**NASA CONTRACTOR REPORT**

NASA CR-1739

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# INVESTIGATIONS OF SOLID CHEMICAL BARIUM RELEASE SYSTEMS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1971

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0060796

| 1. Report No.<br>NASA CR–1739 | 2. Government Accession No. | 3. Recipient's Ca |
|---|---|---|
| 4. Title and Subtitle<br>INVESTIGATIONS OF SOLID CHEMICAL BARIUM RELEASE SYSTEMS | | 5. Report Date<br>August 1971 |
| | | 6. Performing Organization Code |
| 7. Author(s)<br>D. T. Hodder, R. B. Kimball, and W. W. Wrinkle, Jr. | | 8. Performing Organization Report No.<br>SD70-333 |
| | | 10. Work Unit No. |
| 9. Performing Organization Name and Address<br>Space Division<br>North American Rockwell Corporation<br>Downey Calif. | | 11. Contract or Grant No.<br>NAS1-7000 |
| | | 13. Type of Report and Period Covered<br>Contractor |
| 12. Sponsoring Agency Name and Address<br>National Aeronautics and Space Administration<br>Washington, D.C. 20546 | | 14. Sponsoring Agency Code |

15. Supplementary Notes

16. Abstract

An investigation of solid chemical (thermite) barium vapor release systems for geo-magnetospheric measurements is reported. First, the relative barium vapor yield efficiency for the barium-copper oxide/canister system was evaluated as a function of varying physical parameters of the materials and release canister. Second, alternate solid chemical systems were investigated to increase the barium vapor yield efficiency. Tests were conducted under vacuum conditions. Primary measurements of relative barium release efficiency were obtained using a spectrometric technique in which relative intensities of $Ba^o$ and $Ba^+$ resonance emission lines were compared for each formulation or condition. A 75% barium-25% cupric oxide formulation was adopted as a standard for comparison as this formulation had successfully released Ba clouds in several flight tests. The results of these studies indicated that the yield of Ba vapor from the Ba.-CuO systems was essentially insensitive to the parameters tested although some improvements were suggested. Two alternate unoptimized systems showed approximately 2 and 10 times better Ba vapor yields than the Ba-CuO standard mixture. These systems were respectively (1) barium-molybdic oxide mixture and (2) one in which aluminum-molybdic oxide thermite vaporized a quantity of physically separated Ba granules. Hazards and safe handling of Ba and other reactive metals in combination with new chemicals is emphasized.

| 17. Key Words (Suggested by Author(s))<br>Thermite Barium Release Systems<br>Solid Systems-Canister Release<br>Ground Tests and Evaluations<br>Ba-CuO/canister evaluation<br>Improved formulations | 18. Distribution Statement<br><br>Unclassified - Unlimited | | |
|---|---|---|---|
| 19. Security Classif. (of this report)<br>Unclassified | 20. Security Classif. (of this page)<br>Unclassified | 21. No. of Pages<br>68 | 22. Price*<br>$3.00 |

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## RELEASE SYSTEMS

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## SUMMARY

Consistently lower barium (Ba) vapor release yield is obtained with barium-cupric oxide (Ba-CuO)/canister release systems than is predicted by theory (i.e., 1 to 7% actual compared to 28 to 30% theoretical). This investigation was divided into two phases: Phase I which considered possible ways of improving the efficiency of the Ba-CuO/canister system and Phase II which considered alternate solid chemical systems selected on a theoretical yield basis and findings from Phase I. The approaches used in the phases are summarized below:

Phase I - BaCuO/Canister Systems (27 tests)

o The system consists of a canister containing a compressed thermite mixture of Ba and CuO which generates enough heat to vaporize an excess of Ba and rupture a nozzle seal (Figure 2) to release the Ba vapor into a vacuum.

o The relative efficiency of Ba vapor production was determined by measuring the integrated intensity of the 5535Å neutral barium atom (Ba°) and the 4554Å barium ion (Ba+) resonance lines over this period of the canister release output.

o Establish a standard performance index for the German design (3Kg, 75% Ba-25% CuO) canister under a controlled vacuum test environment.

o Determine the effects of scaling down to a small test canister (288 gm.).

o Determine relative improvements in Ba vapor yield resulting from small scale canister tests of:

    o Variation of composition (Ba-CuO weight percent ratios)

    o Variation of compressive force in canister loading

    o Variation of blowout diaphragm strength (0, 53 and 100 atmospheres)

    o Variation of Ba particle size (1 to 3 mm and 0.1 to 0.3 mm)

o **Effects of insulated canister wall and graphite nozzle throat**

Phase II Alternate Chemical Systems (15 tests)

o Using the same type measurements, evaluate the relative yield of Ba vapor from two alternate systems: barium-molybdic oxide (Ba-MoO$_3$) and barium physically separated from an aluminum molybdic oxide thermite (Ba/Al-MoO$_3$)

o Establish a standard for comparison to the 75% Ba-25% CuO mix under same test conditions

The results of the Phase I tests were highly variable and indicated an order of magnitude range in Ba vapor yield under presumably identical conditions for some of the Ba-CuO/canister systems tested. Because of this, it was recognized that major problems existed with the Ba-CuO/canister systems. A significant indication was that the Ba-CuO reaction with an excess of Ba admixed was quenched due to heat loss in the canister. The size and shape of Ba particles used (1 to 3 mm) in the "standard" formulations (most of the Phase I tests) was such that poor mixtures with the smaller sized CuO were produced. This occurred even though incremental pressing and a range of compressive forces were used. This mixture inhomogeneity contributed to the variable results obtained. Another factor responsible for low Ba vapor yields was the solution of Ba in the liquid copper produced by the reaction. This lowered the quantity of Ba vapor available for release. It was also determined that a low pressure nozzle seal – blowout diaphragm gave higher light output than the standard 100 atm. diaphragm.

The Phase II experiments may be regarded as lumped parameter tests in that simultaneous solution of several problems identified in Phase I was attempted. The changes for all Phase II tests included; the removal of the blowout diaphragm, use of similar sized particles of Ba and oxide to insure a more homogeneous mixture and prevent separation when loading into the canister, use of uncompacted mixtures to facilitate ignition and remove potential fire hazards in compression packing, and selection of an alternate oxidizer (MoO$_3$) to minimize Ba-liquid metal solution. The 75% Ba-25% CuO formulation tested under these Phase II conditions served as a reference against which the new chemical systems were compared directly. The Ba-MoO$_3$ system was one of the same theoretical yield as the Ba-CuO system but formed a solid metal product (Mo) instead of the liquid metal Cu. The results were that the relative yield of Ba vapor from Ba-MoO$_3$ was about double that of the Ba-CuO. The Ba/Al-MoO$_3$ was a formulation having a theoretical yield about 1.67 times greater than the Ba-CuO and also as tested, the Ba granules were separated from the Al-MoO$_3$ thermite mixture in the canister. The tests results gave a relative Ba vapor yield for the Ba/Al-MoO$_3$ system of about 10 times that of the Ba-CuO standard of comparison.

# INTRODUCTION

Experimental releases of alkali metal vapors have been successfully conducted for many years in the lower and upper atmosphere (e.g., see reference 1). These releases were directed primarily towards study of the individual photochemical ionization processes as to infer properties and study phenomena of the upper atmosphere and ionosphere, in particular the study of electrical fields. For these studies small rocket releases are generally adequate and no serious technical difficulties exist. Barium vapor releases in interplanetary space have been proposed for the study of the interplanetary medium and fields, and mapping of planetary magnetic fields. Figure 1 presents a recent summary of such experiment concepts. These experiments may in general be characterized as requiring the production of large plasma clouds, whose motion may be studied from earth-based observatories. These lead to the requirement of payloads having higher yield of Ba vapor.

The resonance line of $Ba^+$ ion at $4554\overset{\circ}{A}$ (blue) and the resonance line of $Ba^\circ$ neutral at $5535\overset{\circ}{A}$ (green) are visible at the earth's surface which allows for visual-optical observation and measurements. In space the released Ba vapor is photoionized and both $Ba^\circ$ and $Ba^+$ are excited by solar irradiation to emit their resonance light. The intensity of the resonance radiation, under certain conditions, is proportional to the number of radiating sources and thus can be used to indicate the yield of the release systems.

Lust, Foppl, Haerendel (refs. 2, 3, 4) and others at Max Planck Institute, West Germany had studied several systems and from laboratory and flight evaluations of these systems had determined that the Ba-CuO system was the best.

However, performance of this system as inferred from actual releases is disappointing (i.e., 2 to 7% according to reference 1 and 3). This is not efficient enough when it is recognized that several kg. of free barium are required for production of a barium vapor cloud visible from the earth at even the nearer edge of the geo-magnetosheath (5-6 earth radii).

This study was planned to investigate possible ways of improving the yield of Ba vapor released from solid chemical/canister systems. The Ba-CuO mixture is a thermite mixture with excess Ba to be vaporized by the exothermic heat of reaction:

$$Ba + CuO \longrightarrow BaO + Cu + \Delta H$$

Practically, the efficiency of deflagration and subsequent Ba vapor release from the canister left room for much improvement. It appeared that the physical arrangement and mechanisms operating were inherently of low efficiency.

The experimental part was divided into efforts to improve the performance of the Ba—CuO/canister system (Phase I) and investigation of 2 other systems with theoretical potential (Phase II).

In Phase I an improvement in solid chemical barium release efficiencies was investigated by studies of effects on canister performance of varying the following parameters of the Ba—CuO system:

1. Payload size
2. Chemical formulation
3. Formulation density
4. Particle size
5. Blow-out plug strength
6. Thermal isolation of canister wall

The primary measured parameters used to evaluate canister tests are the following:

o  Ba° – 5535$\overset{\circ}{A}$ Resonance line
o  Ba+ – 4554$\overset{\circ}{A}$ Resonance line
o  Pressure-time traces

Due to the erratic behavior of these parameters in the early tests in the series, additional (and in some cases redundant) measurements were added to obtain a better basis for evaluation of canister performance.

The controlled variables are listed below:

o  Canister configuration (small canister, see figure 2)
o  Diaphragm burst pressure
o  Ba particle size (large 1 to 3 mm or small 0.1 to 0.3 mm)
o  Formulation composition (percent barium to cupric oxide ratio)
o  Speed of window rotation (r.p.m.) Records Ba deposition rate
    – see figure 3
o  Gap/compression (measured at top of canister due to variation
    in compressive force)
o  Presence of thermal insulation (interior)
o  Carbon throat inserts or unlined nozzle for same size opening
o  Number of squibs used for ignition

o Number of layers used in compacting canisters
o Vendor source for barium used
o Weight of charge of Ba-CuO formulation (normally 3 kg for large canister or 288 gm for small canisters)

Additional uncontrolled variables or measurements are given below:

o Blue line (Ba+) intensity, peak and integrated values
o Green line (Ba°) intensity, peak and integrated values
c Peak pressure and pulse duration
o Blue (Ba+)/Green (Ba°) ratio
o Light duration, blue line, green line, and total
o Plume geometry
o Efflux time by three techniques: pressure, light, and window deposits
o Time to diaphragm burst
o Residue condition, size, color, composition
o Buildup of material around nozzle
o Reaction percent of completion by internal residue analysis
o Internal temperature
o Erosion of nozzle

Additional parameters measured periodically are:

o Reflection grating visible range spectrum
o Chemical and physical composition of selected deposits, residue, and nozzle material
o Ba to Cu ratio and time history in sequential window deposits

In Phase II a series of alternate solid chemical barium release systems were tested using the same fundamental measurement techniques. These systems are listed below; they also incorporate certain physical improvements recognized in the course of the Ba-CuO studies.

System A: Ba-CuO, 75% by weight barium and 25% by weight copper oxide

System B: Ba-MoO$_3$, 80% by weight barium and 20% by weight of molybdic oxide

System C: Ba + Al-MoO$_3$, 65% by weight of barium and 35% by weight of a mixture of (2.67 to 1 weight ratio mix of molybdic oxide to aluminum)

The Ba-CuO system was retested to provide a basis for direct comparison.

With this background it is now possible to proceed to a discussion of the experiment methodology.

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## APPARATUS AND PROCEDURES

### Theory of Optical Measurements

The reactions postulated produce sufficient temperature and pressure to raise the barium atoms and ions to excited states upon absorption of that energy. In general, the energy acquired through an absorption process may subsequently be lost in one of several different ways. The most probable and important way (in this case) is by radiative transition into a state of lower energy.

Barium being one of the alkaline earth elements possesses two electrons in its outermost 6s shell. One of the 6s electronic transitions is the "first" singlet transition $1S_0 - 1P_1$ (resonance line). It represents a 6s electron being raised to the first available energy level; lowest common excited state of the atom. From here, the electron can only drop back into its original level, hence returning the atom to its ground state with the release of a photon with a 5535Å wavelength.

If the barium atom is ionized the "resonance" line has a different value. This comes from the fact that the remaining 6s electron is drawn closer to the nucleus due to its unbalanced positive charge. Hence, there is a change in the energy levels. The first ("resonance") line transition is $2S_{\frac{1}{2}} - 2P_{3/2}$, which yields a photon with a 4554Å wavelength. These two wavelengths are easily produced and result from one-step radiative transition. Their intensity is proportional to the number of radiating sources under certain conditions. Thus determinations can be made of the relative vapor concentration from such spectroscopic intensity measurements.

The fundamental objective of this study is a comparison of the relative performance of various physical and chemical formulations and loading techniques in a set canister configuration (see fig. 2). In this sense, the study is not an absolute investigation into the predicted results of such a release at precisely simulated altitudes between 400 km and 5 earth radii. Such a study would require extremely large, ultra-high vacuum chambers and long diffusion time studies in a magnetic field.

In performance of the experimental portion of this study, the primary objective is to simulate only those features necessary to prevent biasing the outcome of the tests so that selection of optimal formulations results.

### Vacuum Techniques

The initial objective is the selection of the proper vacuum range for the test system, weighing factors of realism of simulation versus cost and time for performance of tests. Figure 4 presents the basic trade-offs,

showing vacuum range in relation to realizable system capabilities and
several release altitude simulations.

On the basis of the relationships depicted in figure 4 the minimal
requirement for release altitude simulation does not necessitate ultra-
high vacuum techniques. Further relaxation of vacuum requirements from
the very high vacuum ( $\approx$ 400 km altitude) to the high vacuum ( $\approx$ 100 km
altitude range), permits utilization of mechanical pumps. This may be
done with relative safety since the primary concern is interaction of the
barium plume with free oxygen or other active gases. Since the system is
first purged with argon, this danger is reduced and conditions well above
the 400 km lower limit described above may be adequately simulated.

## Test Chamber

The test chamber is approximately .8m inside diameter and 2.3m long,
having a volume about 1000 liters. It has one viewing window 10mm diame-
ter. The vacuum pump, a Kinney KDH-130, can pump the chamber down to
about $10^{-5}$ torr, and when this chamber is sealed off from the pump it has
a leak rate of $5 \times 10^{-3}$ torr per minute (see figure 3).

The loaded canister was clamped to a metal frame which could be locked
in position in the test chamber to position the canister properly in front
of the tank window. This frame also incorporated a rotating window, a
45 cm diameter disc of 47 mm Lucite, shielded on both sides except for a
circular 10 cm diameter viewing area near its periphery. When the Lucite
disc rotates past the exposed viewing area (ideally the time for 1 revolu-
tion should equal the burn time of the canister being tested) it continuo-
sly exposes fresh Lucite surface to reduce light attenuation by the film
of vapor and debris deposited on the window.

For the small 110 $cm^3$, canister tests on Phase I the axis of the exit
nozzle was 10 cm from the rotating window which was 28 cm from the Lucite
tank window. For the large 3 kg canisters, the jet was 46 cm from the
rotating window.

The spectrometer entrance slit was placed in the center of the tank
window as close to the window as possible (23 cm) and with the optic axis
of the spectrometer perpendicular to the axis of the jet. The spectro-
meter entrance slit was thus 63 cm from the small canister jets and 99 cm
from the large canister jets. All Phase II canisters were 88 cm from the
exit slit. (See figure 3 for a diagram of the test set up and optical
path.)

Spectrographic Measurements (See Figures 3 & 5 for Reference)

In addition to the spectrum lines of ionized and neutral barium in
the luminous jet, there may be considerable contimuum radiation from

incandescent copper particles. Since barium oxide vaporizes at 3000° C, which is only slightly above the reaction temperature predicted from approximate thermodynamic calculations, interference from the BaO bandheads at 5493 and 5644 Å was feared. Because of this, the selective and less costly spectroscopic technique was chosen rather than the use of narrow bandpass interference filters.

A Jarrell-Ash Model 75-000, f/6.3 plane grating spectrograph modified by the addition of a Jarrell-Ash Model 75-010 photoelectric attachment was used to monitor the 5535 Angstrom line for Ba° and the 4554 Angstrom line for Ba+. The spectrograph has a focal length of 750 mm, uses a 5,906 lines/cm grating, and produces a spectrum having a linear dispersion in the first order of 20.5 Å/mm. at 4500 Å. The photoelectric attachment allows 4 calibrated photomultiplier tubes, exit slits, and quartz lenses to be mounted at the focus of the spectrograph in place of the usual photographic film plate. The exit slits, lenses, and tubes may be precisely positioned so each tube monitors only one spectrum line. Exit slits are 0.075 millimeters wide and were filled by the luminous plume, entrance slit is 0.025 mm, tubes are selected 1P28. The wavelength bandpass is 1.54 Å.

Exit slits were first aligned visually using a Westinghouse hollow cathode barium lamp as the light source. Final adjustments for maximum response were done by observing the output of 1P28 tubes whose positions behind the slits had been optimized for output. A voltage of -1000 was used on the tubes. The response of the 2 channels was equalized to give the same response to the Ba 4554 line when the grating was rotated to position this line first at one exit slit and then at the other. The channels were equalized by adjusting the tube load resistances which were potentiometers that could be adjusted then locked in position.

