GE-MTSD -R-064

N72-18967

(THRU)

(NASA-CR-122977) INVESTIGATION OF HAZARDS ASSOCIATED WITH PLASTIC BONDED STARTER MIX MANUFACTURING PROCESSES Final Report (General Electric Co.) May 1971 110 p CSCL 19A

G3/33 20008

FINAL REPORT

INVESTIGATION OF HAZARDS ASSOCIATED WITH PLASTIC BONDED STARTER MIX MANUFACTURING PROCESSES

CONTRACT NAS8-23524

MAY 1971

PREPARED FOR
NATIONAL AERONAUTICS & SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
MISSISSIPPI TEST FACILITY

GENERAL ELECTRIC

110

GE-MTSD-R-064

FINAL REPORT
INVESTIGATION OF HAZARDS ASSOCIATED WITH PLASTIC BONDED STARTER MIX MANUFACTURING PROCESSES

NASA CONTRACT NAS8-23524

MAY 1971

This report has been reviewed and approved by:

J F Pankow

J. F. PANKOW, PROJECT ENGINEER
MATERIEL TESTING AND RESEARCH
MTSD - GENERAL ELECTRIC COMPANY

Paul V King

PAUL V. KING, MANAGER
MATERIEL TESTING AND RESEARCH
MTSD-GENERAL ELECTRIC COMPANY

FOREWORD

The work described in this report was authorized under Contract NAS8-23524 for the National Aeronautics and Space Administration - Mississippi Test Facility.

ACKNOWLEDGEMENT

The author wishes to acknowledge the unselfish and competent help of those people within the General Electric Company without whom this project could not have been accomplished. Special acknowledgement is extended to Mr. P. V. King, Program Director, and to his staff for their contribution and guidance in areas of major concern. Special thanks to Mr. John Dickie of Edgewood Arsenal for his acquisition and information provided with respect to the materials and processes discussed in this report.

ABSTRACT

This report describes the results of investigations conducted by the Materiel Testing and Research Subsection, Technical and Operations Services Department of the General Electric Company. This investigation is concerned with the hazards potential evaluation of Plastic Bonded Starter Mix (PBSM) production process and its ultimate use in M18 and M7A3 grenades.

The investigation indicated:

- Those materials which exhibit the greatest hazard characteristics.
- The process operating stations most likely to introduce initiation stimuli or hazardous conditions.
- The test program necessary to examine ignition characteristics and process hazards.
- The method to handle the accumulated information from testing and system safety analysis.

TABLE of CONTENTS

TABLE of CONTENTS (cont'd)

LIST of ILLUSTRATIONS

SECTION 1

INTRODUCTION AND SUMMARY

1.1 GENERAL

The past few years have seen a rapid increase in the sophistication of weapons and weapons systems relative to manufacture, transportation and storage. At the same time, the bulk and variety of the munitions have greatly increased, concurrent with rising costs of production facilities, causing a disproportionate increase in the costs of handling and storage of special types of ammunition. It is appropriate, therefore, that the criteria used for the determination of "safety distance" and other safety controls be utilized as one of the basis for examination of the recent weapon effectiveness and optimization studies.

While experience has proven the validity of these criteria, they must be re-evaluated from time to time in accordance with current "state-of-the-art" developments in the field of weaponry and techniques in order to assure that the maximum standards of safety, consistent with economic considerations, are being attained.

Requirements as outlined in DOD Instruction 4145.23 dated March 1966, "Quantity Distance Standards for the Manufacturing, Handling and Storage of Mass Detonating Explosives and Ammunition," have been under continual revision. As a result of a number of test programs conducted by a number of governmental and industry groups, these revisions now represent the best that can be done in developing the appropriate hazard criteria, on the basis of existing at-hand information. Despite these efforts, a number of problems remain unsolved, and the costs incurred in meeting criteria which may be overly conservative in specific cases of special application may well run into millions of dollars without assuring a finite degree of protection.

Additionally, it is felt that the demands of the rapidly changing technology are such that safety criteria must be developed in terms of a measurable degree of hazard, since the concept of absolute safety is no longer attainable, if it ever existed.

The basic philosophy governing the tasks accomplished is that maximum benefit in the determination of hazards in specific terms was obtained by a thorough evaluation of past tests, accidents, and basic research into similar munitions. It was necessary, therefore, as discussed further herein, to make maximum utilization of the considerable amount of valid information which has been accrued in the form of investigations, special studies and tests, and of similar information available as a result of other experiments and studies conducted by other governmental and industrial activities.

Major emphasis was placed on the information and methodology contained in the Pyrotechnic Hazards Evaluation and Classification Program conducted for Edgewood Arsenal, particularly in those functions of that program dealing with the environment about the munition. Such information properly used provides valid scaling points. Other significant spin-off benefits resulted from the coincidence of the program.

