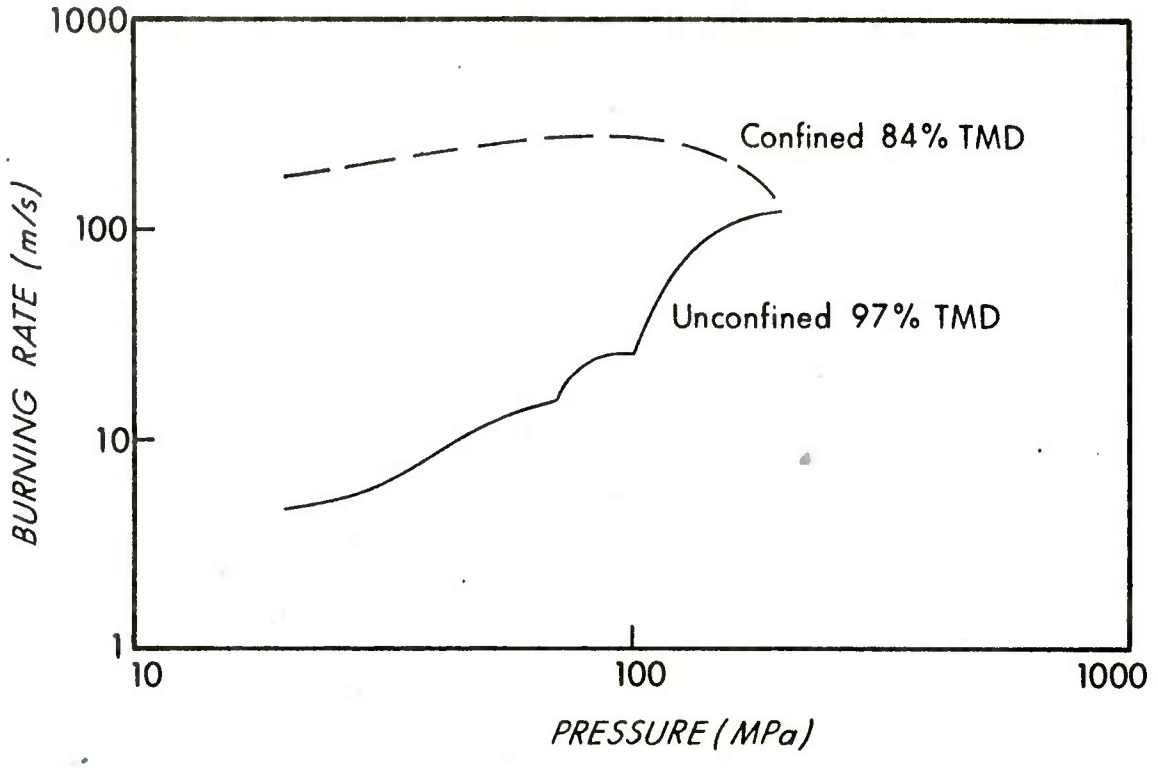

Figure 14. Comparision of Unconfined and Confined Burning Rates of VHBR 1086-8A

respectively, are 84 and 97. At 100 MPa, the burning rates differ by a factor of ten. At lower pressures the difference is greater. Further, the overall slope of the unconfined sample is considerably steeper than the slope of the confined sample. Finally, the bare sample exhibits an increase in burning rate above 100 MPa while the confined sample exhibits a decrease in burning rate. Clearly, for these VHBR samples, burning rate cannot be simply a function of chemical composition. The combined effect of confinement and density variation definitely exerts an influence on burning rate. This may be through any of a number of mechanisms, including possible local overpressures, gas permeation, or grain breakup effects. C. Price[25] has postulated that VHBR propellants burn by rapidly disintegrating into a large number of small particles which then burn according to conventional laminar burning laws. It is the rapid generation of surface area that gives the impression of rapid linear burning. This would certainly seem plausible in light of the initial, largely flat, burning rate vs pressure relationships followed by large

[25] *R. M. Price, "Traveling Charge 40-mm Pellet Production 12 March 1979 - 1 November 1979," Naval Weapons Center Report No. NWCTM 4070, p. 29, November 1979. (See combustion Section of report by C. Price).*

regions of burning rates decreasing with pressure that were frequently observed in this study. Moreover, the increasing burning rate of the bare samples at the same pressures at which the confined sample burning rates decrease could very well correspond to differences in grain breakup patterns and particle burnout effects.