The spectrometer output was recorded by Tektronix type 551 double beam oscilloscopes set to trigger internally on the signal being observed and produce a single sweep. On some of the final tests the line intensities were also recorded with a high input impedance D.C. power amplifier driving oscillograph galvanometers.

Pressure Measurements

In the initial attempts to measure pressure, considerable difficulty was encountered obtaining data, due to condensation of barium vapor or molten reaction mixture in the pressure tube inlet port. The difficulty was overcome by using a recessed pressure port with the end of the pressure tubing isolated from the wall and curved to face away from the reaction mixture.

High pressure steel tubing was used to transmit the pressure from the canister to a Kistler 603A pressure transducer. The transducer was mounted as close as possible to the canister exterior.

For the small canisters, the total length of pressure tubing was 28 cm with the 15 cm near the canister filled with argon, and the other 13 cm filled with Dow Corning 550 silicone oil to protect the transducer. For the large canisters, the total length of tubing was 35 cm, 23 cm filled with argon, and 12 cm with silicone oil. On the large canister tests, the tubing was protected from the heat of the jet by wrapping it with high temperature Mylar tape then with 0.051 mm steel shim stock.

The signal from the transducer was transmitted by a special Kistler high leakage resistance coaxial cable to a Kistler model 566 electrostatic charge amplifier whose output was recorded on a single sweep oscilloscope.

### Time to Diaphragm Burst

The time interval between the electrical pulse to the squib and the rupture of the pressure diaphragm was measured by an oscilloscope which triggered and swept on the firing pulse to the squib and recorded the triggering of the 5535 line intensity oscilloscope by recording its plus gate output. Since the spectrometer oscilloscopes triggered internally, the start of their sweep coincides with the start of the light output from the jet.

### Temperature Measurements

After unsuccessful attempts with commercially available thermocouples, temperature measurements of the canister interior during firing were obtained on small canisters by high temperature thermocouples (tungsten plus 26% rhenium, tungsten plus 5% rhenium) sandwiched between 1 mil Mylar sheets and placed between the o-ring and canister body. The thermocouple junction was 1 cm away from the wall and well away from the squib. Thermocouple output was amplified 100 times (calibrated) by an Epsco DA-102 G D.C. amplifier and recorded on a single sweep oscilloscope. Figure 6 provides a means for converting voltages to temperature data.

### Jet Plume Spectrum

A visible light spectrum was taken of one small canister using a small spectrograph similar to the one described in Reference 5. An Osram cadmium lamp was used as a reference spectrum and the spectrum positions read with a Gaertner traveling microscope.

The oscilloscope records show the relative spectrum line intensities, and from the areas under the curve, the relative integrated light outputs. The ratio of spectrum line intensisities due to ionized and neutral barium was used as a comparative measure of the ratio of concentrations of ionized to neutral barium in the luminous jets. A comparative measure of total emitted barium vapor for the various formulations was obtained by comparing the sums of the time integrated light outputs for both ionized and

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neutral barium obtained during each of the test firings. These numbers are only relative, but they allow optimization of the formulations for maximum ratio of ionized to neutral barium or for maximum total emitted barium. In order to assign absolute values to the ratios of ionized to neutral barium, it is necessary to assume thermodynamic equilibrium in the luminous source, and to assume some value for the temperature and for the pressure, both of which vary along the jet. If these assumptions are made, then the Boltzmann and Saha equations may be used together with the values of the transition probabilities and statistical weights of the atomic states for the spectrum lines to calculate absolute values. Due to the variations in plume geometry and temperature noted, these calculations were not attempted.

A possible source of error in spectroscopic determinations of this type is the self absorption or self reversal of spectrum lines, resulting in lines having either a flat top, or a dip at the top. To evaluate this source of error, a spectrogram was taken on film of one of the luminous jets and the line shape profiles checked by scanning the film in an Applied Research Laboratories Model 22,100 Spectroline Scanner. This microphotometer automatically scans the spectrum lines and produces a strip chart record of photographic density across the lines.

## Jet Plume Geometry

The plume shape or cone angle was determined by taking several open shutter photographs of canister firings, and on one test, by placing a large metal witness plate downrange from the jet and perpendicular to the jet axis and observing the pattern of debris on the plate.

## Canister System

The small size canister system employed is shown in Figure 2. The large size system is identical in all respects save internal volume.

## Outline of Barium Handling Procedures

The safe handling of barium metal, especially in a finely divided particulate form, requires an understanding of its chemical properties and the potential hazards involved. This section describes its safety critical characteristics and outlines the major operational steps followed in this experimental study.

Barium metal has a very strong affinity for oxygen and oxygen containing compounds (one of its major industrial uses is as a "getter" for the removal of traces of gaseous oxygen from electronic vacuum tubes).

Perhaps the most critical safety hazard associated with the normal handling of barium metal occurs when oxygen and small amounts of water or moist air are allowed to come in contact with the barium metal. The chemical

reactions that take place release hydrogen gas and enough localized heat energy to ignite or explode the oxygen and hydrogen gas present.

Halocarbon compounds containing the halogen elements (fluorine, chlorine, bromine, or iodine) in the presence of barium metal, also present a safety hazard because of their strong oxidizing action and explosive potential (see reference 6 for a fuller treatment).

With the careful precaution to maintain the controlled exclusion of free oxygen gas and free water liquid or vapor the particular hazards of concern in this particular experimental study were those associated with the handling of pyrophoric materials (thermite type materials that cannot be extinguished once they are ignited), and a mild toxicity hazard associated with the inhalation of dilute acid soluble barium compounds from airborne contamination.(Barium carbonate has been used as a poison for rodents.)

The following steps outline the procedures followed to avoid these hazards in this experimental study:

1. Barium metal granules were received from the manufacturer in hermetically sealed cans lined with polyethylene plastic bags and containing an inert atmosphere of argon gas (the metal cans are shipped in sturdy boxes according to ICC regulations for Class 1 materials having a high potential fire hazard only).

2. The air tight cans of barium metal were removed from their shipping containers and stored in a metal storage cabinet in a lab adjacent to the test area.

3. In preparation for barium metal screening, weighing, and transfer to sample containers used in remote test operations the necessary clean dry tools, containers, weighing balance, sieving screens, and an air tight can of barium metal were placed in a glove box and purged with dry oxygen-free argon gas (mil - A - 18455E) until the glove box contained less than 0.5% oxygen.

4. After completion of the screening, weighing and barium metal transfer operations, the sealed sample containers of barium metal were placed in a large dessicator, all other barium metal containers sealed, the glove box opened, and all barium containers returned to the metal storage cabinet.

5. In preparation for an experimental test a sealed container of the screened and weighed barium metal sample to be used was attached to the remote handling apparatus within the vacuum test chamber and no further manual handling of the barium metal containers was required during a test firing.

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6. At the completion of a test firing the vacuum test chamber was purged with an air for 30 minutes, the test canister residue was sampled, and then completely immersed in water to hydrolyze any unreacted barium metal particles, while excluding free oxygen present in the air.

## Remote Handling Apparatus, Phase II

Because of hazards experienced (appendix A & B) it was decided that remote handling was required for conducting Phase II experiments. Thus due to the increased impact sensitivity determined for System B, as compared to System A, a remote mixing, canister loading, positioning, and firing system was developed for all Phase II tests (see figure 7). The unloaded canister is first placed in the support fixture (9. figure 7).

For Systems "A" and "B", a previously weighed and sealed sample bottle of barium is then placed into the remote handling vacuum chamber fixture. An oxidizer sample bottle is also placed in its fixture. For System "C", the thermite mixture (aluminum metal powder and molybdenum trioxide) is mixed in air and placed in the canister with the aluminum tube assembly—canister cavity insert (15. figure 2). The thusly loaded canister is inserted in holder (9. figure 7) and Ba bottle is loaded. Then for all systems the mechanical and electrical connections are attached (10. figure 7) and the system is pumped down to 30 torr. Small-scale laboratory tests indicated that systems A and B may ignite spontaneously and burn partially or completely as a vacuum chamber pressure between 30 and 1 torr is approached in pumping down.

The two separate sample bottles of Ba metal and oxidizer for System "A" or "B" tests (single Ba sample bottle for System "C" tests) are remotely opened and poured into a lucite drum mixer, and mixed for 10 minutes. Then the thoroughly mixed Ba metal and oxidizer are dumped into the canister through the funnel (11. figure 7), the funnel is removed and the canister releasing solenoid is activated to position the canister for firing.

## RESULTS AND DISCUSSION

### Barium Cupric Oxide Systems (Phase I)

The intensities of the Ba° (5335Å, green) line and the Ba+ (4554Å, blue) line were recorded and the integrated intensities over the period of emission were used as the primary evidence for inferring systems relative performance. Table I and figure 9 presents a summary of the integrated line intensities for all Phase I tests and indicates the principal parameters investigated. The ratio of intensities of Ba+ and Ba° at any

instant is an index of the plume temperature and hence the chemical reaction efficiency when other system parameters can be assumed to remain fixed. Evaluation of this ratio in Table I indicates that of these parameters, the integrated Ba° and Ba+ line intensities provide the best index of performance for presumable identical small canister tests. However, the integrated intensities of the large canister tests are unsuitable for characterizing performance due to the range of variations obtained. The "standard" large canister tests were more erratic than any of the "identical" small canister systems tested as indicated by variable nozzle erosion, changes in condensed plasma residue, color and quantity, and internal pressure variations. It should be noted that in comparisons of the spectral intensities for the large and small canisters, self reversal of the Ba° lines in the plume and the different viewing geometry for the large canister tests introduced some question as to the validity of such comparisons. (See Table I)

The test results of Table II indicate that a higher pressure reaction is occurring in the small size Ba (0.1 to 0.3 mm) tests. Photographs and deposition pattern analysis indicate that, in sharp contrast to the "standard" 1 to 3 mm. size Ba whose plume subtends a 7° angle at the end of the tank and widens to 30° where it exits the nozzle, the plume for the 0.1 to 0.3 mm size Ba essentially fills the vacuum chamber. This difference indicates that small and large size Ba tests cannot be compared on an equal basis by comparing the measured line intensities. The ratio of intensities of blue to green line (Table I) indicates that the plasma temperature was higher for the small size Ba tests adding to the complexity of analysis. Figure 10 shows a photograph of a small canister plume.

Analysis of a visible range spectrogram shows that the plume exhibits continuum as well as resonance line radiation and that variable optical absorption (self reversal) occurs. Using a large aperture grating spectrograph reference, the spectrogram of the jet showed a continuum or bands extending from the red down to about the cadmium green line. The only line feature in the spectrum was an absorption line (lighter than background). Further, such spectrograms might permit the calculation of the temperature difference but the problem of the unknown variation in the plume geometry for the high pressure, small barium size systems prevents such analysis. Alternate approaches not implemented are the emission of the plume into a pressurized neutral gas environment to confine the plume. However, a temperature difference would still be expected and would have to be accounted for.

Figure 9 depicts the dependence of integrated light intensity on test parameters. The light emitted by the plume from the barium canister was recorded at 5535Å and 4554Å, (the wavelengths of resonance lines of Ba I and Ba II) and the time integrated intensity in these wavelength regions was used as a relative measure of the amount of barium atoms released (relative reaction efficiency). Figure 11 depicts representative data

traces. Absolute content of Ba found in the residue incrementally deposited on the rotating window is also given. The Ba deposit was taken to be a relative measure of instantaneous Ba concentration released since each section of the window was covered immediately after exposure. The agreement between Ba deposition and spectral light measured is good, especially for test #25. This tends to confirm experimentally the validity of the relationship between spectral light intensity and Ba vapor yield upon which our analysis relies. While the lime intensities may be a qualitative indication of reaction efficiencies, certain factors, to be discussed below, seriously complicate any simple quantitative analysis.

The major findings from evaluation of the results listed in Table II are as follows:

1. Highly variable test results were obtained for "identical" Ba—CuO systems.

2. Excessive heat loss to both excess barium and the canister wall resulted in quenching of this reaction. (Use of an insulated canister liner did not solve this problem; hence, the excess barium is regarded as the principal heat sink, e.g., see figure 12 large white chips are barium.)

3. Blow-out plug failure was by temperature and pressure effects.

4. Chemical analysis of the canister internal residue indicated that the chemical reaction varies from 16 to 60% completion.

5. Solution of barium in copper lowers vapor pressure preventing Ba vaporization. This was found by chemical and microscopic analysis of flow residue external to the canister (e.g., see figure 13).

6. Barium/copper alloy condensation on exit nozzle was observed.

7. Erosion of the exit nozzle of the full scale (3 kg.) canisters was significant compared to the small scale canisters (see figure 14).

8. The apparently anomalous intensity data obtained for the large canister tests and the small particle size Ba tests were considered to be due to the different pressures and plume geometries observed.

Based upon the variability of results of these experiments using Ba-CuO systems, there appeared to be no reliable way of obtaining uniform results with the Ba—CuO systems tested; although possible improvements to system performance were indicated, e.g.:

o Use of either a metal foil partition or physical separation of the excess barium from the thermite mix.

o Use of a low-strength blowout diaphragm (this single parameter
apparently produced the highest observed yield in Phase I based
upon integrated green light intensities).

o Use of both smaller sized barium and oxidizer grains to insure a
uniform mix which would not separate on loading.

Implementation of these changes would presumably solve at least to
a degree the problems of test variability. However, in no case did chemical
analysis of canister internal residue indicate that such changes would
achieve a completion of the desired chemical reactions. Moreover, reference
to figure 9 and Table II shows that from the integrated light value criterion
some of the best performance was achieved for systems exhibiting the lower
range of chemical reaction completion (i.e., 16%) and which did not even
fully evacuate (i.e., partially melted excess barium was found internal
to the canister). Factors such as these would indicate that from an abso-
lute standpoint only extremely low barium vapor yields were realized
in Phase I tests (estimated to be well below 1% of the total barium weight).
If this interpretation were correct then there are apparently inherent
difficulties with the Ba-CuO system which cannot be resolved merely by
physical changes.


Molybdic Oxide Thermite Systems (Phase II)

Having defined the major problems of the Ba-CuO/canister system, con-
sideration of alternate chemical formulations was undertaken. A primary
objective was to obtain a thermite reaction not producing an intermediate
liquid phase metal which would potentially extract liquid barium from
the system by solution. The failure to prevent the observed Ba-CuO al-
loying was considered a primary problem of earlier systems.

Additional factors to be considered were the existence of explosive
or other hazardous handling characteristics, the production of a luminous
phase which would interfere with the desired $Ba^\circ$ and $Ba^+$ spectroscopic
measurements, and being essentially a low pressure reaction which would
provide a plume geometry comparable to the Ba-CuO system (proved to be
essentially a low pressure reaction) so as to permit direct comparison.

From evaluation of systems listed in Table I, two were chosen for
analysis in Phase II tests. It was first necessary to verify experimentally
that the anticipated reactions would occur and that no unanticipated hazards
existed with these new systems. Such tests were completed (Appendix A) and
indicated that although one of the systems ($Ba-MoO_3$) showed an enhanced
pyrophoric reaction probability (and hence required remote handling) the
tests could be completed. Not all problems recognized in Phase I were
studied here however. An example was the observed condensation of (pre-
sumably vapor phase) barium produced by expansion and cooling associated

with the canister nozzle. However, Phase I showed that since this type reaction is low pressure and progresses according to the high temperature involved, such a nozzle and blow-out diaphragm are unnecessary. Hence, although beyond the scope of this study, nozzle and closure optimization could have been considered. Tests of an unsealed canister system were indicated to be the most reasonable approach.

Use of a remote handling system (figure 7) necessitated moving the canister assembly some 25.4 cms further from the Jarrel-Ash spectroscope viewing port than was the case for Phase I tests. As a result the occultation of the rotating Lucite window in front of the viewing port was almost negligible for the barium cupric oxide systems, although in Phase I with only about 50% more material in an identical canister the occultation was heavy. Deposition of material inside of the vacuum chamber was essentially equivalent for Phase I and Phase II. Spectral, temperature and pressure measurement techniques and equipment were identical to those used for Phase I tests. Table III provides a summary of the parameters and results of the series of 15 tests. Systems A and B were ignited readily in these tests and there was one incident of pre-ignition on System A, test #5. Test A-6 was to replace that test where no data was obtained. The pre-ignition occurred when the barium cupric oxide cylinders opened prematurely in the mixer (see figure 15) due to their internal pressure (1 atmosphere), while the test chamber was under vacuum.* To prevent this occurrence on subsequent tests, the pre-argon purge vacuum pumpdown was limited to no less than 30 torr. There were no more pre-ignitions although premature openings of the barium and oxidizer cylinder within the mixer were observed again.

The first test of System C (C-1) produced barely measureable blue and green light and pressure. After implementation of the test abort procedure, it was determined by examination of the flame front conductor that the igniter had indeed fired and the reaction initiated, however, it was quenched immediately. Subsequent System C tests were performed using two igniters and a chamber pressure from 6 torr to 25.4 torr of argon. The range of chamber pressures was employed due to the extremely long delay noted between igniter firing and peak reaction exotherms. It was felt that the lower chamber pressures might result in the reaction again quenching. Despite the bimodal nature of the System C light curves (see figure 16), inspection of the interior of the canisters showed normal evacuation. It should be noted that the measurement of the weight of the interior residue for the C System was discontinued due to the extreme difficulty encountered in removing this material.

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*Note:  Appendix A - This spontaneous ignition effect
        was noted for all cases of the System A and B
        small scale tests conducted independently by NR.

Figures 17, 18, and 19 depict the interior and exterior views of typical systems A, B and C canisters, respectively, after firing. Study of these figures reveals that thermal quenching was minimized and canisters were normally evacuated (with the exception noted). Further comparison of the exterior canister lids for systems A and B show that the Ba—CuO alloying/condensation problem was indeed minimized by use of the $MoO_3$ oxidizer. On the other hand the clinkery material observed to be plugging the nozzle on System B (interior view) is typical and constitutes a potential hazard. Note that in all three cases the thermocouple may be observed to have survived the test intact testifying to the reality of the temperature data.