Since quantitative information appropriate to the "Safety" problem may differ by an order of magnitude from that information generated for the pyrotechnic starter mix problem, it follows that variables in the Plastic Bonded Starter Mix (PBSM) situation may assume significant importance in determing the factors of safety required for acceptable safety criteria. For this reason, all factors governing pyrotechnic starter mixes were carefully re-examined.

1.2 BACKGROUND

The proposed introduction of a plastic bonded starter mix disk into the manufacturing process for M-18 color smoke and M7A3 C/S grenades generated the requirement to undertake an investigation into the potential hazards of PBSM during the process of its manufacturing, transportation, and storage.

Limitations introduced by the rapid turnaround from concept to production applications, utilizing the PBSM disk, necessitated an abbreviated examination of the potential hazards and the development of a comprehensive test plan to be applied later. Finally, the need for a mathematical simulation of the planned tests to enable assessment of the potential hazards completed the initial requirements for examination into the PBSM.

1.3 RECORDS AND EXPERIENCE ANALYSIS

This section contains the findings, recommendations, and conclusions of a search of the various records and technical documents containing significant data and information relative to pyrotechnic hazards classification and evaluation used for the research into the properties and hazards of various plasticized compositions.

The objectives of this segment were to:

a. Review the findings relative to the characteristics of pyrotechnics and starter mixtures as established by tests and the literature search and also to identify and attempt to resolve any anomalous findings or to determine the course of further studies and/or tests.

b. Contact all available sources for the accumulation of records of accident/incident experiences in pyrotechnic and related industries, and to analyze this data with particular reference to:

- Causes - procedures, human error, training, skills, equipment, or facilities.

- Type of initiation stimuli - static, friction, dust, impact, heat, shear, pinching, etc.
- Source of stimuli - machinery, air, or human
- Propagation, communication, and transition reactions
- Type and degree of damage - fire, blast, and fragmentation
- Identification of major damaging factor(s)
- Probability, in gross terms, of various types of accidents
- Correlation of damage data with "quality distance" criteria specified in AMR 385-224

c. Direct particular attention toward little known reactions, imcompatibilities, contaminants, evidence of synergism, and effects of geometric configurations during the review, and to analyze pyrotechnic incidents.

d. Use the results of this analysis as the basis for the formulation of the test program.

Approximately 310 related technical handbooks, reports, manuals, references, and other documents were reviewed for applicability to the immediate program and also to the potential program. Appendix A of this report contains a bibliographical listing of the documents reviewed and classifications for each based on these two criteria.

The documents researched were obtained from the following primary sources:

- Defense Documentation Center
- General Electric Technical Information Retrieval System
- Bureau of Mines Technical Reports
- Bureau of Explosives Reports
- Chemical Propulsion Information Agency Reports
- Picatinny Arsenal Publications
- Army Materiel Command Safety Office Reports (including Edgewood Arsenal and Pine Bluff Arsenal Reports)
- Ballistics Research Laboratory Reports
- NASA Scientific and Technical Information Facility, College Park, Maryland
- Department of the Army Publications
- Department of the Navy Publications
- Department of Defense Publications

The documents searched were selected from sources cited previously and present a very wide spectrum of the field. Much of the literature consists of reports and technical papers on the pyrotechnic and high explosive industries. However, it was found that a large percentage of the literature does not contain sufficient technical detail. The results and conclusions reported in some of the technical literature indicate that the industry may need more exact test methods, test equipment, and instrumentation. In addition, a systems approach to the overall problem of hazards evaluation is lacking. Much of the literature is redundant and is concerned with obsolete methods and procedures.

The value of a literature search such as this is difficult to ascertain in specific terms. The obvious advantage to performing a literature search is that it provides a technical and scientific basis upon which to plan and conduct a program and avoids possible costly duplication of effort.

1.4 MATERIAL HAZARD ANALYSIS

1.4.1 INTRODUCTION

Quantitative chemical analysis of the raw materials, bulk compounds, and the final plastic bonded starter mix for concentrations of likely contaminants and compounds that could potentially increase the sensitivity of the product to initiation by those stimuli found during production processes was deemed impractical during this initial examination of the PBSM although highly desirable to be undertaken in a follow-on program. In lieu of the chemical analysis, examination into the chemical constituents of the PBSM and their properties was undertaken for familiarization purposes and development of a comprehensive test program.

The essential ingredients comprising the PBSM are as follows:

	Approximate Proportion by Weight
• Potassium Chlorate	39
• Sodium Bicarbonate	9
• Acra Wax C - filler	3
• Santicizer 141 - plasticizer	5
• NC 1845 polymercaptan - crosslinker	20
• XD2679 resin	20

Preparation of the ingredients and the final mix is undertaken wherein all the solids are presifted, mixed and then slowly added to the blended liquid materials.