The burning rates computed for the large diameter samples ranged from 1 m/s to 300 m/s. Highest burning rates were computed for sample 8A above 270 MPa. Two lots of formulation 7B were fired, so replicate data exists for this formulation. All other samples were fired singly. A summary of burning rate data for these firings is given in Table 11. The superimposed burning rate curves for formulation 7B, lots 4 and 5, are given in Figure 15. The

TABLE 11. APPARENT BURNING RATES OF LARGE DIAMETER SAMPLES

Sample	Burning Rate (m/s)		
	50 MPa	100 MPa	150 MPa
29-51A	116.3	117.9	100.7
29-51A (M4)	103.6	108.0	112.5
29.51A (M7)	25.2	34.1	26.6
30-4A	54.7	40.53	53.5
1086-5A	86.4	95.1	91.5
1086-7B (Lot 4)	2.4	5.0	13.2
1086-7B (Lot 5)	1.4	3.3	10.7
1086-8A	1.1	57.3	146.1

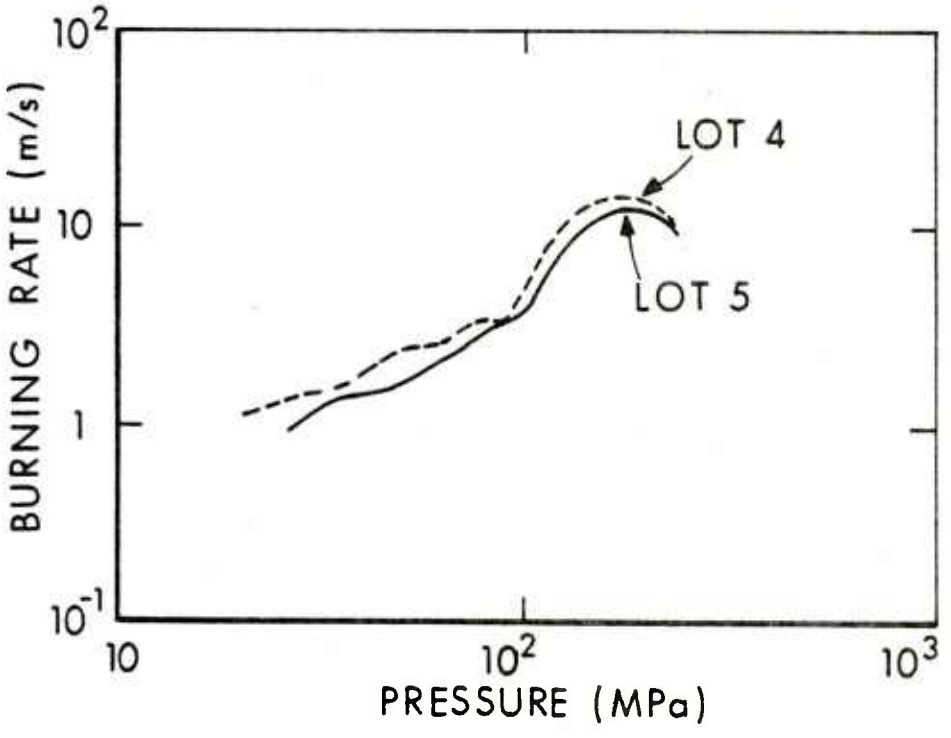

Figure 15. Apparent Burning Rates of VHBR 1086-7B, Large Diameter Samples

reproducibility of these data, though not as good as for the steel-cased samples, is reasonable enough to permit comparisons with the small diameter confined and unconfined firings as seen in Figure 16. The effect noted here