# CONCLUDING REMARKS

The determinations of this study lie in two principal categories, the first concerned with Ba-CuO/canister systems, and the second with alternate solid chemical release systems.

A better understanding of the functioning of solid Ba release canister has been obtained. The "standard formulation" Ba-CuO/canister system of German design appears not to be a high pressure system. Even in a sealed canister the pressure rise is only a few atmospheres. High pressure (100 atmosphere) systems do result when fine (0.1 to 0.3 mm) size Ba is used (figure 20). However it is not clear from spectrometric or chemical analyses that this high pressure aids either the completion of the chemical reaction or the production of Ba vapor, although it produces a faster reaction and a high temperature. One effect of the higher pressure appears to be the faster dispersal of the reactants and excess Ba.

By making improvements in the "standard" Ba-CuO/canister system suggested by the findings of Phase I, the erratic behavior was minimized in the Phase II tests of that system, in that repeatable $Ba^+$ to $Ba^\circ$ integrated intensity ratios were obtained. However, there appear to be inherent difficulties with even the "optimized" Ba-CuO/canister system. Ba-CuO alloy is still deposited in substantial quantities outside of the canister nozzle (droplets of alloy as large as a few mm. have been noted). Rapid heat loss by radiative transfer in space coupled with the increased difficulty of evaporating the Ba in solution, implies a loss of Ba vapor even assuming superheated droplets. In any case, there is indirect evidence to show that even for the "optimized" Ba-CuO system, in which the chemical reaction appears complete, the efficiency of release of Ba vapor remains poor.

With regard to the alternate solid chemical Ba release systems, it has been demonstrated that it is feasible to obtain significantly higher Ba vapor yields in a vacuum release than with the "optimized" Ba-CuO system. Theoretical studies indicated that the $Ba-MoO_3$ (System B) should have the same maximum Ba vapor yield as the Ba-CuO system (System A) but that Ba alloying should not be a problem with $Ba-MoO_3$. In the experimental tests this appeared to be at least partially true since the integrated Ba light intensities for System B were about twice as large as for comparable Ba-CuO (System A). The other inherent inefficiencies of Ba thermite/canister systems noted were, however, still present.

The $Ba/Al-MoO_3$ (System C) was formulated as one which theoretically has a maximum Ba vapor yield of 1.67 times that of Ba-CuO. In the experimental tests the thermite $Al-MoO_3$ mixture was separated physically from the Ba granules (1-3 mm size) to minimize any reactions of Ba with the thermite or its reaction products. This arrangement produced

integrated Ba light intensities of about 10 times that of the comparable Ba-CuO (System A) tests. The segregation of the Ba metal from the heat producing thermite mixture is believed to be an important factor in the observed improvement. It should be noted that Ba-liquid metal alloying should also be absent. Larger size Ba particles were used in System C than in Systems A and B (1 to 3 mm as compared to 0.2 to 0.5 mm for Systems A and B). The use of a finer sized thermite mix and smaller Ba particles might improve the performance of System C.

Concerning the relative hazards of the systems studied in Phase II, it should be noted that the System C thermite mixture ($Al-MoO_3$) was virtually inert and implicitly much safer to handle than Ba containing thermite mixtures such as Systems A and B, which have an erratic but extremely low, impact ignition threshold (Appendix A). Other undesirable aspects found for all Ba thermite mixtures evaluated were hazards of moisture sensitivity (ignition) and spontaneous ignition at a vacuum threshold of from 1 to 30 torr, pressure of either air or argon when being pumped down (Appendix A). This latter effect has not been previously reported in the literature to our knowledge, but has been repeated in our laboratory on numerous occasions. This spontaneous vacuum ignition effect is extremely critical if unsealed canisters are ever considered for flight or testing. One explanation might be that the Ba-oxide reaction is continuously proceeding at a very low rate at room temperature and the better thermal insulation provided by a vacuum over a porous mixture allows isolated portions to reach ignition temperature whereas with gas present (1 atmosphere) to conduct heat away, the hot spots do not develop.

Techniques and apparatus for evaluating the relative performance of Ba release systems in a vacuum chamber have been developed in which the hazards of handling Ba and other reactive metals and their mixtures with oxides have been minimized.

The results of Phase I and Phase II cannot be directly compared because of the differences in the canister release systems which produce plumes of different geometry and optical viewing. In Phase I, the Ba-CuO mixtures were compressed in the canister with very little ullage and they were fired with 100 atmosphere blowout plugs sealing the nozzles. In Phase II, the mixtures were of powders of similar size, well mixed and only compacted by gentle shaking (essentially loose powder) and were fired from canisters with a nozzle open to the vacuum chamber. They also contained about one-half as much mixture as the Phase I canisters.

In summary, evidence has been obtained which indicates that the Ba-CuO/canister system is inherently inefficient for releasing Ba vapor. The evidence developed on two alternate solid systems shows that improvements of from 2 to 10 times more Ba vapor can be released by these systems than by the Ba-CuO system. It should be emphasized that these two systems, $BA-MoO_3$ and $Ba/Al-MoO_3$ have not been optimized for release efficiency and may very well be capable of greater improvement.

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# APPENDIX A

## Hazard Evaluation Tests on Barium, Aluminum, and Molybdic Oxide Mixtures

### Mixtures Tested

The following mixtures were subjected to impact sensitivity,* and pyrophoric reaction probability tests according to the Detailed Test and Operational procedures for NAS1-7000 Phase II.

A) Barium (84.5%) and Molybdic Oxide (15.5%)
B) Aluminum (27.1%) and Molybdic Oxide (72.9%)
C) Barium (68.3%), Aluminum (8.6%), and Molybdic Oxide (23.1%)

Mixtures of particles of sizes in the range of 0.1 to 0.3 mm were tested.

### Impact Sensitivity

Sample Preparation

Samples for impact sensitivity test were prepared as follows:

| Sample No. | BARIUM | | $MoO_3$* | ALUMINUM | |
|---|---|---|---|---|---|
| | % | Particle Size | % | % | Particle Size |
| $A_1$ | 84.5 | 0.1 - 0.3 mm | 15.5 | - | |
| $A_2$ | 84.5 | 1.0 - 3.0 mm | 15.5 | - | |
| $B_1$ | - | | 72.9 | 27.1 | 0.2 - 0.5 mm |
| $B_2$ | - | | 72.9 | 27.1 | 0.1 - 0.3 mm |
| $C_1$ | 68.3 | 0.1 - 0.3 mm | 23.1 | 8.6 | 0.2 - 0.5 mm |
| $C_2$ | 68.3 | 1.0 - 3.0 mm | 23.1 | 8.6 | 0.2 - 0.5 mm |

*($MoO_3$ particle sizes less than 0.1 mm in all cases)

These samples were prepared in an argon-filled dry box.

Samples were prepared by weighing out individual ingredients on beam balance (Accuracy ± 0.05 gm) in dry box, dumping ingredients into 118 cc screw-top glass sample bottles, closing top and shaking bottle until sample appeared thoroughly mixed by visual observations.

Samples containing coarse (1.0-3.0 mm) barium or coarse aluminum segregated extensively after mixing, making selection of representative samples rather difficult. The samples containing barium, prepared as previously noted, were further sampled for sensitivity analyses by extracting small (0.1-0.2 gm) representative samples from the master blend and placing these smaller samples in approximately 10 cc plastic vials. Each of the plastic vials was sealed inside the dry box so that the atmosphere around the sample would be only argon. Five each such sample vials were prepared from master batches, $A_1$, $A_2$, $C_1$, and $C_2$. The five vials from each batch were further sealed by placing them in a 118 cc screw-top glass bottle also sealed in the dry box under argon to provide maximum protection from the atmosphere. Individual vials could thus be used for impact tests without exposing the rest of the composition to the atmosphere. Samples $B_1$ and $B_2$, containing no barium, were not sealed in small vials since the Al-$MoO_3$ mixture should not be particularly moisture or $O_2$ sensitive.

The $MoO_3$ and Al materials were dried at 94° C for about 20 hours before placing them in the dry box for preparing samples. All ingredients and samples were weighed and mixed in the dry box including $B_1$ and $B_2$.

### Impact Sensitivity Tests and Results

Tests in Air. Initial tests were performed in the atmosphere. Samples were extracted from sample vials, placed on an anvil, and impacted as quickly as possible to minimize air contact and barium oxidation. All samples containing barium ($A_1$, $A_2$, $C_1$, and $C_2$) gave sparks when impacted with a 2.27 kg ball from heights as low as 10 cm (minimum practical test height with a 2.27 kg ball). Samples $B_1$ and $B_2$ gave no reaction at 127 cm (maximum height capability) with the 2.27 kg ball. It was tentatively concluded that sparks noted with samples $A_1$, $A_2$, $C_1$ and $C_2$ were merely a result of rapid air oxidation of barium from freshly exposed surface created by impact energy. Samples of pure (Ventron material) barium of both large and small particle size gave results comparable to those noted with Samples $A_1$ and $A_2$. Samples $C_1$ and $C_2$ gave noticeably brighter flashes than $A_1$ and $A_2$, presumably because of ignition of aluminum particles. Bright streamer-type flashes were emitted from impact area indicative of burning particle paths.

Impact Tests Under Argon. In order to eliminate the barium-air reaction from ocurring and thus minimizing the $MoO_3$-Ba reaction, the impact apparatus was enclosed in a plastic tent with glove bag attached. The atmosphere in the enclosure was purged with argon until the J-WO$_2$ meter indicated less than 1% $O_2$ in the atmosphere. Test samples were impacted in this atmosphere with the following results.

Impact Tests Under Argon

| Sample No. | Impact Height, Centimeters | Number of Tests Performed | Number[1] of Positive Results | Comments[2] |
|---|---|---|---|---|
| A₁ | 127.0 | 1 | 1 | |
| | 45.7 | 1 | 1 | |
| | 35.6 | 1 | 1 | |
| | 17.8 | 1 | 1 | The apparent ano- |
| | 15.2 | 1 | 1 | maly here may have |
| | 12.7 | 3 | 1 | been a result of |
| | 10.2 | 1 | 1 | non-representative |
| | 7.6 | 9 | 6 | sampling. |
| | 7.6 | 10 | 5 | |
| | | | | |
| A₂ | 22.9 | 1 | 0 | |
| | 17.8 | 1 | 0 | |
| | 10.2 | 1 | 0 | |
| | 7.6 | 1 | 0 | |
| | | | | |
| B₁ | 127.0 | 5 | 0 | |
| | | | | |
| B₂ | 127.0 | 7 | 2 | |
| | 122.0 | 3 | 2 | |
| | 117.8 | 5 | 0 | |
| | 101.4 | 5 | 0 | |
| | | | | |
| C₁ | 12.7 | 2 | 2 | |
| | 10.2 | 2 | 2 | Using 771 gm ball |
| | 7.6 | 10 | 4 | |
| | | | | |
| C₂ | 127.0 | 2 | 2 | |
| | 91.5 | 3 | 2 | |
| | 61.0 | 3 | 2 | |
| | 30.5 | 2 | 2 | |
| | 15.2 | 3 | 2 | |
| | 10.2 | 3 | 2 | |
| | 7.6 | 4 | 0 | |

(1) A positive result is indicated by a visible flash or spark at impact. No explosions or detonations with audible results occurred as would occur with primary explosives.

(2) All tests were conducted with a 2.27 kg impact ball unless otherwise noted.

It is apparent from the results that the fine barium reacts quite readily with the $MoO_3$ and is easily initiated. Samples $A_1$ and $C_1$ are so sensitive that the minimum impact energy required to initiate them could not be adequately determined on our apparatus. The minimum height attainable with the apparatus is 7.6 cm because of the physical design of the safety enclosure surrounding the impact area. Smaller weights than 771 grams could potentially be utilized but the electromagnet used to hold the weight in place prior to drop has sufficiently magnetized the surrounding metal so that even the 771 gram ball cannot reliably be released by turning off the electro-magnet. Therefore it is impractical if not impossible to utilize smaller weights with this apparatus. Typically, materials that are rated as extremely impact sensitive have impact sensitivity values of 5 to 8 cms, with a 2 kg weight. The reported values of some sensitive explosive materials are noted below.

### Reported Impact Sensitivities

| Material | Picatinny[1] Arsenal Apparatus | Bureau of[1] Mines Apparatus | Jet Propulsion[2] Laboratory Apparatus |
| --- | --- | --- | --- |
| Lead Azide | 7.6 cm | 9.9 cm | — |
| Lead Styphnate | 7.6 cm | 17.0 cm | — |
| Nitroglycerin | — | 15.0 cm | — |
| Mercury Fulminate | 5.1 cm | 5.1 cm | — |
| Composition B | 35.6 cm | 75.0 cm | 20.3 cm |

(1) Using 2.00 kg ball

(2) Using 2.27 kg ball - the Rocketdyne device was a JPL apparatus

Different values are routinely obtained on different apparatus, with the JPL device almost always indicating a lower impact height for initiation thus implying greater sensitivity. The reason for obtaining lower values on the JPL device can probably be attributed to the smaller surface area available for impact. A standard No. 6 Allen socket-head cap screw (surface area 0.13 $cm^2$) is used as the piston tip with the JPL apparatus. These tips gave the most reproducible results in tests performed by JPL on standard TNT samples.

The significance of this apparently extreme sensitivity is difficult to evaluate. Obviously any samples containing barium and molybdic oxide must be protected from impact. This may also mean that it is unsafe to

mix and press mixtures of Ba and $MoO_3$.

Abrasion Sensitivity Testing. Prior abrasion sensitivity tests utilized the Esso, Inc. friction tester on barium-cupric oxide mixtures. This was the first use of this tester at the Santa Susanna Field Laboratories. There was no reaction of the mixture although enough torque was applied during the test to completely flatten the sample between the stainless steel faces of the apparatus. No grit was used with these samples during these tests. Further calibration tests using this tester and a known sensitive primary explosive (PETN) and pyrotechnic squib mix produced no positive reactions. Even when grit was added to the sensitive material, no initiation occurred with this tester. Hence no reliable abrasion sensitivity test data are available at the present.

Anomalous Vacuum Sensitivity. When mixtures of powders of Ba and metal oxides (Ba thermites) are placed in a vacuum chamber and pumped down, a pressure is reached at which the mixture spontaneously ignites. The pressure range was found to be from 1 to 30 torr, varying with mixture and particle sizes, but repeatable for a given system.


Pyrophoric Reaction Probability Tests

Samples Tested. Both fine material (0.1 to 0.3 mm) and coarse material (0.2 to 0.5 mm) was tested for a worst case analysis. Samples were prepared under argon. Five 1 gram samples of each of the following mixtures were prepared and tested.

| Mixture | Ba. Wt. % | $MoO_3$ Wt. % | Al. Wt. % |
|---|---|---|---|
| $A_3$ (fine) $A_4$ (coarse) | 84.5 | 15.5 | — |
| $B_3$ (fine) $B_4$ (coarse) | — | 72.9 | 27.1 |
| $C_3$ (fine) $C_4$ (coarse) | 68.3 | 23.1 | 8.6 |

Pyrophoric Reaction Probability Tests and Results. The five samples of each mixture were sequentially subjected to the following tests within a fume hood:

(1) The samples were heated in air in an uncovered Vycor crucible over a Meker burner until reaction occurred or until the maximum temperature attainable was reached. In those instances where ignition did not occur ($B_3$) direct ignition with an oxy-acetylene torch and later a magnesium ribbon was also attempted.

(2) Identical to (1) above with the exception that the crucible was flooded with argon while heating.

(3) Identical to (1) with the exception that the crucible was flooded water saturated air initially at room temperature while heating.

(4) A 1-gram sample was exposed to dry air in a desicator charged with silica gel. Rate and nature of reaction was observed.

(5) A 1-gram sample was exposed to moist air in a desicator whose base is filled with distilled water. Rate and nature of reaction was observed. At the end of the week droplets of water were applied directly to unreacted mixture and the results observed.

(6) Samples were heated to ignition in air and under argon to determine ignition temperature, reaction rate (duration) and peak reaction temperature (unconfined).

The results of these tests are summarized below:

| Mix | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 |
|-----|--------|--------|--------|--------|--------|--------|
| $A_3$ | Thermite reaction when slight heat applied. Bright flash. Scattered sample. Approx. 5 secs to ignition. | Same as Test #1. Appeared to be more spectacular than 1 or 3. Approx. 5 secs to ignition. | Same as 1 except it seemed to require more heat. Approx. 30 secs to ignition. | No reaction. | No reaction with moist air or liquid water. | Reaction Rate*: 8 secs. Ignition Temp(C°): 140 Peak Temp(C°): 942 |
| $A_4$ | ←————————————— SAME RESULT AS TEST $A_3$ ABOVE —————————————→ | | | | | Reaction Rate*: 25 secs. Ignition Temp(C°): 233 Peak Temp(C°): 1176 |
| $B_3$ | No ignition—MoO$_3$ sublimes. Some black residue formed. Repeated with glass torch with same result. Mixture glowed cherry red. | See Test #1 | See Test #2 | No reaction. | No reaction with moist air or liquid water. | Reaction Rate*: No visible reaction – slight exotherm, 5 secs. Ignition Temp(C°):None Peak Temp(C°): 733 |
| $B_4$ | No reaction. | No reaction. | No reaction. | No reaction. | No reaction. | Reaction Rate*: No reaction. Ignition Temp(C°):None Peak Temp(C°): 895 |
| $C_3$ | Thermite reaction when slight heat applied. Bright flash approx. 5 secs to ignition. | Same as #1. Approx. 5 secs to ignition. | Same as 1. Approximately 10 secs. to ignition. | No reaction. | No reaction with moist air. Initial flash delayed(1 sec) with liquid water. | Reaction Rate*: 4 secs. Ignition Temp(C°): 122 Peak Temp(C°): 444 |
| $C_4$ | Thermite reaction when slight heat applies. Bright flash approx. 10 secs to ignition. | Same as Test #1 | Same as Test #1 | Same as Test #1 | No reaction with moist air. Flashed immediately with liquid water. | Reaction Rate*: 15 secs. minor activity.                28 secs. major activity. Ignition Temp(C°): 233 Peak Temp(C°): 1428 |

RESULTS OF PYROPHORIC REACTION PROBABILITY TESTS

*Reaction Duration

Evaluation of Potential Gas Forming Hazards Arising from Sublimation of
Molybdic Oxide. Plotting molybdic oxide vapor pressure as a function of
reaction temperature indicates that for the anticipated thermite temperature
(i.e., 1000 to 2000° Centigrade) no pressure hazard should exist.