1.4.2 PREPARATION

An appropriate weight of resin material is added directly into a vertical planetary mixing bowl. The plasticizer is then added to the material and mixed slowly to avoid splashing and loss of the plasticizer. Mixing is continued until homogeneous and recycled as necessary to assure total blending of all the resin.

Dry potassium chlorate is screened through a 60-mesh screen and placed in a double cone blender along with screened sodium bicarbonate and Acra Wax C that has been screened respectively through 60-mesh and 30-mesh screens. The blended materials are stored in a Velostat bag and sealed until use.

Liquid preblend is combined with the crosslinker in a planetary blender. A well ventilated area is mandatory because of the extremely pungent and objectionable odor. The proper quantity of solid preblend is slowly added and blended. The mix is then poured (as soon as possible) into polyethylene M18 or M7A3 starter mixture molds which hold approximately 15 grams. The pot life of the material is approximately three hours after addition of the crosslinker (NC1845). Batches of PBSM prepared as above approximate 30 pounds of material.

The poured mix is cured in an oven at 70°C for two hours. When cured, the material is not extremely hard, but will have a rubber-like consistency and can be touched without sticking.

1.4.3 HAZARDS IDENTIFICATION

Examination of the process for production of the PBSM as outlined above provides some insight into those periods when the process inherently is more hazardous than other periods and which would identify potential test methods to explore the hazards and initiation sensitivities to be proposed in the test program.

Individually, the constituents of the PBSM each offer some degree of hazards. Identification of those which could be determined during the records and experience analysis are discussed below. Others for which no immediate information is available would be researched more thoroughly in a follow-on program.

1.4.3.1 Potassium Chlorate

Potassium chlorate is composed of transparent, colorless crystals that decompose at approximately 400°C with the liberation of oxygen. Differential thermal analysis (DTA) shows the decomposition point to be 362.2°C ± depending on the factors that influence DTA. When $KClO_3$ is mixed in stoichiometric amounts with sulfur, DTA shows that decomposition occurs at 179.1°C ±.

During the thermal decomposition of $KClO_3$, products are formed through the following intermediates:

- $2KClO_3 = KClO_2 + KClO_4$
- $KCl_2 = KCl + O_2$
- $KClO_4 = KCl + 2O_2$

The crystal lattice structure of $KClO_3$ is of tremendous importance in determining what actually causes increases sensitivity. If the crystal lattice structure can be loosened by different solvents, catalysts, and by recrystallization from water, decomposition will occur at a lower temperature. CuO, NiO, and MnO_2 are recognized as good catalysts and lower decomposition temperature considerably.

1.4.3.2 NC1845 Polymercaptan

The exact formula for this material is not known; however, comparison to normal mercaptan substances should indicate that this material exhibits the following hazardous characteristics:

- Toxic hazard rating from moderate to high and could produce unconsciousness in high concentrations with cyanois, cold extremities and rapid pulse.
- When heated to decomposition, mercaptans are dangerous and emit highly toxic fumes of oxides of sulfur.

Regarding the polymercaptan as a sulfur, the process combination with potassium chlorate creates the highly reactive starter mix (PBSM).

Sulfur itself is known to exist in two stable crystalline forms and at least two amorphous and two liquid forms. One crystalline form is ordinary (rhombic, octahedral, alpha, S_8) sulfur that is stable at room temperature but undergoes transition to the Beta form at 94.5°C with a melting point of 112.8°C. The other crystalline form is Beta-sulfur (monoclinic, prismatic) which slowly changes to the Alpha-sulfur form below 94.5°C but has a melting point of 119.3°C.

Once sulfur approaches the liquid form in the 100-110°C range, volume changes become very pronounced. This volume change could cause considerable crystal lattice loosening of the $KClO_3$ -polymercaptan mixture, thereby increasing reactivity of the mixture.

Not much research has been performed on the effect of contaminants on the decomposition of potassium chlorate-sulfur mixes with the exception of the work of Tanner, who found that a stream of sulfur dioxide flowing into a $KClO_3$-S mix ignited it immediately.

It should be pointed out that $KClO_3$-S mixes are very sensitive to H_2SO_4. It has been found that a drop of H_2SO_4 on 0.5 gram of a $KClO_3$-S mix caused an explosion because of both chloric acid ($HClO_3$) and heating effects. It was also determined that SO_2 has produced an explosion with $KClO_3$-S at 100°C.