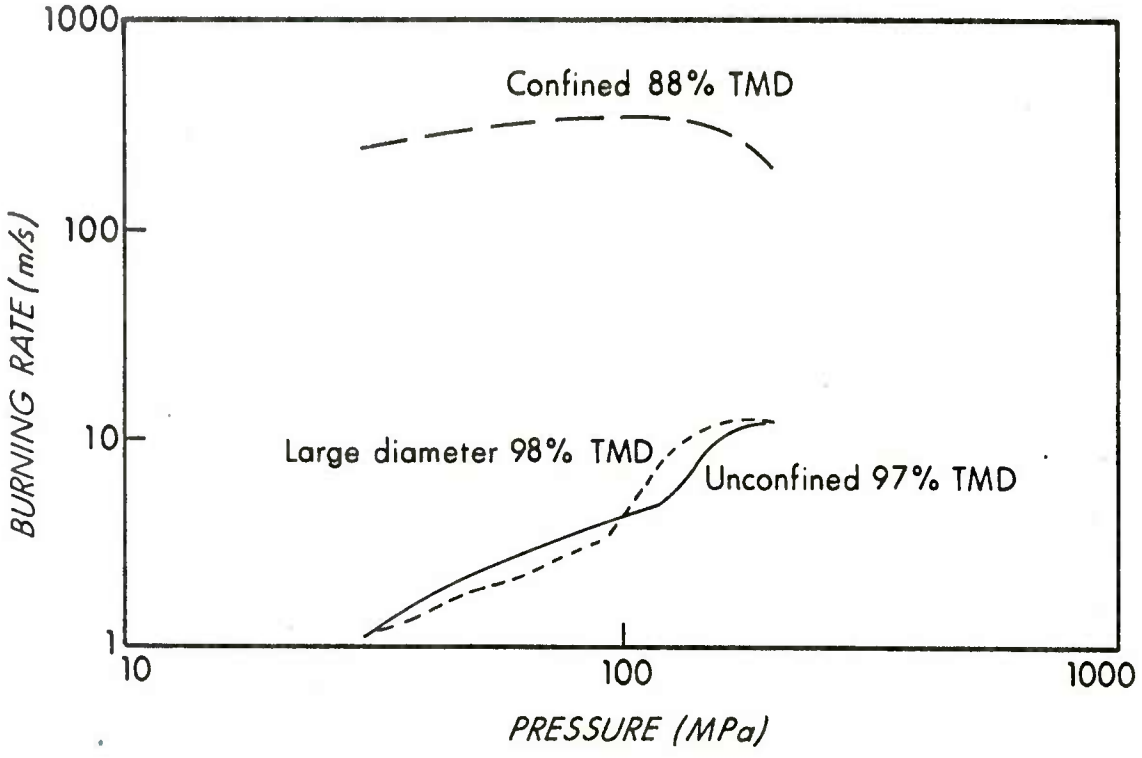

Figure 16. Apparent Burning Rates of VHBR 1086-7B,

is similar to that observed for sample 8A fired in the bare and confined configuration (Figure 14). The confined sample appeared to burn two orders of magnitude faster than the unconfined and the large diameter samples. Since the large diameter samples were bonded into steel sleeves, they could be expected to burn more like the confined sample. On the other hand, the densities of the bare and large diameter samples were identical, while the cased sample was much more porous. Both the porosity differences and the confinement could have affected the burning. The decreased porosity of the higher density samples may inhibit flame front propagation. The presence of the confining steel sleeve, however, could channel product gases to augment sample breakup. At this point it is not clear what the difference is due to.

Burning rate comparisons involving the large diameter, 1086-5A and 1086-8A, samples are handicapped by the fact that only one firing was performed per formulation. Hence, no variability data on the large sample burning rates are available. A comparison of the burning rate curves for one of these compositions in the various configurations is, nevertheless, interesting. Figure 17 compares burning rate data for formulation 1086-8A. Both the cased and uncased samples burned quite reproducibily, so the difference in their burning properties is clearly established. If the large diameter sample burning rate data can be believed, then at 35 MPa the cased sample of 8A burns a thousand times faster than the large diameter sample. This difference is truly enormous and points to a burning mechanism in which physical effects can