Summary

Comparison of the impact sensitivity results obtained with all mixtures
containing barium and molybdic oxide indicate that there is a pyrophoric
hazard associated with this mixture which is greater than that derived from
the barium-cupric oxide mixture, however, in no case did the mixtures tested
indicate an explosive hazard problem. Based upon these findings, it is
recommended that at least the packing of such mixtures be conducted as a
remote operation. Further, to protect operating personnel, additional
protective measures should be adopted for transport and handling of
canisters loaded with this problem.

Problems encountered in igniting the aluminum molybdic oxide mixture
may be solved by reducing both particle sizes to the 0.149 mm (or finer)
size range.

Alternative solutions to the sensitivity of the barium-molybdic oxide
mixtures that should be considered are the following:

a. Investigation of possible de-sensitizing binders to lower the
   sensitivity thresholds of the barium-molybdic oxide mixtures tested.

b. Consideration of alternative mixtures such as aluminum iron oxide
   thermite mixture of barium tungsten oxide mixtures.

Special Ignition Tests of Alternate Size Ranges for Aluminum-Molybdic Oxide
Mixtures. The results of tests conducted upon 0.149 mm aluminum and molyb-
dic-oxide mixtures to investigate the feasibility of igniting smaller sized
mixtures are summarized below:

| Mixture/Test Description | Ignition Temperatures | Peak Reaction Temperatures | Reaction Duration |
|---|---|---|---|
| 0.149 mm Al – 1 gram not packed – hot flame – open crucible | 1011 C° | 1205 C° | 45 seconds |
| 0.149 mm Al – 2 grams packed – low flame – covered crucible | No Reaction | No Reaction | No Reaction |
| 0.149 mm Al – 2 grams open crucible – not packed – very hot flame | 605 C° | 678 C° | 32 seconds |

## APPENDIX B

### Barium—Cupric Oxide Impact Sensitivity Tests

Impact sensitivity was determined in two ways. Initially, as a rough measure of sensitivity, a pinch of the mixture was put on a steel block and subjected to repeated hammer blows with a steel hammer. There were no sparks, no flame, no indication of any kind of reaction.

For a more sophisticated and quantitative measure of the impact sensitivity of the barium cupric oxide (0.1 to 0.3 mm particle size) mixture, tests were run on the JPL impact sensitivity tester. The results with a 2.27 kg ball, and conducted under atmospheric conditions, were as shown below:

| Ht. (Centimeters) | Result |
|---|---|
| 127.0 | Sparks, partial burning |
| 127.0 | Sparks, flash, apparently complete burning |
| 91.4 | Slight sparking, partial burning |
| 91.4 | Flash, complete burning |
| 61.0 | 0 |
| 61.0 | 0 |
| 61.0 | Moderate sparking, partial burning |
| 50.8 | 0 |
| 50.8 | Sparks, complete burning |
| 40.6 | Moderate sparks, incomplete burning |
| 40.6 | 0 |
| 40.6 | Sparks, flash, complete burning |
| 40.6 | No sample, blank test, no sparking |
| 30.5 | Good sparks |
| 25.4 | 0 |
| 25.4 | 0 |
| 25.4 | Small spark |
| 20.3 | Small spark |
| 15.2 | 0 |
| 15.2 | Small spark |
| 10.2 | 0 |
| 10.2 | Very faint spark |
| 10.2 | 0 |
| 10.2 | 0 |

The results indicate that the mixture is somewhat erratic in behavior toward impact. However, there was very little reactivity below 30.5 cm. The sparks or flash were orange, not like the green barium flame obtained with barium/halocarbon mixtures. Nor was there the loud noise associated with a "go" during the barium/halocarbon testing for impact sensitivity.

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# TABLE I. INTEGRATED LIGHT INTENSITY IN UNITS OF VOLT SECONDS
## (Phase I)

TEST # (#1 Through #3 were Sealed Canister Tests)

| Description | V.SEC 5535A Green° (avg) | V.SEC 5535A Green° | V.SEC 4554A Blue+ (avg) | V.SEC 4554A Blue+ | LIGHT RATIO $\frac{V_B}{V_G}$ |
|---|---|---|---|---|---|
| # 4 Std. Fml. - No Blow-out Plug | | .165 | | .027 | 0.15 |
| # 6 " " - 100 Atm, Blow-out Plug | .110* | .060 | .039* | .037 | 0.5 |
| # 7 " " - 53 Atm, " " " | | .105 | | .052 | 0.175 |
| # 8 " " - 100 Atm, " " " | | .098 | | .071 | 0.214 |
| # 9 " " - " " " " " | .067* | .014 | .047* | .017 | 0.400 |
| #10 " " - " " " " " | | .089 | | .053 | 0.289 |
| #11 70% Ba 30% CuO | | .050 | | .041 | 0.858 |
| #12 " " " " | .042* | .034 | .033* | .023 | 0.584 |
| #13 " " " " | | .041 | | .035 | 0.355 |
| #14 78.5% Ba 21.5% CuO | | .0023 | | .0014 | 0.444 |
| #15 " " " " | .0504* | .0711 | .0227* | .0356 | 0.180 |
| #16 " " " " | | .0779 | | .0311 | 1.06 |
| #19 Single Stroke Std. Formulation 18,144 Kg compressive force | | .033 | | .001 | 0.429 |
| #20 " " " " · 22,675 Kg " " | .020* | .013 | .013* | .024 | 1.50 |
| #21 " " " " 18,144 Kg " " Graphite throat | | .013 | | .015 | <0.550 |
| #17 Full Scale Canister, Std. Formulation | | .066 | | .066 | 0.857 |
| #18 Full Scale Canister, Std. Formulation | | .004 | | .022 | 2.75 |
| #22 Full Scale Canister, Std. Formulation, graphite throat | .088* | .0016 | .093 | .0032 | 0.737 |
| #23 " " " " " " " | | .126 | | .252 | 1.00 |
| #24 " " " " " " " | | .0225 | | - ? - | 1.23 |
| #25 Small Scale Canister, Small Size Ba, Ziconium Oxide Liner, Graphite | | .0019 | | - ? - | no data |
| #26 " " " " " " " " " Throat | .0009* | .0005 | .0003* | .0002 | 1.00 |
| #27 " " " " " " " " " " | | .0004 | | .0003 | 0.357 |

*Average

## TABLE IIA. PHASE I TEST DATA

| | Test No. | 4 | 6 | 7 |
|---|---|---|---|---|
| | Controlled Parameters | | | |
| 1. | Diaphragm Burst Pressure | 2 ATM | 100 ATM | 53 ATM |
| 2. | Particle Size of Ba | Large | Large | Large |
| 3. | Formulation Percent Composition (Ba) | 75% | 75% | 75% |
| 4. | Speed of Window Rotation | 6 RPM | 40 RPM | 40 RPM |
| 5. | Gap/Compression | 5 mm | Full | 5 mm |
| 6. | Interior $ZrO_2$ Coated | No | No | No |
| 7. | Carbon Throats | No | No | No |
| 8. | No. of Squibs | 1 | 2 | 1 |
| 9. | No. of Increments Pressed | 8 layers (2.8 gm/cm$^3$) | 8 layers (2.8 gm/cm$^3$) | 8 layers (2.8 gm/cm$^3$) |
| 10. | Vendor Source for Barium | Ventron | Ventron | Ventron |
| 11. | Weight of Charge | 288 g. | 288-24 = 264 g. | 288 g. |
| 12. | Blue Line Intensity Peak, Integrated | .15 v. .027 v. sec. | 0.1 v. .037 v. sec. | .35 v. .052 v. sec. |
| 13. | Green Line Intensity Peak, Integrated | 1.0 v. .165 v. sec. | 0.2 v. .060 v. sec. | 2.0 v. .105 v. sec. |
| 14. | Peak Pressure & Duration | No Data | 0.54 ATM 0.5 sec. | 1.42 ATM 2. sec |
| 15. | Blue/Green Ratio | 0.15 | 0.5 | 0.175 |
| 16. | Light Duration Blue, Green and Duration | B: .4, 1.4 $\epsilon = 1.8$ G: .4, .8, 2.2 $\epsilon = 3.4$ | B: 0.66 sec. G: 0.66 sec. | B: 1.1 sec. G: 1.6 sec. |
| 17. | Plume Geometry | | | |
| 18. | Efflux Time: Pressure, Light and Window | P: 2.2 sec. L: 5 sec. W: .75 sec. | P: .5 sec. L: .66 sec. W: 0.6 sec. | P: 2 sec. L: 1.6 sec. W: 1 sec. |
| 19. | Time to Diaphragm Burst | No Data | <.1 sec | .077 sec. |
| 20. | Residue Condition | 2-3 mm & larger (up to 1 cm.) CU Nuggets | Fine CU Colored Dust | Fine CU Colored Powder |
| 21. | Nozzle Buildup | 4 cm. Diam. 1 cm. High | | |
| 22. | % of Reaction Completion | Coated to Depth of 3 to 8 mm | | Hollow shell-stuck to top (Photo) |
| 23. | Internal Temperature | | 5000 F | |
| 24. | Nozzle Erosion | | | |

## TABLE IIB. PHASE I TEST DATA

| | Test No. | 8 | 9 | 10 |
|---|---|---|---|---|
| **Controlled Parameters** | | | | |
| 1. Diaphragm Burst Pressure | | 100 ATM | 100 ATM | 100 ATM |
| 2. Particle Size of Ba | | Large | Large | Large |
| 3. Formulation Percent Composition (Ba) | | 75% | 75% | 75% |
| 4. Speed of Window Rotation | | 40 rpm | 40 rpm | 40 rpm |
| 5. Gap/Compression | | Full | Full | Full |
| 6. Interior $ZrO_2$ Coated | | No | No | No |
| 7. Carbon Throats | | No | No | No |
| 8. No. of Squibs | | 1 | 1 | 1 |
| 9. No. of Increments Pressed | | 8 layers (2.8 gm/cm$^3$) | 8 layers (2.8 gm/cm$^3$) | 8 layers (2.8 gm/cm$^3$) |
| 10. Vendor Source for Barium | | Ventron | Ventron | Ventron |
| 11. Weight of Charge | | 288-4 = 284 g. | 288-8 = 280 g. | 288-11 = 277 g. |
| 12. Blue Line Intensity Peak, Integrated | | .16 v. .071 v. sec. | 0.8 v. .017 v. sec. | .52 v. .053 v. sec. |
| 13. Green Line Intensity Peak, Integrated | | .75 v. .098 v. sec. | 2.0 v. .015 v. sec. | 1.8 v. .089 v. sec. |
| 14. Peak Pressure & Duration | | 2.04 ATM 0.4 sec. | 7.15 ATM 1.4 sec. | 1.49 ATM 0.4 sec. |
| 15. Blue/Green Ratio | | 0.214 | 0.400 | 0.289 |
| 16. Light Duration Blue, Green and Duration | | B: 0.9 sec. G: 0.9 sec. | B: .18 sec. G: .03 sec. | B: 0.48 sec. G: 0.76 sec. |
| 17. Plume Geometry | | | | Photo Dep. Pattern Cone Angle 7° |
| 18. Efflux Time: Pressure, Light and Window | | P: 0.4 sec. L: 0.9 sec. W: 1 sec. | P: 1.4 sec. L: .18 sec. W: .23 sec. | P: 4 sec. L: .76 sec. W: .23 sec. |
| 19. Time to Diaphragm Burst | | No Data | 1 sec. | .27 sec. |
| 20. Residue Condition | | | | |
| 21. Nozzle Buildup | | | | |
| 22. % of Reaction Completion | | | | After firing, can still half full |
| 23. Internal Temperature | | 5000 F | | |
| 24. Nozzle Erosion | | | | . |

## TABLE IIC.  PHASE I TEST DATA

| | Test No. | 11 | 12 | 13 |
|---|---|---|---|---|
| **Controlled Parameters** | | | | |
| 1. | Diaphragm Burst Pressure | 100 ATM | 100 ATM | 100 ATM |
| 2. | Particle Size of Ba | Large | Large | Large |
| 3. | Formulation Percent Composition (Ba) | 70% Ba | 70% Ba | 70% Ba |
| 4. | Speed of Window Rotation | 40 rpm | 40 rpm | 40 rpm |
| 5. | Gap/Compression | | | Full |
| 6. | Interior $ZrO_2$ Coated | | | |
| 7. | Carbon Throats | | | |
| 8. | No. of Squibs | 1 | 1 | 1 |
| 9. | No. of Increments Pressed | 8 layers $(2.8 \, gm/cm^3)$ | 8 layers $(2.8 \, gm/cm^3)$ | 8 layers $(2.8 \, gm/cm^3)$ |
| 10. | Vendor Source for Barium | Ventron | Ventron | Ventron |
| 11. | Weight of Charge | 288 g. | 288 g. | 288 g. |
| 12. | Blue Line Intensity Peak, Integrated | 1.8 v. .041 v. sec. | .7 v. .023 v. sec. | .64 v. .035 v. sec. |
| 13. | Green Line Intensity Peak, Integrated | 2.1 v. .050 v. sec. | 1.2 v. .034 | 1.8 v. .041 |
| 14. | Peak Pressure & Duration | 10.2 ATM 2 sec. | 4.76 ATM .5 sec. | 2.58 ATM .6 sec. |
| 15. | Blue/Green Ratio | 0.858 | 0.584 | 0.355 |
| 16. | Light Duration Blue, Green and Duration | B: .07 sec. G: .07 sec. | B: .04 sec. G: .1 sec. | B: .1, .05 = .15 sec. G: .1, .05 = .15 sec. |
| 17. | Plume Geometry | | | |
| 18. | Efflux Time: Pressure, Light and Window | P: 2 sec. L: .07 sec. W: 0.3 sec. | P: .5 sec. L: .1 sec. W: .6 sec. | P: .6 sec. L: .5 sec. W: .5 sec. |
| 19. | Time to Diaphragm Burst | 1.1 sec. | .38 sec | .44 sec. |
| 20. | Residue Condition | Fine CU Colored Powder | | |
| 21. | Nozzle Buildup | | | |
| 22. | % of Reaction Completion | | | Some orange colored mater. in residue |
| 23. | Internal Temperature | | | |
| 24. | Nozzle Erosion | Hole burned in pressure tube | Hole burned in in pressure tub. near nozzle | |

## TABLE IID. PHASE I TEST DATA

| Test No. | 11 | 15 | 16 |
|---|---|---|---|
| **Controlled Parameters** | | | |
| 1. Diaphragm Burst Pressure | 100 ATM | 100 ATM | 100 ATM |
| 2. Particle Size of Ba | Large | Large | Large |
| 3. Formulation Percent Composition (Ba) | 78.5% Ba | 78.5% Ba | 78.5% Ba |
| 4. Speed of Window Rotation | 40 rpm | 40 rpm | 40 rpm |
| 5. Gap/Compression | Full | Full | Full |
| 6. Interior $ZrO_2$ Coated | No | No | No |
| 7. Carbon Throats | No | No | No |
| 8. No. of Squibs | 1 | 1 | 1 |
| 9. No. of Increments Pressed | 8 layers $(2.8 \text{ gm/cm}^3)$ | 8 layers $(2.8 \text{ gm/cm}^3)$ | 8 layers $(2.8 \text{ gm/cm}^3)$ |
| 10. Vendor Source for Barium | Ventron | Ventron | Ventron |
| 11. Weight of Charge | 288 g. | 288-10 = 278 g. | 288-5 = 283 g. |
| 12. Blue Line Intensity Peak, Integrated | .16 v. .0014 v.sec. | .18 v. .0356 v.sec. | 1.9 v. 0.311 v.sec. |
| 13. Green Line Intensity Peak, Integrated | .36 v. .0023 | 1.0 v. .0711 | 1.8 v. .0779 |
| 14. Peak Pressure & Duration | 6.80 ATM 2 sec. | 1.63 ATM .3 sec. | 2.04 ATM .4 sec. |
| 15. Blue/Green Ratio | 0.444 | 0.180 | 1.06 |
| 16. Light Duration Blue, Green and Duration | B: .02 sec. G: .01 sec. | B: .5 sec. G: .6 sec. | B: .3 sec. G: .6 sec. |
| 17. Plume Geometry | | | |
| 18. Efflux Time: Pressure, Light and Window | P: 2 sec. L: .02 sec. W: .6 sec. | P: .3 sec. L: .6 sec. W: .4 sec. | P: .4 sec. L: .6 sec. W: .4 sec. |
| 19. Time to Diaphragm Burst | >2 sec. | .18 sec. | .28 sec. |
| 20. Residue Condition | | | |
| 21. Nozzle Buildup | | | |
| 22. % of Reaction Completion | | Unreacted Ba residue 196 g. | Unreacted Ba residue 204 g. |
| 23. Internal Temperature | | | |
| 24. Nozzle Erosion | | | |