It has been proposed a reaction mechanism where polythionic acid is the "trigger" to start the reaction with the exothermic reaction mass. Four reactions were proposed:

- $H_2S_nO_6 = H_2SO_4 + SO_2 + (N-2)S$ - Reaction (1)
- $SO_2 + 2KClO_3 = 2ClO_2 + K_2SO_4$ - Reaction (2)
- $2ClO_2 + 4S = 2SO_2 + S_2Cl_2$ - Reaction (3)
- Expressing Reactions (2) and (3) as one reaction,
  $SO_2 = 2KClO_3 + 3S = 2SO_2 + S_2Cl_2 + K_2SO_4$ - Reaction (4)
  Chain Reaction

Reaction (1) is significant in that air oxidation produces sulfurous acid on the surface of the sulfur. This acid, however, reacts quickly with sulfur to form polythionic acids ($H_2S_nO_6$). Reaction (1) is also significant in that a sudden rise in temperature will produce additional sulfur dioxide and sulfuric acid. Sulfuric acid, because it is hygroscopic, favors additional production of polythionic acids. As long as the temperature continues to rise, reaction (1) is not reversible, but a drop in temperature causes a reverse reaction. Sulfuric acid tends to coat the surface of chlorate as it is produced resulting in formation of chloric acid. Reaction (4) is a chain reaction which produces more sulfur dioxide than is consumed.

Sulfur changes from a solid form to the liquid form, and finally, to gas. Sulfur will decompose in the presence of oxygen as long as sufficient heat exists to sustain the decomposition. Reactions are as follows:

- $S + O_2 = SO_2$
- $2S + 3O_2 = 2SO_3$

SO_3 reacts with H_2O to form sulfuric acid.

$$2SO_3 + 2H_2O = 2H_2SO_4$$

From this, it is recognized that considerable care must be taken during the process to reduce the potential of exposure of the potassium chlorate and polymercaptan to undersirable environments which could increase the sensitivity of the compounds.

1.4.3.3 Santicizer (R) 141 Plasticizer

Santicizer (R) 141 plasticizer, a compound of alkyl aryl phosphate manufactured by the Monsanto Chemical Company, "combines into one compound the non-flammability, the efficiency, and permanence of other vinyl plasticizers." Its low temperature flexibility, moisture and resistance, and electrical properties appear to make it an excellent compound for use in the PBSM product. It has also received Federal Drug Administration approval as a non-toxic plasticizer for food packaging.

Its characteristics imply that in its use with the other constituents in the PBSM, a relatively stable compound would result.

Since this material replaces Alorcol 1500 Plasticizer which has according to the manufacturer's technical information sheet a "high dielectric strength and resistivity," the electrostatic ignition hazard potential should be thoroughly studied.

1.4.3.4 Role of Moisture

The actual role that water vapor plays in pyrotechnic reactions is very complex and not well understood. It has been postulated that water molecules, in their escape from the reaction zone, are likely to cause fissures and erosion effects on the $KClO_3$ crystal which facilitate diffusion. In addition, water catalyzes the formation of polythionic acids.

One might predict, then, that the presence of water in the system would increase the sensitivity. However, it was discovered in the pyrotechnic hazards program that ingredients of pyrotechnics stored at 60 percent relative humidity before mixing were desensitized relative to dry mixes.

1.4.3.5 Sodium Bicarbonate

This compound is the desensitizing agent utilized to control the reaction mechanism of the potassium chlorate and polymercaptan. Its contribution to the final plastic bonded starter mix is such that no identifiable hazard is exhibited by the sodium bicarbonate by itself.

It must be postulated that the other ingredients added to the composition have decreased the sensitivity of the $KClO_3$-S mixture. The sodium bicarbonate tends to coat the crystals of the $KClO_3$ and makes them insensitive to any reaction that could cause a rise in temperature. It must be assumed that if a rise in temperature occurs, the ions or atoms in any crystal will become excited and increase in such amplitude about their position in the lattice that diffusion is encouraged and the particles can exchange positions. This results in a phase shift, and when solid substances undergo a transformation of this type, atoms are in a "loosened" state.

1.4.4 SYSTEM SAFETY ENGINEERING QUANTITATIVE HAZARD ANALYSIS

Behind nearly all accidents is a cause that can be identified and eliminated. Inherent in the role of safety analysis is the responsibility for properly identifying and eliminating accident causes before they occur.

There are various qualitative and quantitative techniques which are used in analyzing data acquired from hazard analysis, safety tests, safety reviews, and accident reports. Based on a review of safety analysis procedures, one or more techniques may be used with equal success. The necessary criterion for depth and adequacy of the technique employed is traceability; i.e., cause to effect or effect to cause.

Safety analysis techniques which are tailor-made to tie in with research testing programs have been developed as a practical approach for evaluating processing hazards. The techniques are based essentially on accident investigations and emphasize both the quantitative and qualitative assessment of process conditions in standard engineering terms and establishment of material response to stimuli found in the process.