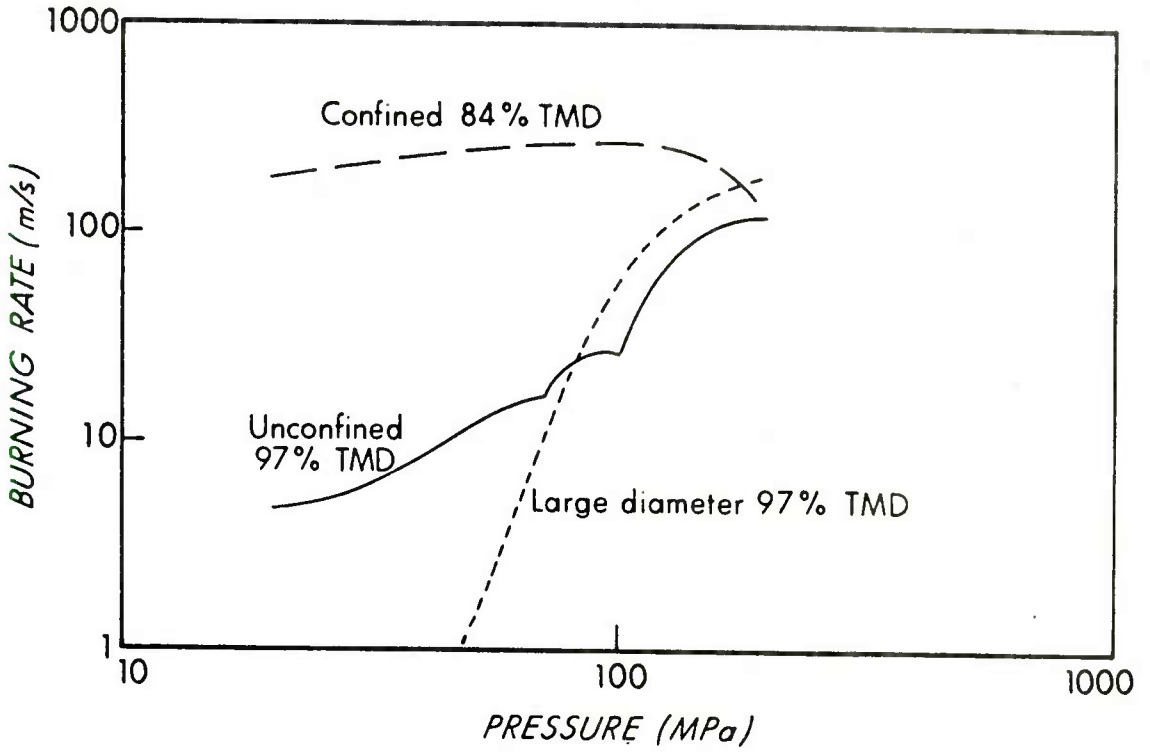

Figure 17. Apparent Burning Rates of VHBR 1086-8A

completely override chemical effects. Comparison of the uncased diameter sample with the larger diameter sample indicates a crossover in burning rates around 75 MPa. This cannot be explained on the basis of chemical effects. If different modes of grain breakup due to porosity or confinement differences are postulated, then the data may be rationalized on the basis of instantaneous surface area exposed as a result of more or less complete sample breakup.

C. Experimental Impetus

The theoretical impetus values computed for the formulations were quite promising (Table 3). Experimental impetus calculations were made using measured maximum pressures and thermodynamically calculated covolumes. The presence of igniter/ignition aid was accounted for in the calculations. The experimental impetus values obtained from initial firings were originally lower than the theoretical values by as much as 40 percent. This discrepancy resulted in a very close scrutiny of both the experimental and computational techniques. Besides heat loss, part of the difference was traced to chamber volume errors, part to assumptions made for the theoretical performance calculations, and part has not yet been accounted for.

The treatment of possible condensed-phase combustion products was found to have significant effect on predicted impetus values. In those cases where large amounts of solid boron nitride form, far higher impetus values are obtained. The formation of liquid B_2O_3 has a similar effect, though the differences in impetus are less. Impetus values for several compositions under condensed-phase-permitted and condensed-phase-forbidden conditions are given

in Table 12. The condensed phase impetus values are higher due to the liberation of the energy of condensation with a subsequent increase in the internal energy of the gaseous combustion products.

TABLE 12. EFFECTS OF CONDENSED PHASE PRODUCTS ON VHBR PROPELLANT THEORETICAL IMPETUS

Sample	Impetus J/g	Principal Condensed Products Moles/kg		Impetus Condensed Phase Suppressed J/g
		BN	B_2O_3	
30-4A	1103.6	6.6	0.86	832.4
29-51A	1053.5	5.3	1.40	824.6
29-51A-Mod 4	1057.0	5.9	0.99	813.2
29-51A-Mod 7	1057.4	6.3	1.0	801.8
1086-5A	1124.7	---	1.30	1068.2
1086-7B	1084.4	---	1.9	1045.3
1086-8A	1119.1	---	1.4	1068.5

The values for the experimental impetus computed were little affected by whether the covolume used came from condensed-phase-allowed or condensed-phase-not-allowed calculations. Typically, the variation in experimental impetus caused by this was 1 percent or less. The experimental impetus values presented are calculated using an average of the values computed using the two covolume values. Table 13 shows the comparison of theoretical and experimental impetus results. On the average, for samples 5A through 8A, the experimental impetus is on the average 75 percent of theory for the condensed theoretical

TABLE 13. DISCREPANCY BETWEEN EXPERIMENTAL AND THEORETICAL IMPETUS FROM LARGE DIAMETER VHBR TESTS

Sample	Experimental Impetus J/g	% Theory (Condensed Phase Allowed)	% Theory (Condensed Phase Suppressed)
1086-5A	773.6	69	72
1086-7B	865.0	80	83
1086-8A	866.0	77	81
29-51A	877.7	83	106
29-51A Mod 4	917.5	87	113
29-51A Mod 7	866.5	82	108
30-4A	804.9	73	97

impetus values and 79 percent of theory for the uncondensed theoretical impetus values. For the NWC samples, however, comparisons yield on the average 81 percent of theory for the condensed phase thermochems and 107 percent of