## TABLE IIE.  PHASE I TEST DATA

| | Test No. | 17 | 18 | 19 |
|---|---|---|---|---|
| **Controlled Parameters** | | | | |
| 1. | Diaphragm Burst Pressure | 100 ATM | 100 ATM | 100 ATM |
| 2. | Particle Size of Ba | Large | Large | Large |
| 3. | Formulation Percent Composition (Ba) | 75% | 75% | 75% |
| 4. | Speed of Window Rotation | 6 rpm | 40 rpm | 40 rpm |
| 5. | Gap/Compression | .5 gap | Same as 17, misfire, no CU on surface | 9 mm gap 20 ton |
| 6. | Interior $ZrO_2$ Coated | No | No | No |
| 7. | Carbon Throats | No | No | No |
| 8. | No. of Squibs | 1 | 1 | 1 |
| 9. | No. of Increments Pressed | 15 layers ($2.8\,gm/cm^3$) | 15 layers ($2.8\,gm/cm^2$) | 1 stroke |
| 10. | Vendor Source for Barium | Ventron | Ventron | Ventron |
| 11. | Weight of Charge | 3000 | 3000 | 288 g. |
| 12. | Blue Line Intensity Peak, Integrated | .30 v. .066 v. sec. | .22 v. .022 v.sec. | .12 v. .001 v.sec. |
| 13. | Green Line Intensity Peak, Integrated | .35 v. .066 | .08 v. .004 | .28 v. .033 |
| 14. | Peak Pressure & Duration | 0.61 ATM 1.7 sec. | 5.45 ATM >5 sec. | No Data |
| 15. | Blue/Green Ratio | 0.857 | 2.75 | 0.429 |
| 16. | Light Duration Blue, Green and Duration | B: .8 sec. G: .8 sec. | B: .02 sec. G: .02, .02 $\epsilon$ = .04 sec. | B: .01, .01 $\epsilon$ = .02 sec. G: .7 sec. |
| 17. | Plume Geometry | | Photo, Cone angle of jet 25-30° | |
| 18. | Efflux Time: Pressure, Light and Window | P: 1.7 sec. L: .8 sec. W: 1.5 sec. | P: >5 sec. L: .04 sec. W: 1.5 sec. | P: No data L: .7 sec. W: 1.1 sec. |
| 19. | Time to Diaphragm Burst | .8 sec. | 1.2 sec. | >2 sec. |
| 20. | Residue Condition | Pink dust | Dark brown and gray | |
| 21. | Nozzle Buildup | | | |
| 22. | % of Reaction Completion | | | |
| 23. | Internal Temperature | | | |
| 24. | Nozzle Erosion | From 11 mm to 22 mm burned pressure tube | | |

## TABLE IIF.  PHASE I TEST DATA

| Test No. | 20 | 21 | 22 |
|---|---|---|---|
| **Controlled Parameters** | | | |
| 1.  Diaphragm Burst Pressure | 100 ATM | 100 ATM | 100 ATM |
| 2.  Particle Size of Ba | Large | Large | Large |
| 3.  Formulation Percent Composition (Ba) | 75% | 75% | 75% |
| 4.  Speed of Window Rotation | 40 rpm | 40 rpm | 40 rpm |
| 5.  Gap/Compression | 9 mm gap 20 ton | 15.5 mm gap 25 ton | 15 mm gap |
| 6.  Interior $ZrO_2$ Coated | No | No | No |
| 7.  Carbon Throats | No | Graphite Throat | Graphite Throat |
| 8.  No of Squibs | 1 | 1 | 1 |
| 9.  No. of Increments Pressed | 1 stroke | 1 stroke | 15 layers (2.8 $gm/cm^3$) |
| 10.  Vendor Source for Barium | Ventron | Ventron | Ventron |
| 11.  Weight of Charge | 288 g. | 288 g. | 3000 |
| 12.  Blue Line Intensity Peak, Integrated | .15 v. .024 v.sec. | 1.1 v. .015 v.sec. | .28 v. .0032 |
| 13.  Green Line Intensity Peak, Integrated | .10 v. .013 | >28 v. saturates .013 | .38 v. .0016 |
| 14.  Peak Pressure & Duration | 4.08 ATM .7 sec. | 13.6 ATM .5 sec. | No data |
| 15.  Blue/Green Ratio | 1.50 | <0.550 | 0.737 |
| 16.  Light Duration Blue, Green and Duration | B:  .9 sec. G:  .2, .2 $\epsilon$ = .4 sec. | B:  .7 sec. G:  .2, .04 $\epsilon$ = .24 sec. | B:  .05 sec. G:  .04 sec. |
| 17.  Plume Geometry | | | |
| 18.  Efflux Time:  Pressure, Light and Window | P:  .7 sec. L:  .9 sec. W.  .9 sec. | P:  .5 sec. L:  .7 sec. W:  .7 sec. | P:  No Data L:  .05 sec. W:  .5 sec. |
| 19.  Time to Diaphragm Burst | .2 sec. | .1 sec. | 1.25 sec. |
| 20.  Residue Condition | | | Dark residue Smoldered grey dust |
| 21.  Nozzle Buildup | | | 5.7cm x 0.76cm |
| 22.  % of Reaction Completion | | | |
| 23.  Internal Temperature | | | |
| 24.  Nozzle Erosion | | | To 1.59 cm |

## TABLE IIG.  PHASE I TEST DATA

| | Test No. | 23 | 24 | 25 |
|---|---|---|---|---|
| **Controlled Parameters** | | | | |
| 1. | Diaphragm Burst Pressure | 100 ATM | 100 ATM | 100 ATM |
| 2. | Particle Size of Ba | Large | Large | Small |
| 3. | Formulation Percent Composition (Ba) | 75% | 75% | 75% |
| 4. | Speed of Window Rotation | 55 rpm | 55 rpm | 55 rpm |
| 5. | Gap/Compression | 15 mm gap | 15 mm gap | 3 mm gap est. |
| 6. | Interior $ZrO_2$ Coated | | | Yes |
| 7. | Carbon Throats | Graphite Throat | Graphite Throat | Graphite Throat |
| 8. | No. of Squibs | 1 | 1 | 1 |
| 9. | No. of Increments Pressed | 15 layers (2.8 gm/cm$^3$) | 15 layers (2.8 gm/cm$^3$) | One stroke |
| 10. | Vendor Source for Barium | Ventron | Alfa | Alfa |
| 11. | Weight of Charge | 3000 | 3000 | 228 g. |
| 12. | Blue Line Intensity Peak, Integrated | .25 v. .252 | .38 v. | No Data |
| 13. | Green Line Intensity Peak, Integrated | .25 v. .126 | .31 v. .0225 | .7 v. .0019 |
| 14. | Peak Pressure & Duration | 1.70 ATM .3 sec. | 11.82 ATM >2 sec. | 137.2 ATM .15 sec. |
| 15. | Blue/Green Ratio | 1.00 | 1.23 | No Data |
| 16. | Light Duration Blue, Green and Duration | B: .094 sec. G: .047 sec. | B: .15 sec. G: .15 sec. | B: No Data G: .06 sec. |
| 17. | Plume Geometry | | | |
| 18. | Efflux Time: Pressure, Light and Window | P: .3 sec. L: .09 sec. W: 1.1 sec. | P: > 2 sec. L: .15 sec. W: 1 sec. | P: .15 sec. L: .06 sec. W: short |
| 19. | Time to Diaphragm Burst | No data | 1.9 sec. | .08 sec. |
| 20. | Residue Condition | Dark material and grey dust | Dark Material and pink dust | Fine red-pink powder |
| 21. | Nozzle Buildup | 7.0cm x 0.96cm | 6.0cm x 0.96cm | Assymetrical lump 0.32cm |
| 22. | % of Reaction Completion | | | |
| 23. | Internal Temperature | | | |
| 24. | Nozzle Erosion | 1.43 cm | 1.43 cm | 1.1 cm |

## TABLE IIH.  PHASE I TEST DATA

| | Test No. | 26 | 27 |
|---|---|---|---|
| Controlled Parameters | | | |
| 1.  Diaphragm Burst Pressure | | 100 ATM | 100 ATM |
| 2.  Particle Size of Ba | | Small | Small |
| 3.  Formulation Percent Composition (Ba) | | 75% Ba | 75% Ba |
| 4.  Speed of Window Rotation | | 55 rpm | 55 rpm |
| 5.  Gap/Compression | | 3 mm gap est. | 3 mm gap est. |
| 6.  Interior $ZrO_2$ Coated | | Yes | Yes |
| 7.  Carbon Throats | | Graphite throat | Graphite throat |
| 8.  No. of Squibs | | 1 | 1 |
| 9.  No. of Increments Pressed | | One stroke | One stroke |
| 10.  Vendor Source for Barium | | Alfa | Alfa |
| 11.  Weight of Charge | | 228 g. | 228 g. |
| 12.  Blue Line Intensity Peak, Integrated | | 2 v. .0002 | .25 v. .0003 |
| 13.  Green Line Intensity Peak, Integrated | | 2 v. .0005 | .7 v. .0004 |
| 14.  Peak Pressure & Duration | | 163.0 ATM .1 sec. | 146.0 ATM .1 sec. |
| 15.  Blue/Green Ratio | | 1.00 | 0.357 |
| 16.  Light Duration Blue, Green and Duration | | B:  .01 sec. G:  .01 sec. | B:  .0016 sec. G:  .0016 sec. |
| 17.  Plume Geometry | | | |
| 18.  Efflux Time:  Pressure, Light and Window | | P:  .1 sec. L:  .01 sec. W:  Short | P:  1 sec. L:  .0016 sec. W:  Short |
| 19.  Time to Diaphragm Burst | | .06 sec. | .07 sec. |
| 20.  Residue Condition | | Fine red-pink powder | Fine red-pink powder |
| 21.  Nozzle Buildup | | Assymetrical lump 0.32cm | 2.5cm x 0.24cm |
| 22.  % of Reaction Completion | | | |
| 23.  Internal Temperature | | | |
| 24.  Nozzle Erosion | | To 1.1 cm | To 0.96 cm |

## TABLE III.   SUMMARY OF EXPERIMENT RESULTS OF PHASE II

| SYSTEM TEST | PRESSURE (ATM) | INTERNAL TEMP | (4554Å) BLUE PEAK | (5535Å) GREEN PEAK | BLUE INTEGRATED (VOLT-SECONDS) | GREEN INTEGRATED (VOLT-SECONDS) | RATIO INTE-GRATED BLUE TO GREEN | RESIDUE |
|---|---|---|---|---|---|---|---|---|
| A/1 | 0.65 | | 0.55V | 0.30V | $0.50 \times 10^{-2}$ | $1.94 \times 10^{-2}$ | 0.257 | 57 gm |
| A/2 | 0.15 | 65 MV | 0.08V | 0.30V | $1.07 \times 10^{-2}$ | $3.63 \times 10^{-2}$ | 0.295 | 70 gm |
| A/3 | | 80 MV | 0.07V | 0.38V | $0.55 \times 10^{-2}$ | $3.07 \times 10^{-2}$ | 0.179 | 59 gm |
| A/4 | 2.24 | 160 MV | 0.14V | 0.40V | $1.82 \times 10^{-2}$ | $6.23 \times 10^{-2}$ | 0.298 | 66 gm |
| A/6 | 2.24 | 210 MV | 0.10V | 0.23V | $1.18 \times 10^{-2}$ | $3.43 \times 10^{-2}$ | 0.344 | 52 gm |
| B/1 | 1.97 | 75 MV | 0.20V | 0.64V | $2.13 \times 10^{-2}$ | $6.46 \times 10^{-2}$ | 0.330 | 71 gm |
| B/2 | 3.33 | 80 MV | 0.34V | 0.80V | $2.80 \times 10^{-2}$ | $7.10 \times 10^{-2}$ | 0.394 | 71 gm |
| B/3 | 1.71 | 85 MV | 0.22V | 0.64V | $2.52 \times 10^{-2}$ | $7.50 \times 10^{-2}$ | 0.336 | 78 gm |
| B/4 | 1.97 | 60 MV | 0.28V | 0.62V | $2.44 \times 10^{-2}$ | $6.50 \times 10^{-2}$ | 0.376 | 71 gm |
| B/5 | 1.80 | 55 MV | 0.20V | 0.48V | $2.64 \times 10^{-2}$ | $6.82 \times 10^{-2}$ | 0.387 | 91 gm |
| C/1 | ** | | ** | ** | | | | |
| C/2 | 3.52 | | MORE THAN 1V* | MORE THAN 1.5V* | GREATER THAN $10.4 \times 10^{-2}$ | GREATER THAN $7.90 \times 10^{-2}$ | ** | 70 gm |
| C/3 | 2.78 | 220 MV | 5.00V | 1.50V | $5.52 \times 10^{-2}$ | $2.96 \times 10^{-2}$ | 1.87 | 50 gm |
| C/4 | | | 1.00V | 3.28V | $1.18 \times 10^{-2}$ | $8.20 \times 10^{-2}$ | 0.144 | *** |
| C/5 | 1.37 | 200 MV | 7.20V | 3.23V | $11.00 \times 10^{-2}$ | $7.40 \times 10^{-2}$ | 1.49 | *** |

*ESTIMATED (SIGNAL SATURATED)
**ESTIMATED VALUE EXCLUDED
***UNABLE TO REMOVE
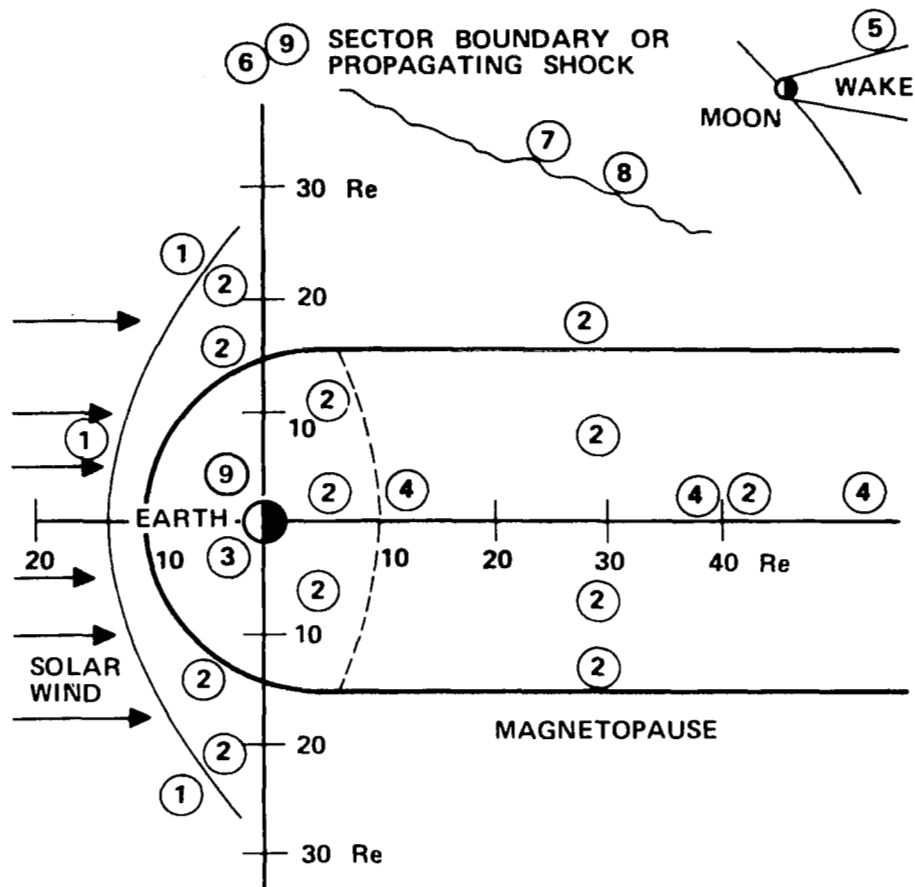
VIEW LOOKING NORMAL TO ECLIPTIC PLANE
SYMMETRY ASSUMED FOR SIMPLICITY

◯ = EXPERIMENT LOCATION

1. ACTIVE BOW SHOCK
2. MULTIPLE DIAGNOSTIC
3. POLAR REGION, NEUTRAL POINTS
4. MAGNETOTAIL
5. LUNAR WAKE
6. INTERPLANETARY DIAGNOSTIC
   AND ARTIFICAL SHOCK