As spelled out in the Air Force System Command Design Handbook on Safety, the System Safety Engineering Hazard Analysis and Matrix is a standardized systems safety analysis (which basically encompasses a failure mode and effect analysis) and is oriented toward a nine-step method that can be adopted to a variety of situations. The results can therefore be written in a nine-column matrix with accompanying diagrams. As shown in Figure 1-1, the nine-step approach utilized during a theoretical program includes:

- Prepare system block or functional flow diagrams representing the basic conceptual breakdown of the process, job operation, sequence of events, or physical movement of material.
- Determine the number of accidents in which each individual component was involved and compare to the overall processing operation.
- Determine all envisioned malfunctions, failure or error modes for each component, step, or functional interface.
- Determine the chain of events that might follow an error or malfunction so that likely secondary failures or difficulties are identified.
- Determine the resultant effects or consequences to the system and identify all personnel hazards in terms of blast, fragmentation, and fire.
- Determine the corrective action and list all recommendations, such as design changes and procedural changes.

A sample application of System Safety Engineering Quantitative Hazard Analysis is shown in Appendix B.

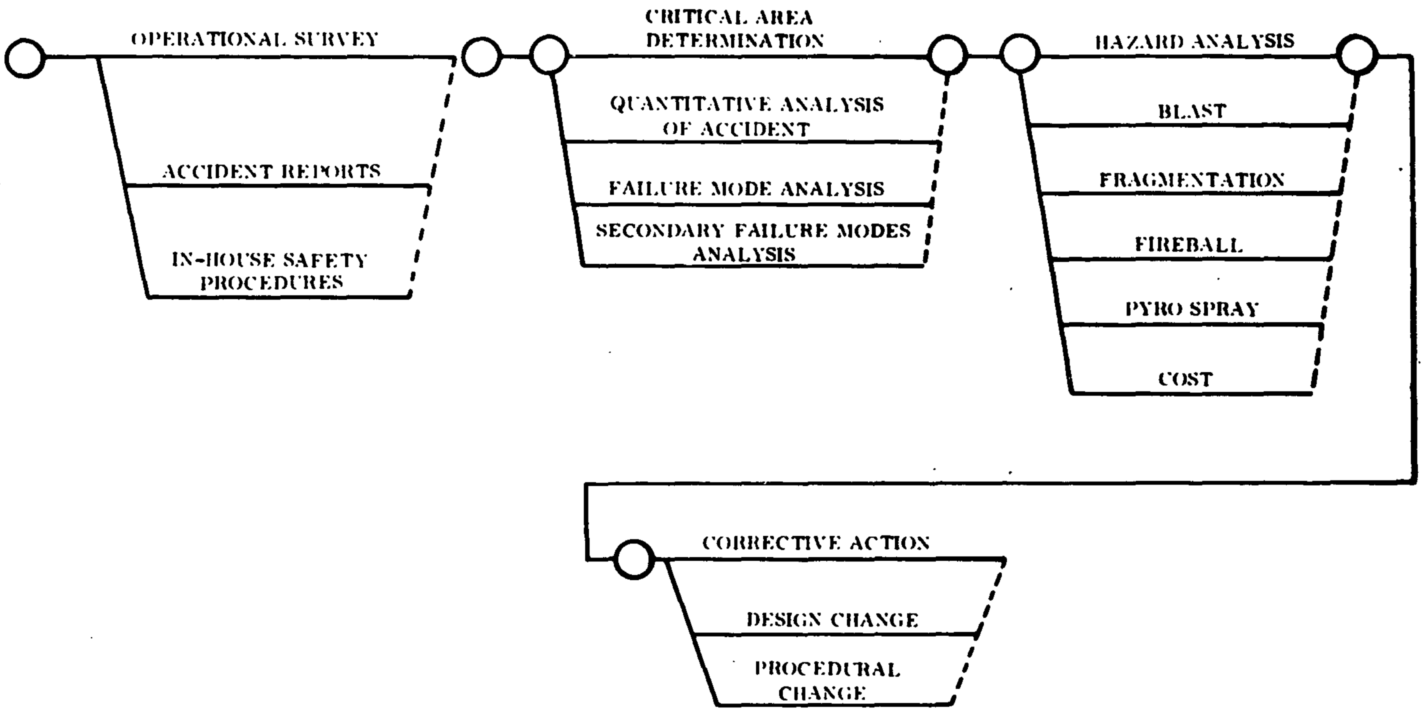


Figure 1-1. Typical Hazard Analysis and Matrix Sequence Chart

SECTION 2

TEST PLAN DEVELOPMENT

2.1 TECHNICAL APPROACH

Diagraming the process operation, as previously outlined, and combining this information with known hazards associated with normal starter mix compounds, a cross reference from operation to test can be postulated and utilized in the development of the potential test program to examine the actual production hazards, transportation safety requirements and storage conditions applicable to the PBSM. Testing of normal starter mixes was carried out in the Phase I Hazards Evaluation and Classification Program and is reflected in Appendix C.