theory for the uncondensed thermochems. It is likely therefore, that, for the NWC samples, a partial condensation of BN had occurred. It is difficult, however, to account for the 20 to 25 percent difference between theory and experiment for the rest of the samples. Closed chamber experiments on conventional gun propellants typically result in 95 percent or better agreement with theory. Whether the impetus discrepancy is due to experimental errors that have gone unrecognized or whether the theoretical estimates are high due to incorrect product selection or possibly incorrect heat-of-formation data for some of the VHBR propellant ingredients is at this time unclear. If the formation of condensed phase products is slow compared to the combustion time, then the heat release of the condensation process could be effectively neutralized by the normal heat losses typically observed in closed bomb firings. The "Blake" code assumes, of course, that thermochemical equilibrium is achieved. Hence, some of the difference observed may be due to nonequilibrium effects.

One final observation concerning experimental impetus values is in order. Steel-cased samples ordinarily yielded experimental impetus values on the average of 65 percent of theory. The bare and large diameter samples yielded average experimental impetus values of approximately 75 percent. The reason for the difference is not clear. It may be due to work performed by the combustion gases in deforming sample tubes or possible increased heat loss effects due to the presence of the steel sleeves.

D. Residue

Throughout the study it was noted that significant amounts of solid residue were formed on combustion of the VHBR propellant samples. A partial collection of residues was made for examination throughout the study. Infrared spectral examination of residues revealed curves resembling boric acid and boron nitride.

An effort was made to do a complete collection of residues from the large diameter pellet firings. Table 14 lists the percent solid residue by weight collected for these samples.

TABLE 14. RESIDUE FROM VHBR PROPELLANT FIRINGS

Sample	Residue (%) Measured	Residue (%) Predicted	% Hivelite in Formulation	% Boron in Formulation	Predicted Products
1086-5A	6.2	10.7	8.8	4.8	B_2O_3
1086-7B	14.7	13.0	10.5	4.25	B_2O_3
1086-8A	0.7 (?)	10.9	8.6	4.8	B_2O_3
29-51A	(Not Collected)	26.1	16.2	10.9	BN, B_2O_3
29-51A Mod 4	29.9	25.4	16.2	10.9	BN, B_2O_3
30-4A	21.5	26.8	16.2	11.4	BN, B_2O_3

The amount of residue collected appears to correlate strongly with the amount of boron in the formulation and the predicted presence of boron nitride in the combustion products. It is possible that the lower experimental residue figures for formulations with only B_2O_3 as the predicted product are a result of the solubility of the hydrated oxide species in water.

A more detailed residue study, including collection of aqueous as well as solid combustion products coupled with more complete qualitative as well as quantitative analysis, would be of interest. It is important to know, from a systems point of view, the nature and extent of residues formed by the VHBR propellants. A more complete knowledge of the residues may also help to guide product selection in thermochemical calculations.

V. CONCLUSIONS

The results of the burning rate studies indicate that, although the VHBR propellant formulations examined can burn reproducibly under the right conditions, no generalized burning rate laws characteristic of given sample compositions can be derived for them. Sample size, porosity, physical integrity, and confinement effects exert a strong influence on VHBR propellant combustion characteristics. In other words it has not been possible to measure an intrinsic linear burning rate that is independent of physical or geometry considerations. It may not be important from a practical end-use point of view to understand how all the details of the experiment affect the measured apparent burning rates. However, in order to allow intelligent tailoring of the VHBR propellant formulations, it is essential to have a clear understanding of the mechanism of combustion. More information is needed to clarify the mechanisms by which these effects exert their influence. Experiments such as flash x-ray diagnostics and super-high speed cinematography will be essential to providing a much needed physical description of VHBR propellant burning processes. In the mean time, closed chamber experiments can provide useful "quickness" type of information on VHBR propellant samples having the same formulation, porosity, confinement, and dimensions as the propulsion packages under consideration.

The results of the experimental impetus computations indicate that both our pressure measurement technology and our theoretical performance calculations need to be re-examined. The differences between the measured and computed impetus values need to be resolved. This will require additional closed chamber experiments, a re-examination of the heats of formation of major VHBR propellant ingredients, and further thermochemical calculations with new assumptions on product species and their physical states. An examination of condensation kinetics is also essential.

VI. ACKNOWLEDGMENTS

We wish to acknowledge the important contributions made by Mr. R. Bowman for his support of the closed bomb experiments. We are grateful to Dr. E. Freedman who was responsible for the many thermochemical performance calculations. Dr. J. Walbert was invaluable in his efforts to help with the Fourier analysis of the closed bomb data.

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