7. SECTOR BOUNDARY
8. PROPAGATING SHOCK
9. CLOSED FIELD DIAGNOSTIC
10. SOLAR WIND DISTANCE VARIANCE

FIGURE 1. POSSIBLE PLASMA CLOUD EXPERIMENTS
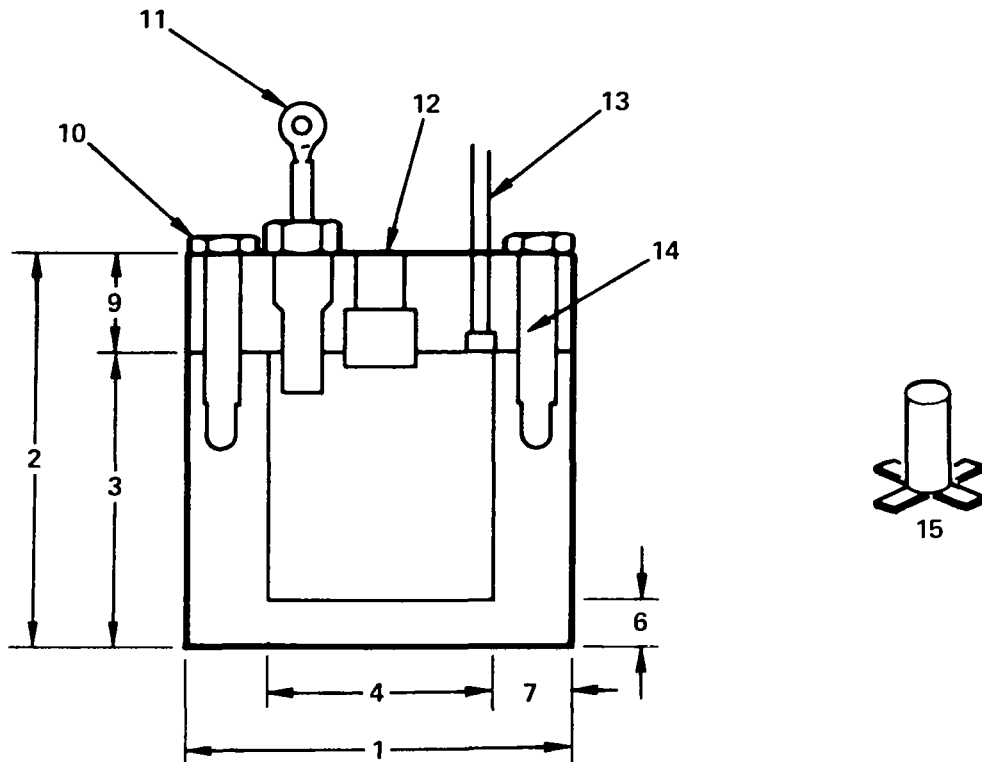
1. CANISTER OUTSIDE DIAMETER, 3.375" (8.572 CM)
2. CANISTER HEIGHT, 3.50" (8.89 CM)
3. CANISTER INTERNAL HEIGHT, 2.218" (5.634 CM)
4. CANISTER INTERNAL DIAMETER, 1.968" (4.999 CM)
5. CANISTER AND COVER MADE OF STAINLESS STEEL
6. CANISTER BOTTOM THICKNESS, 0.402" (1.021 CM)
7. CANISTER WALL THICKNESS, 0.704" (1.788 CM)
8. CANISTER TOTAL VOLUME OF INTERNAL CAVITY, 110 CM$^3$ (NOMINAL)
9. CANISTER COVER THICKNESS, 0.88" (2.235 CM)
10. CANISTER COVER BOLTS
11. CANISTER IGNITER
12. CANISTER NOZZLE OPENING, 0.437" DIAMETER (1.110 CM)
13. PRESSURE TRANSDUCER LINE-CONNECTION
14. "O" RING SEAL
15. ALUMINUM TUBE ASSEMBLY-CANISTER CAVITY INSERT FOR SYSTEM C TESTS (IGNITER FLAME PASSAGE THROUGH BARIUM METAL UPPER LAYER TO THE THERMITE MIX BOTTOM LAYER)

FIGURE 2. STAINLESS STEEL CANISTER ASSEMBLY SCHEMATIC

EXPOSED PORTION OF WINDOW

16 CM

16 CM

22.5 CM

G
ROTATING
WINDOW
DETAIL

0.8 M

E

A

G

B

2.3 M

F

D

C

VACUUM
TANK SET-UP
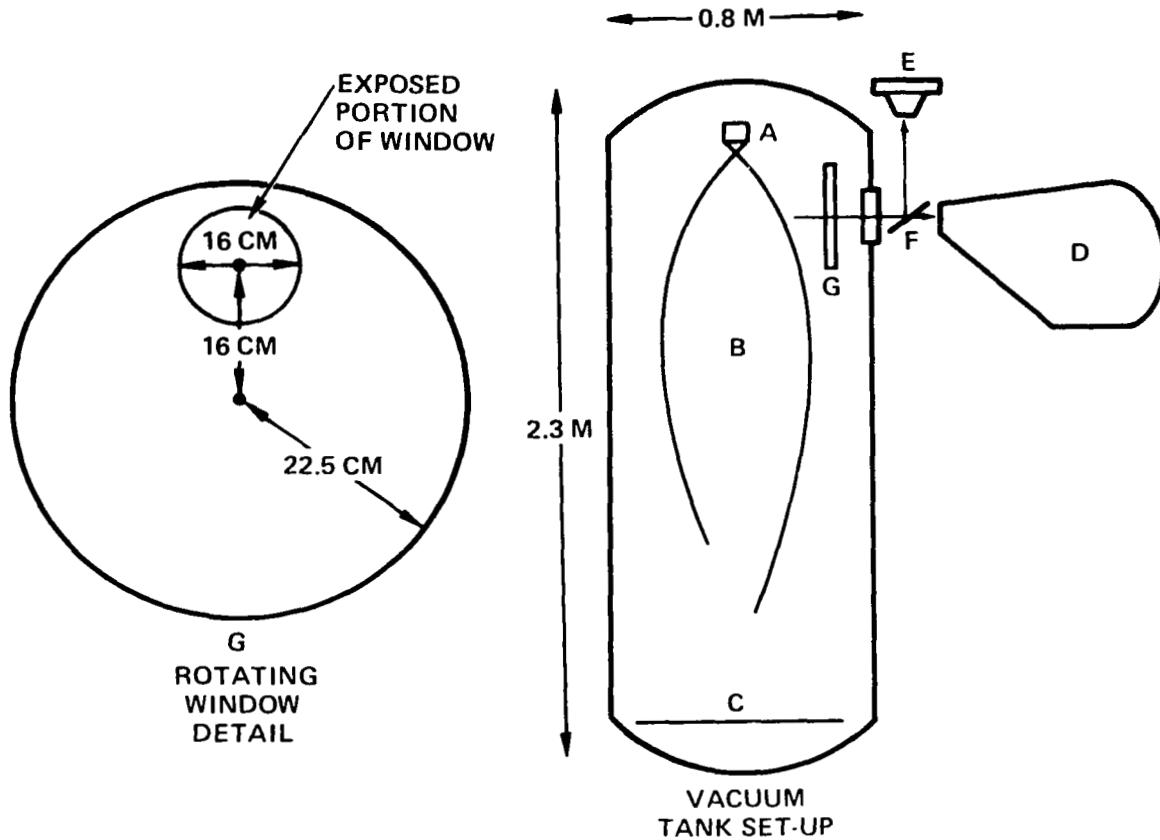
KEY:    A - CANISTER
        B - PLUME
        C - WITNESS PLATE
        D - JARREL-ASH GRATING SPECTROGRAPH
        E - CAMERA OF VISIBLE RANGE SPECTROGRAPH
        F - HALF SILVERED NEUTRAL DENSITY BEAM-SPLITTER
        G - ROTATING WINDOW (LUCITE)

OPTICAL PATH (PERPENDICULAR TO PLUME AXIS, i.e., B, F, D)

PHASE I

- SMALL CANISTERS - 63 CM
- LARGE CANISTERS - 99 CM

PHASE II

ALL -88.4 CM

FIGURE 3.   TEST SET-UP AND OPTICAL PATH

43
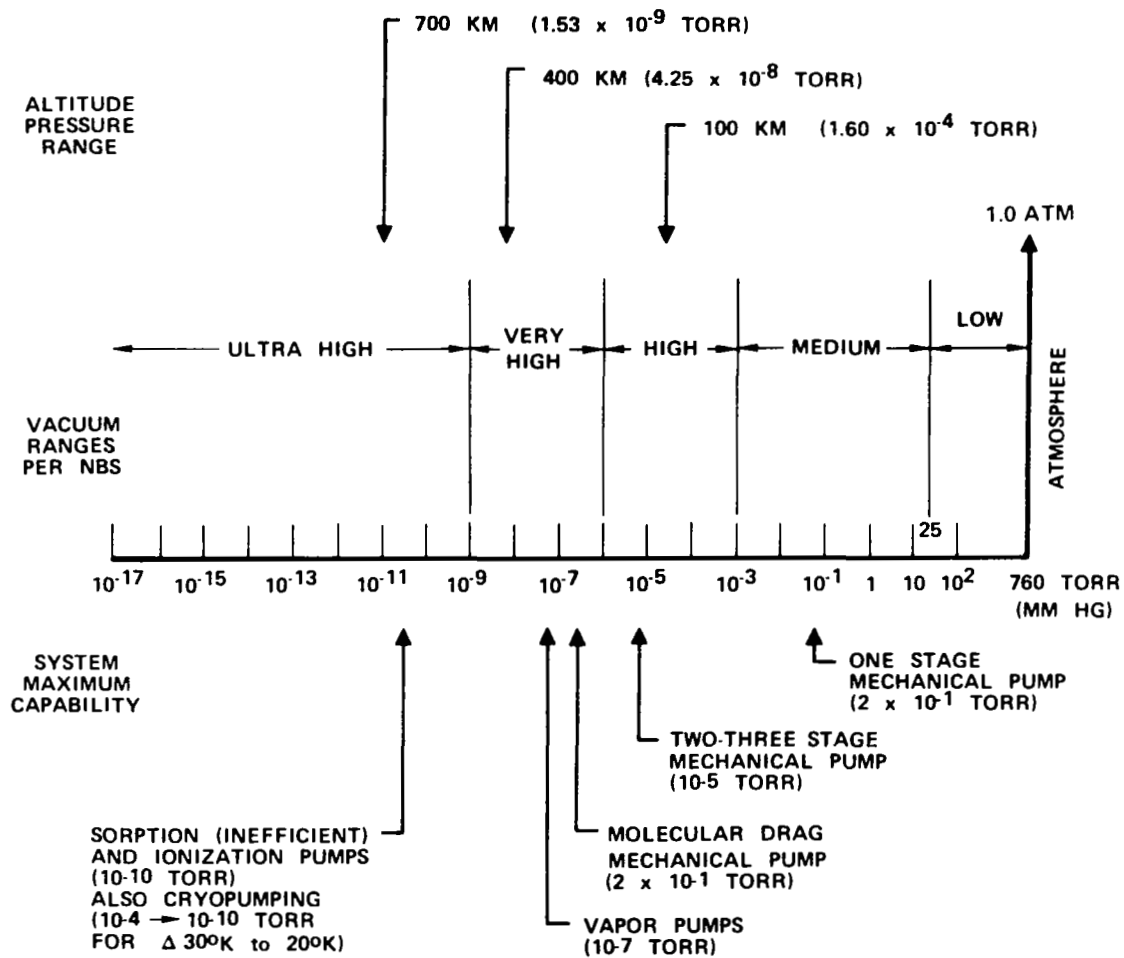
FIGURE 4. SUMMARY COMPARISON OF VACUUM REQUIRE-
MENTS AND SYSTEM CAPABILITIES

CHEMICAL & PHYSICAL
ANALYSIS OF RESIDUE

● INTERNAL PRESSURE

● TIME TO BLOW OUT
   DISK RUPTURE

TEMPERATURE AT
TOP OF CANISTER

TEMPERATURE IN
BOTTOM OF
FORMULATION

● 4544$\overset{\circ}{A}$ Ba$^+$ LINE INTENSITY

● 5535$\overset{\circ}{A}$ Ba$^0$ LINE INTENSITY

● EFFLUX TIME

● PLUME SPECTRUM

● PLUME PHOTOGRAPHY
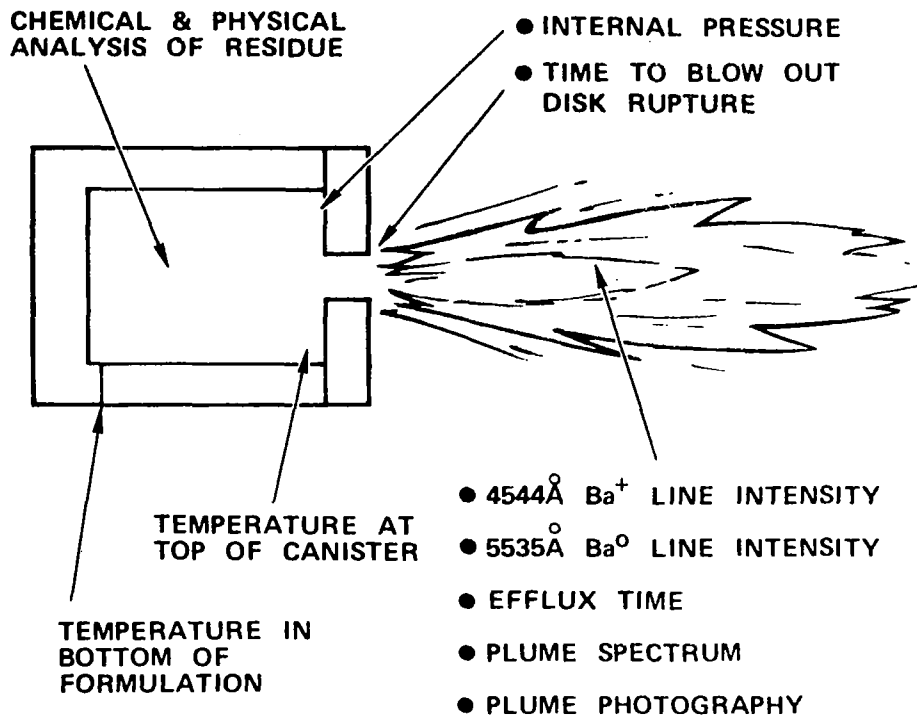
FIGURE 5.  SCHEMATIC OF TEST CANISTER AND PARAMETERS MEASURED
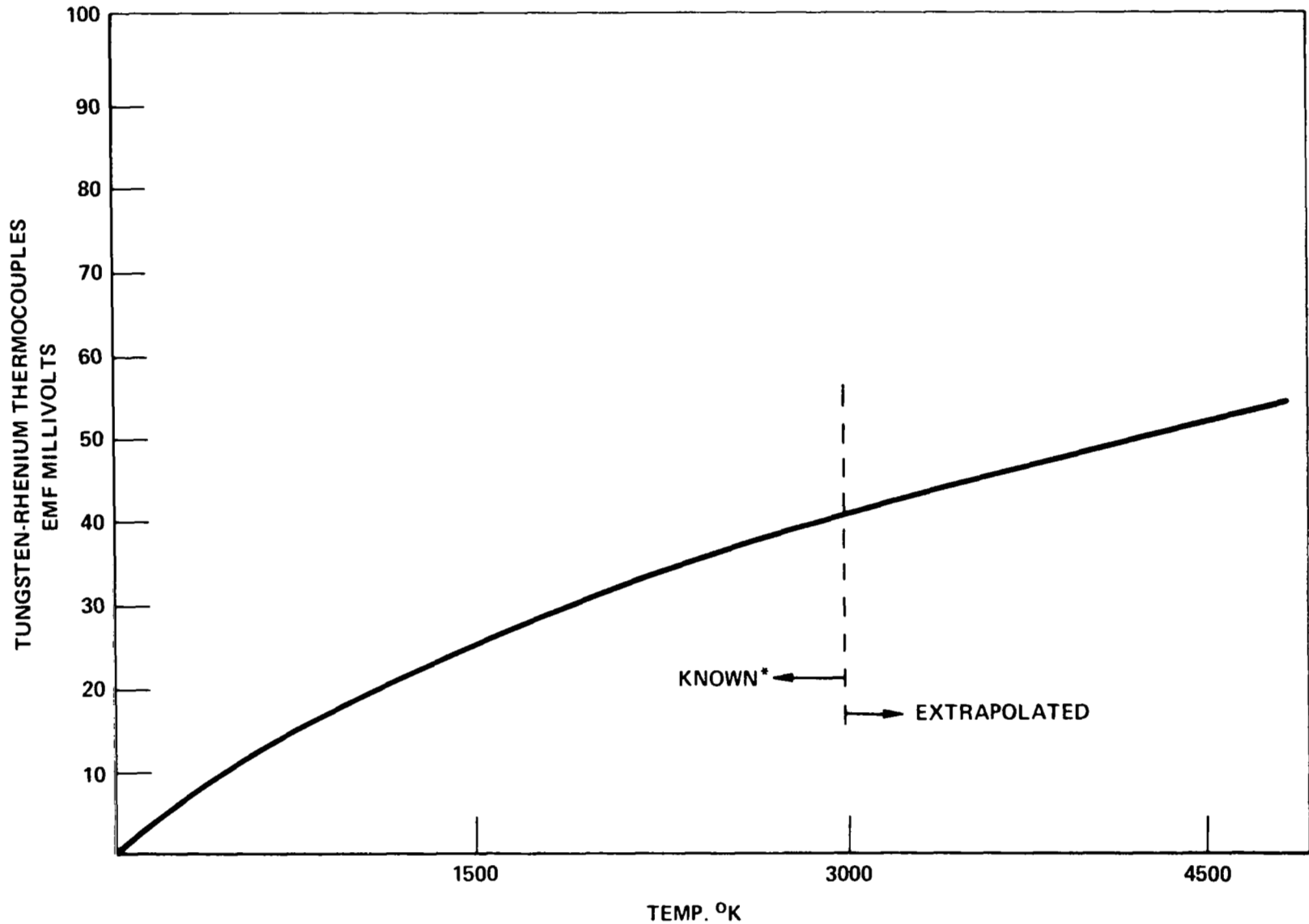
FIGURE 6. TUNGSTEN RHENIUM THERMOCOUPLE CONVERSION DATA
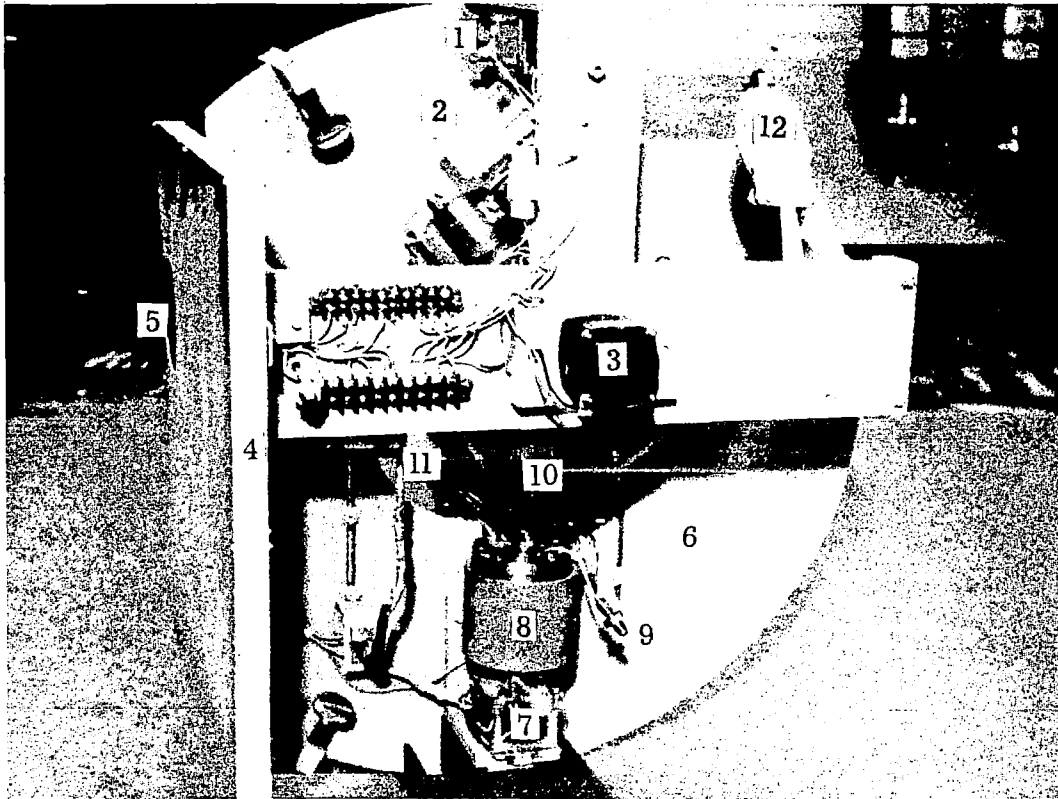
1. SAMPLE BOTTLE OPENING SOLONOID
2. SEPARATE SAMPLE BOTTLES FOR BARIUM AND OXIDIZER
3. MIXER AND DRIVE MOTOR ASSEMBLY
4. ROTATING WINDOW COVER
5. SPECTROMETER VIEWING WINDOW TUNNEL
6. MAIN SUPPORT MOUNTING BRACKET
7. CANISTER SHAKER SOLONOID ASSEMBLY
8. CANISTER AND HOLDER
9. PRESSURE TRANSDUCER HYDRAULIC LINE
10. CANISTER LOADING FUNNEL
11. MIXER POSITIONING MOTOR
12. FUNNEL VIEWING MIRROR (PART OF EXTERNAL VACUUM
    CHAMBER VIEWING ASSEMBLY)