2.2 PLANNING

The entire planning phase is predicated on the logical diagraming of the information available and must, by necessity, be extended to include the overall project plan which comprises all segments of the work undertaken or to be undertaken. Therefore, attention is drawn to Figure 2-1 which presents a step by step approach to the solving of the basic objectives of the PBSM project.

The objectives of the test plan developed for the conduct of the PBSM Program are as follows:

a. To develop cost effective, reproducible simulations of those incidents/accidents determined by the foregoing studies, analysis, etc., to be major hazards to the manufacture of PBSM pyrotechnics;

b. To establish "worst case" conditions in terms of the potential severity of the incidents concerned.

c. To provide a logical rationale to permit conversion with related tests and studies in in the field.

d. To identify areas where "follow-on" tests (beyond the scope of the current program) are necessary to present, insofar as is practicable, a standard test geometry to permit the reduction of replicate tests to the minimum required for cost/effective solutions.

e. To identify those factors, initiating stimuli, degree of confinement, etc., which are controlling or overriding in a given situation.

It has been determined that in any given accident/incident a number of initiating stimuli may be available and that those stimuli may occur under various environmental conditions of material confinement, geometry, or consolidation. The philosophy used herein has been to consider the

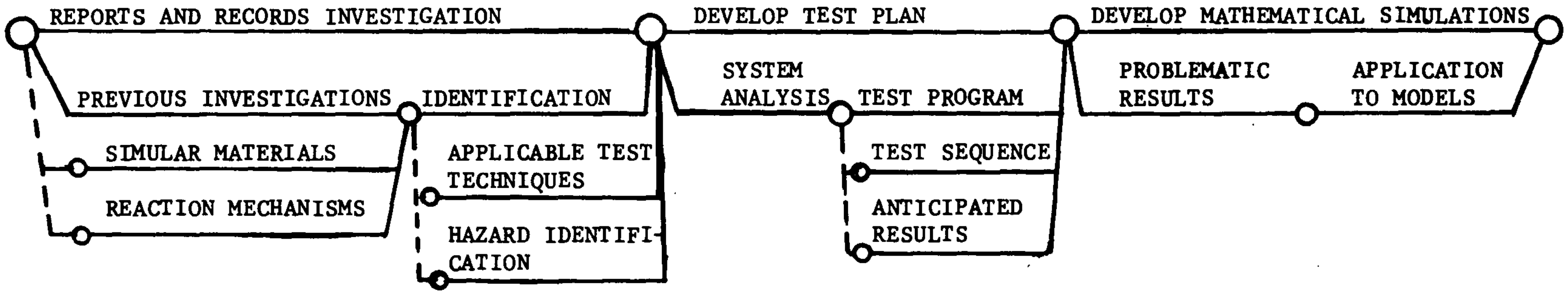


Figure 2-1. PBSM Project Summary

worst case condition in order to obtain a rough order of magnitude approximation of potential severity, with the intuitive feeling that the "worst case" or "maximum credible" incident determination will prove to be amenable to control or preventive actions of a comparable magnitude with those controls applicable to reactions of lesser severity. In the event that this proves not to be the case, i.e., if the preventive or control criteria necessary for the maximum credible incident is not "cost effective" in terms of the "maximum probable" incident, additional tests will be conducted to the less restrictive criteria.

As an example, for this reason the method of initiation (stimuli) chosen has been the initiation of materials by a J-2 cap, which provides a shock wave, and a shaped charge effect with sufficient energy release to detonate high explosives. Similarly, the degree of confinement, geometry, and combinations of materials have been related, on the basis of preceding tests, as those which will result in the highest level of reaction.

Examination of the process operation for the PBSM as diagramed in Figure 2-2 shows the following primary areas of hazard:

- Blending of liquids and solids
- PBSM disc molding and container recycle
- Drying and associated off-gassing
- Mold recycle
- Transportation and storage

The test program developed as a result of the system analysis activity is presented in Figure 2-3 and is durther discussed in the following paragraphs.

2.3 TESTING ACTIVITY

2.3.1 INTRODUCTION

This section presents the testing program to determine whether specific plastic bonded starter mixes compositions are safe to handle, transport, or store. The proposed testing program will determine the reaction to specific initiating influences.

The following discussion deals with the various tests to be performed on laboratory samples of bulk compositions and mixes. These sample compositions, and/or sufficient raw material to blend or mix the compositions, will be provided by the Edgewood Arsenal.

2.3.2 LABORATORY CHEMICAL ANALYSIS

Quantitative chemical analysis of the raw materials, bulk compounds, dyes, and starter mixes for the concentrations of contaminants in the form of metals will be carried out utilizing atomic absorption spectrophotometric analysis.