FIGURE 7. REMOTE HANDLING APARATUS
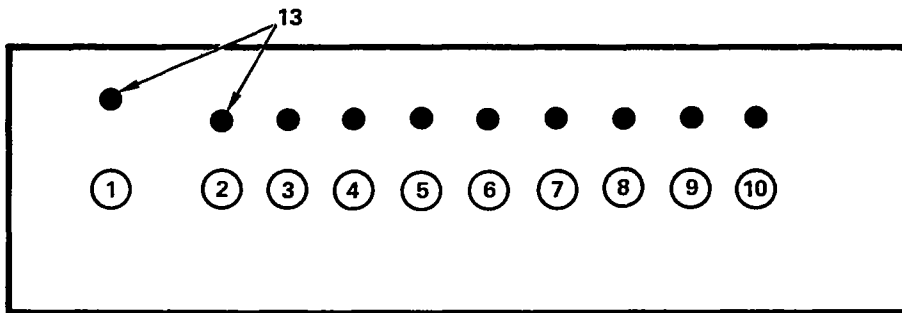
REMOTE CONTROL PANEL

FIRING PANEL

CHARGE
OFF
FIRE
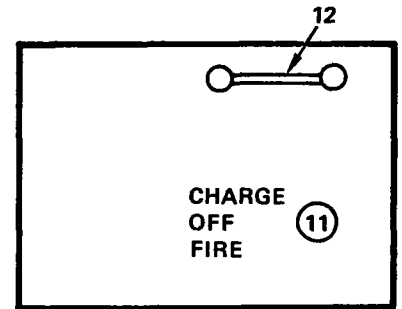
SEQUENCE OF OPERATIONS & KEY
1. MAIN POWER SWITCH FOR CONTROL PANEL
2. SAMPLE BOTTLE OPENING SWITCH
3. MIXER POSITIONING SWITCH
4. MIXER OPERATION SWITCH
5. SAMPLE DUMPING SWITCH
6. CANISTER AND FUNNEL SHAKER SWITCH
7. FUNNEL OBSERVATION LIGHT SWITCH
8. FUNNEL REMOVING SWITCH
9. CANISTER UNLOCKING AND POSITIONING SWITCH
10. BACK-UP CANISTER POSITIONING MOTOR SWITCH
11. FIRING CIRCUIT CAPACITOR CHARGE AND FIRING SWITCH
12. FIRING PANEL SHORTING BAR
13. TEN INDICATOR LIGHTS

FIGURE 8. SCHEMATIC OF REMOTE HANDLING SYSTEM CONTROL PANEL
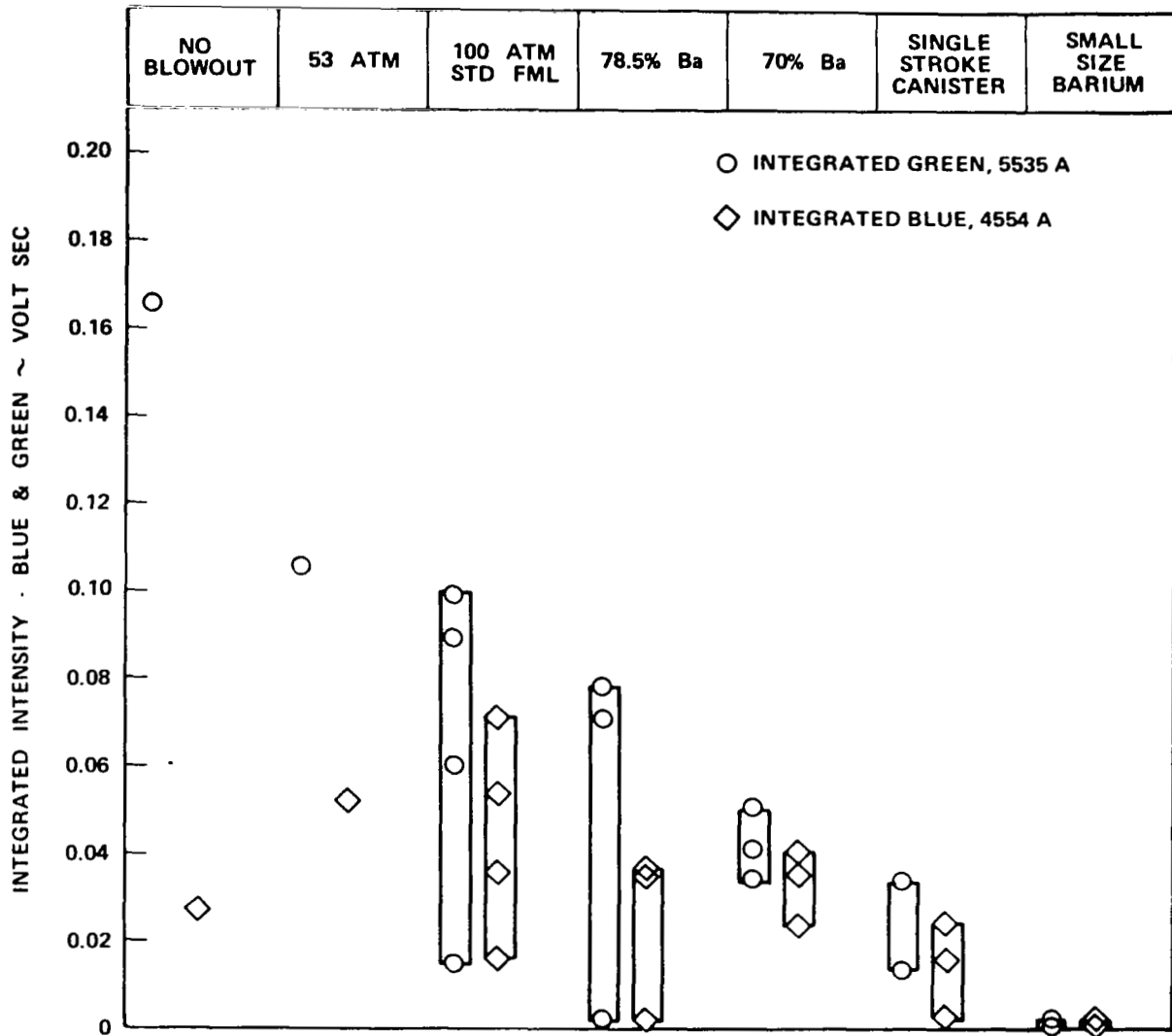
FIGURE 9. RELATIVE PERFORMANCE BASED UPON INTEGRATED LIGHT OUTPUT

49
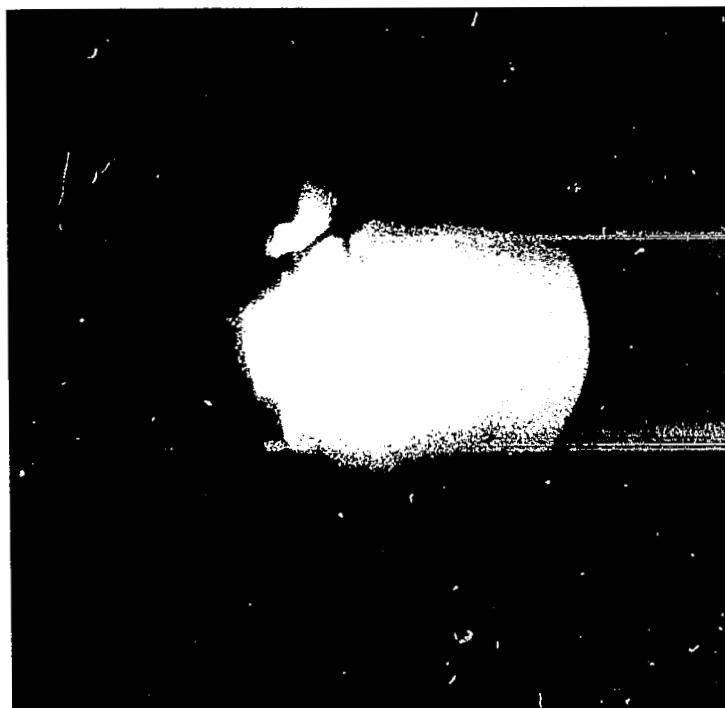
FIGURE 10. SMALL CANISTER PLUME

TEST NO. 24

PPM Ba    9  6  28 153 62  86  26    (WINDOW DEPOSITION, PPM Ba)

5535Å
0.1 SEC/CM
0.1 V/CM

PRESSURE
0.2 SEC/CM
0.5 V/CM

4554 Å
5 MSEC/CM
0.1 V/CM

TEST NO. 25

4554 Å
5 MSEC/CM
0.1 V/CM
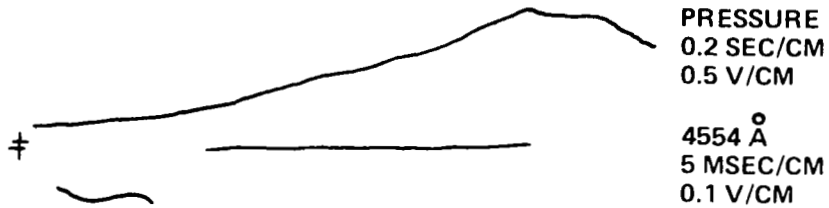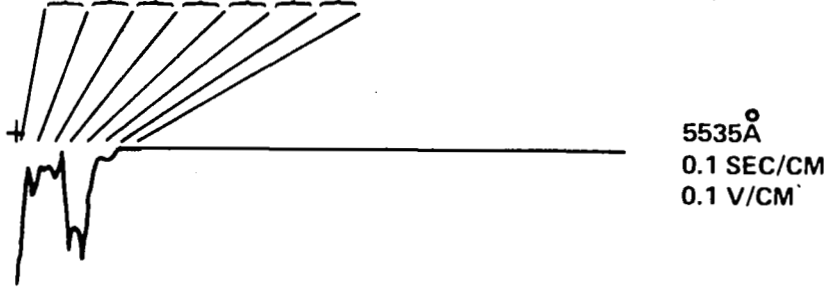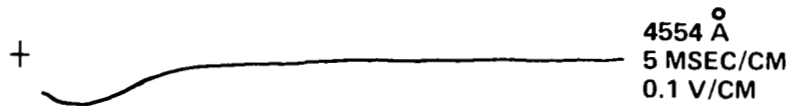
PPM Ba    44    30    17    25    34    5    9    (WINDOW DEPOSITION,
                                                  PPM Ba)

5535 Å
5MSEC/CM
0.1 V/CM
FILTER FACTOR OF 10
(10% TRANSMISSION)

PRESSURE
0.1 SEC/CM
1 V/CM
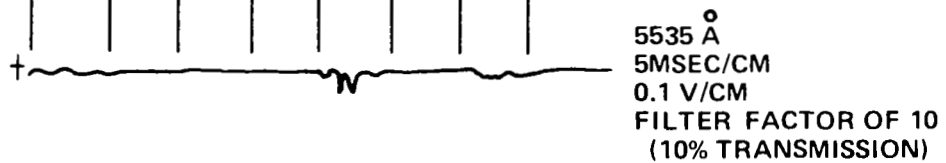
FIGURE 11.  REPRESENTATIVE DATA TRACES FROM PHASE I FIRINGS

FIGURE 12. RESIDUE FROM A CANISTER WHERE QUENCHING OCCURRED
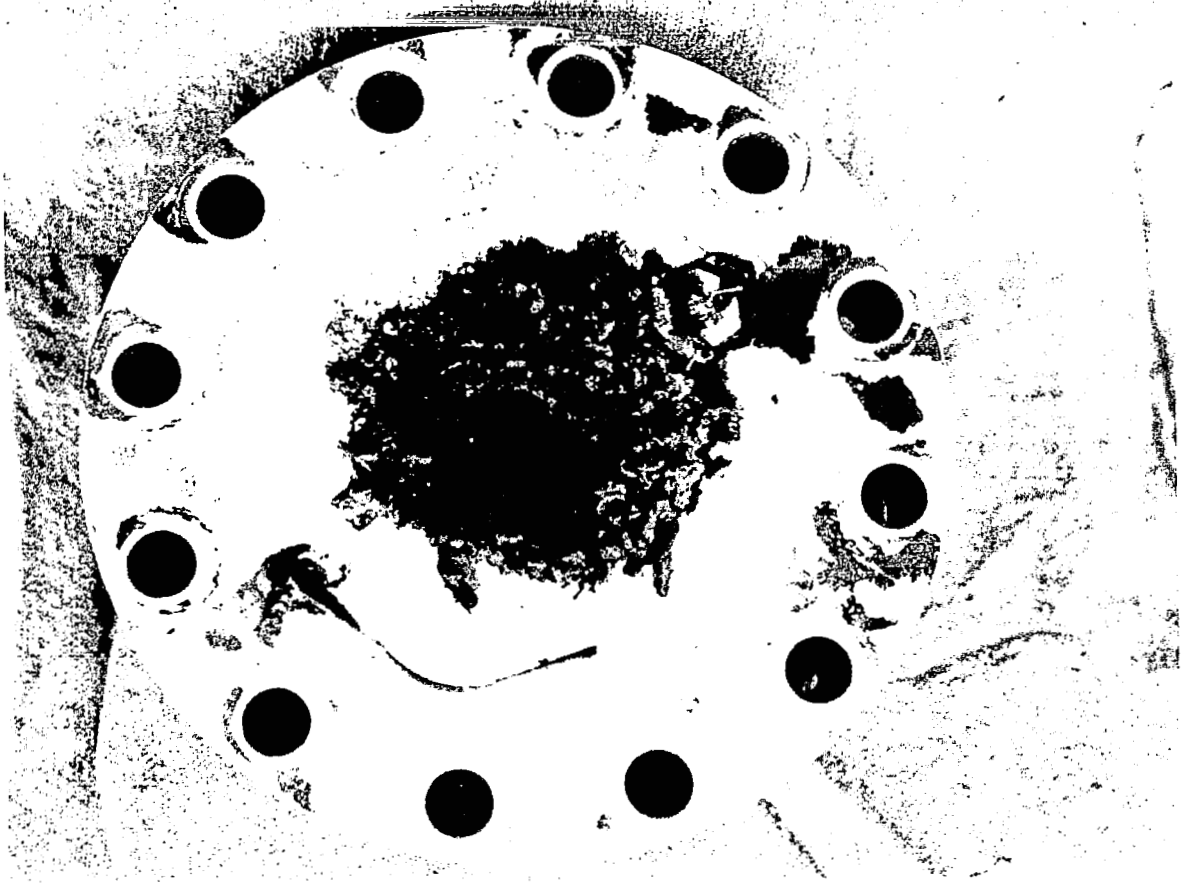
FIGURE 13. NOZZLE EROSION AND BARIUM CONDENSATION
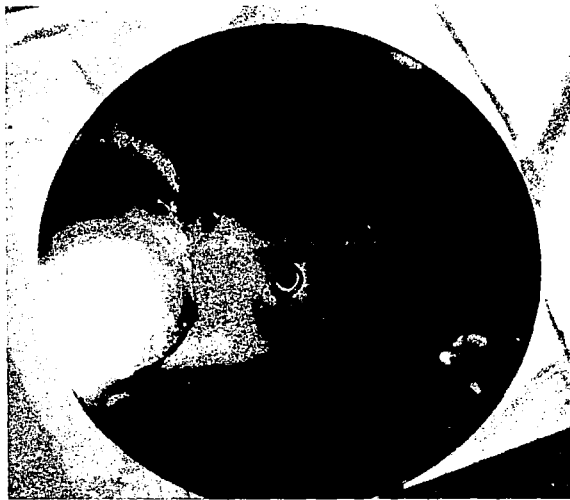
ROTATING WINDOW
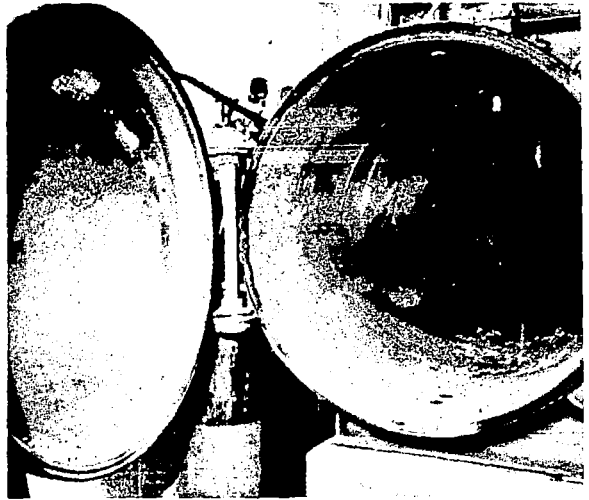


TEST CHAMBER INTERIOR
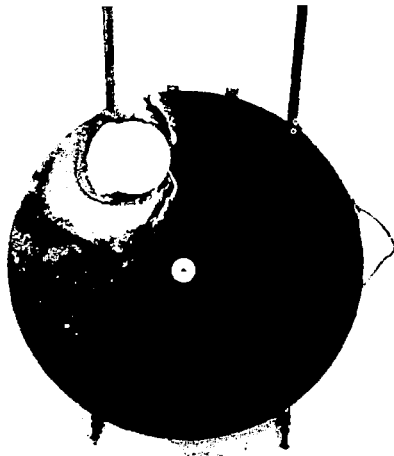


ROTATING WINDOW FRAME
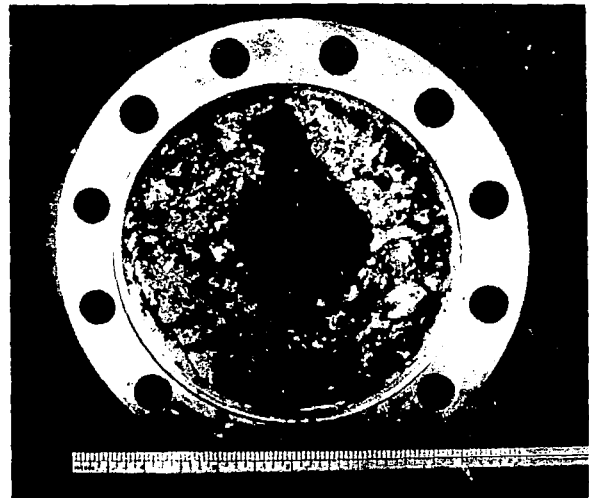


NOZZLE EROISION

FIGURE 14. EFFECTS OF LARGE CANISTER FIRING

FIGURE 15. BARIUM-CUPRIC OXIDE SYSTEM
PRE-IGNITION

SYSTEM A, TEST NO. 6
- CHART SPEED 10.2 CM/SEC
- ALL CHANNELS: SENSITIVITY = 0.0985 VOLTS/CM

SYSTEM B, TEST NO. 2
- CHART SPEED 10.2 CM/SEC
- ALL CHANNELS: 0.0985 VOLTS/CM

SYSTEM C, TEST NO. 5
- CHART SPEED, 10.2 CM/SEC
- NEUTRAL DENSITY 0.7 FILTER USED, FILTER FACTOR = 5
- BLUE CHANNEL 0.5 VOLTS/INCH
- GREEN CHANNEL 0.0985 VOLTS/CM

BLUE LINE

GREEN LINE

PRESSURE

TIME 1 CM
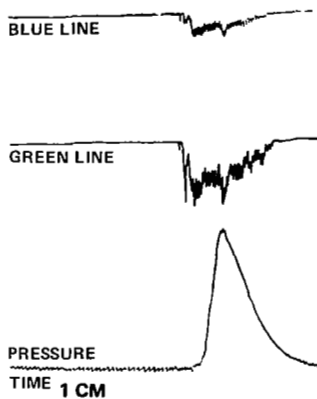
THERMOCOUPLE TRACE
- 50 MILLISEC/CM.
- UPPER 0.2 V/CM.

BLUE LINE

GREEN LINE
TEST NO. 8
SYST. B

PRESSURE
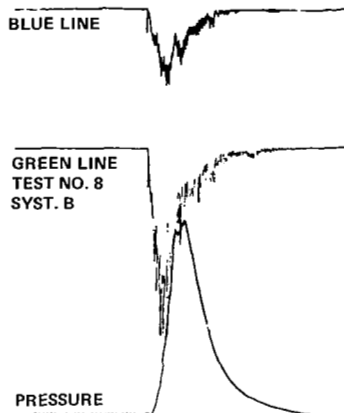
CANISTER THERMOCOUPLE
- 50 MILLISEC/CM.
- LOWER .05 V/CM.

BLUE LINE

GREEN LINE
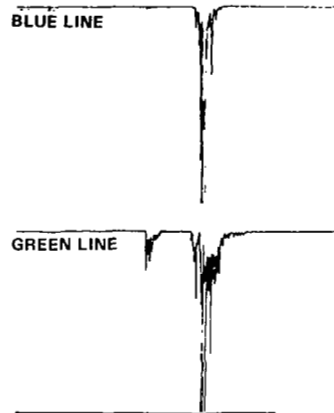
CANISTER THERMOCOUPLE
- 0.2 SEC/CM.
- LOWER .1 V/CM.

FIGURE 16. COMPARISON OF PHASE II SYSTEMS
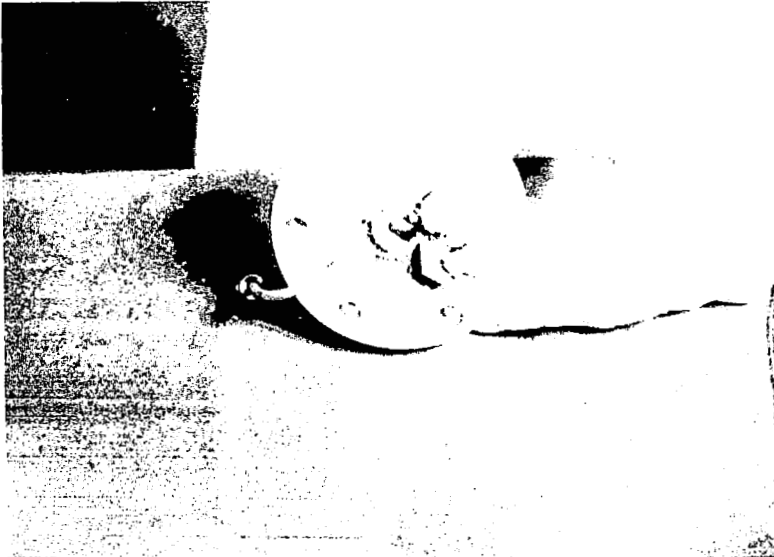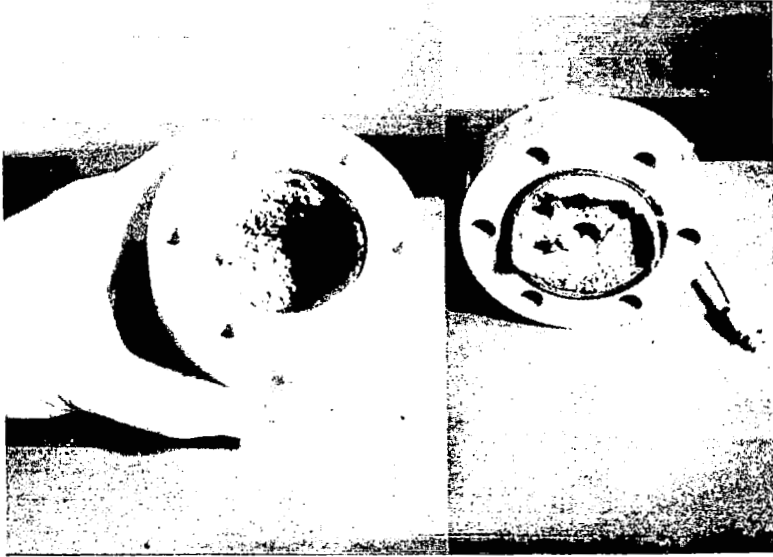
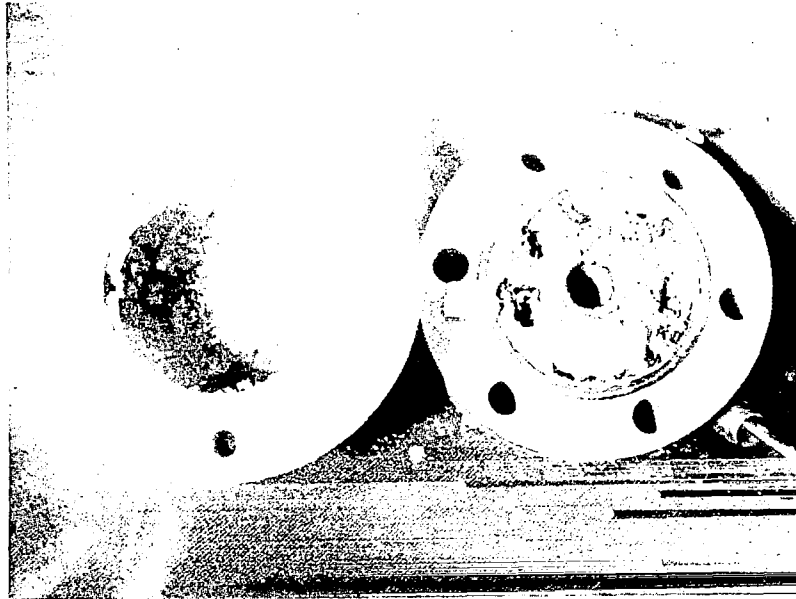FIGURE 17. CANISTER, SYSTEM A TEST 1
(BARIUM CUPRIC OXIDE)

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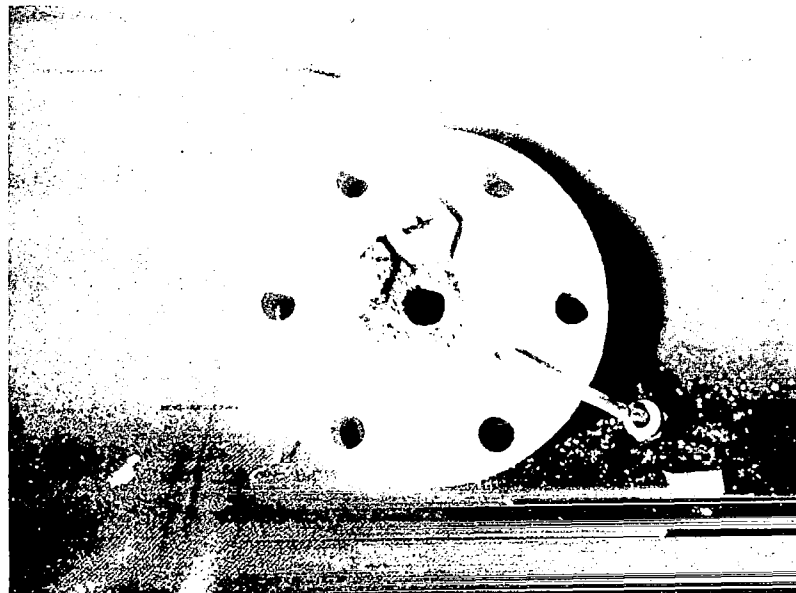
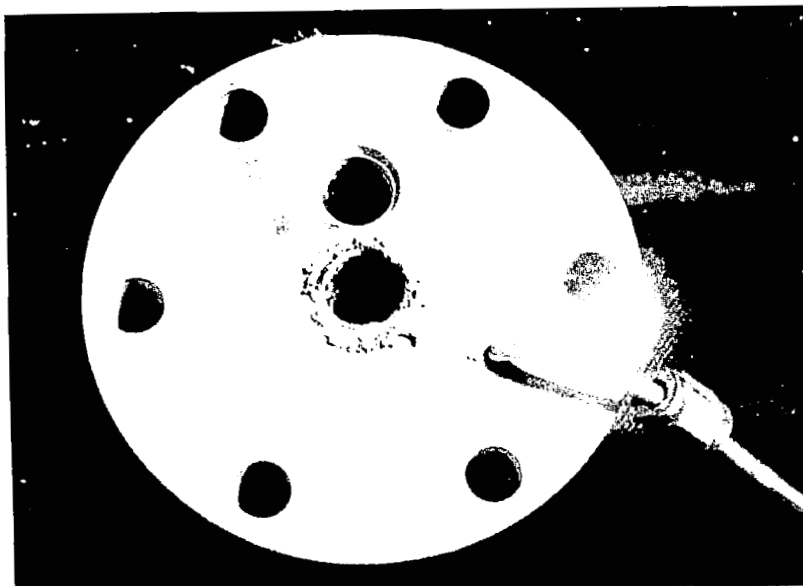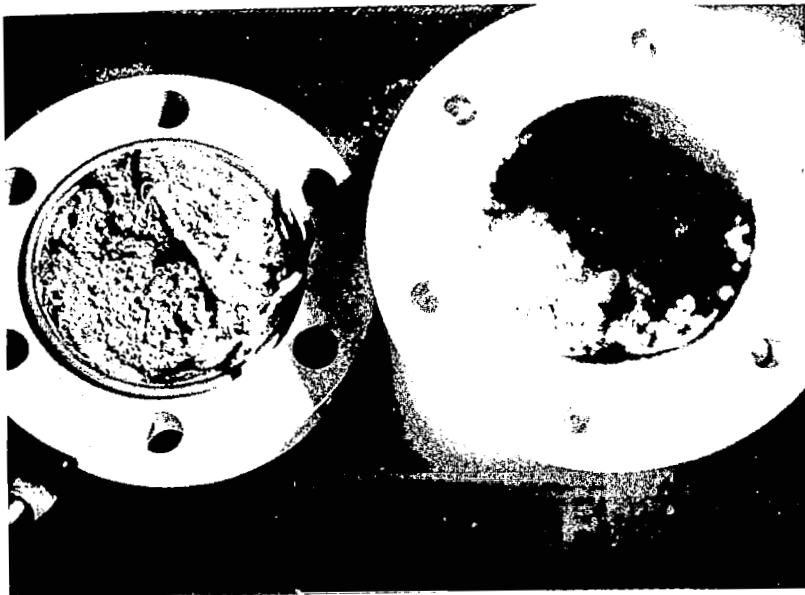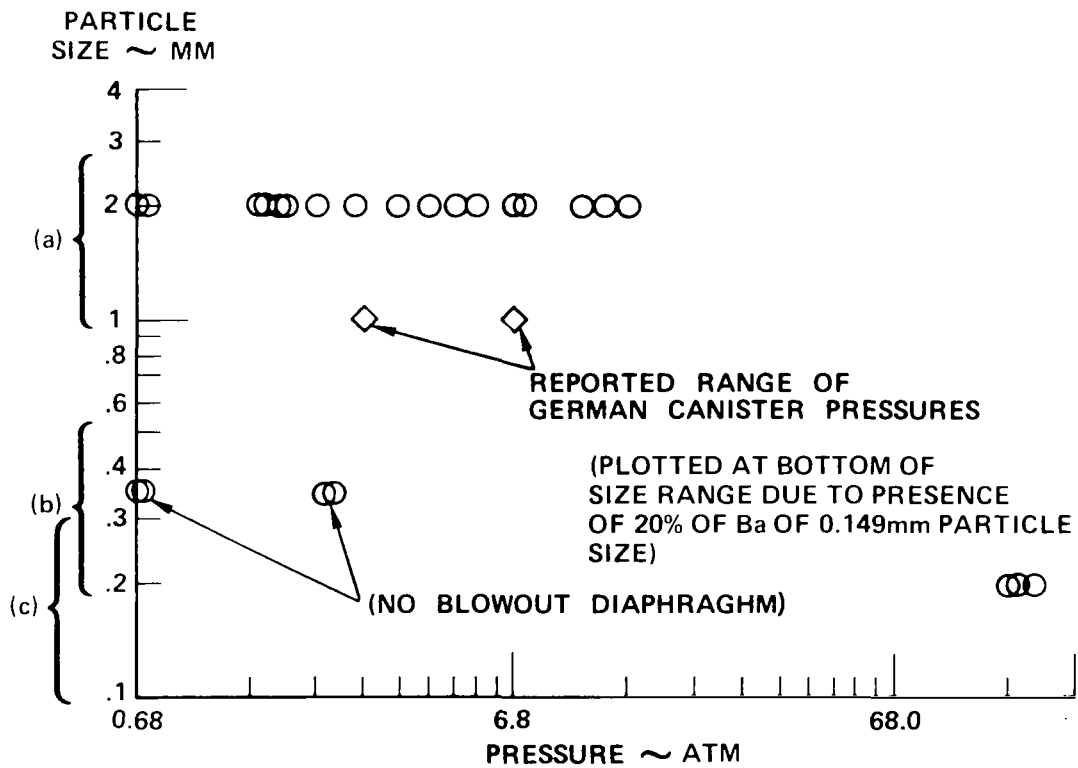FIGURE 18.  CANISTER, SYSTEM B TEST 1
(BARIUM MOLYBDIC OXIDE)

FIGURE 19.  CANISTER, SYSTEM C TEST 3
(BARIUM, ALUMINUM MOLYBDIC OXIDE)

PARTICLE
SIZE ~ MM

(a) PARTICLE SIZE RANGE USED FOR STANDARD Ba-CuO FORMULATION
(b) PARTICLE SIZE RANGE USED FOR PHASE II
(c) PARTICLE SIZE RANGE USED FOR SMALL SIZE Ba, PHASE I TESTS

FIGURE 20. PARTICLE SIZE VERSUS PEAK PRESSURE