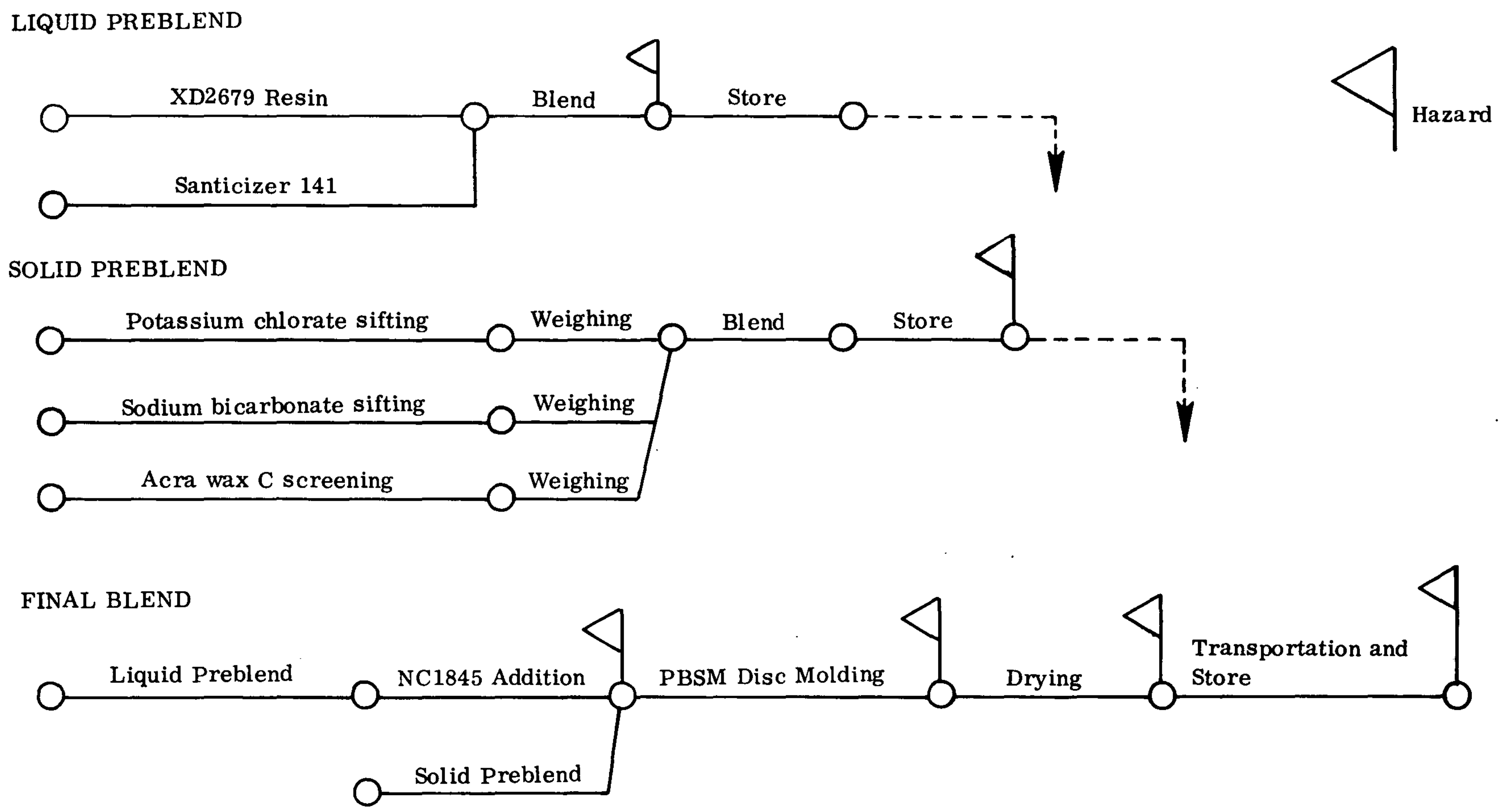


Figure 2-2. Process Operation Critical Path

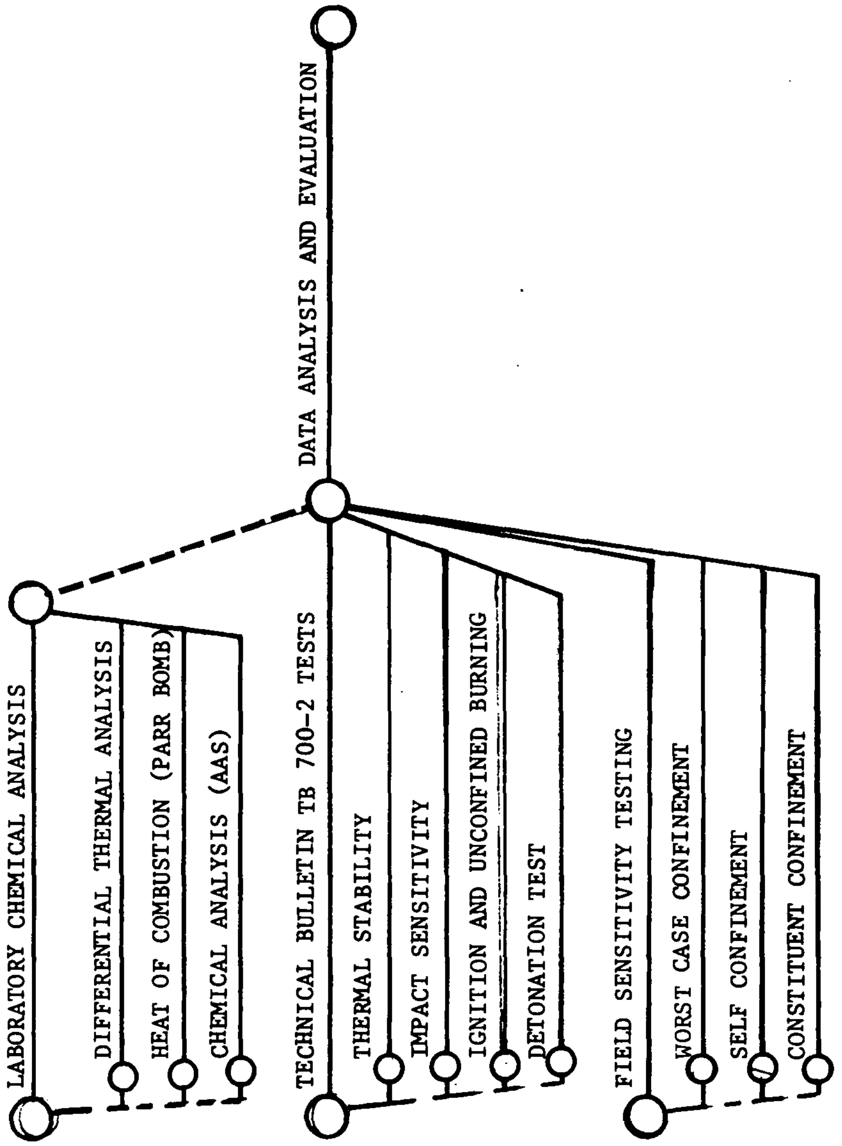


Figure 2-3. Potential Test Program

The theory and practical application of atomic absorption spectrophotometric analysis is well known. Basically, the principle of this method is the aspiration of a solution containing the sample into a flame, resulting in a large proportion of the metal atoms becoming ground-state or neutral atoms. Actual passage of a resonant beam of monochromatic light through such a flame will result in reduction of its intensity by absorption of a portion of the light by the neutral or ground-state atoms.

Because the absorption is proportional to the concentration of neutral atoms in the flame, measurement of the absorption can be used as a quantitative determination of the concentration of the metallic element in the original solution. Measurement of the absorption of radiation in the ground-state or neutral atoms of the atomized sample occurs at a wave-length that is specified and characteristic of the element under consideration.

Because the measurement made is a reduction of an initially greater intensity, it is called a spectrophotometric measurement. Concentration of the neutral atoms in the flame can be varied by many methods, including burner gas flow and the chemistry of the sample itself.

Standard solutions containing several concentrations of metallic elements are used as standard reference material for the spectrophotometric determination. Atomic absorption spectrophotometric determinations are unquestionable applicable to materials with concentrations of various metallic elements present in minute quantities.

The analytical program for atomic absorption spectrophotometric analysis is designed to provide metallic concentration of iron, manganese, copper, chromium, nickel, and cobalt on the following:

- Raw materials
- Starter mixes

As indicated, further testing will consist of certain special tests designed to assess the physical and chemical characteristics of the sample material through the following tests.

2.3.3 DIFFERENTIAL THERMAL ANALYSIS

Differential Thermal Analysis will be used to determine physical and chemical reactions that might occur when the material is subjected to a rise in temperature. Fischer Series 200 Differential Thermal Analyzer or equivalent will be used.

DTA measurements are used extensively to detect any exothermic or endothermic changes that might occur in a chemical system by measuring the temperature difference between a sample and a thermally inert reference material as both are heated at a constant rate of increase of temperature. A reference material will be selected which did not undergo any thermal reaction over the temperature range under investigation, so that any exothermic or endothermic change occurring within the sample will cause its temperature to either exceed (exothermic) or lag (endothermic) behind that of the reference material during the course of a physical or chemical reaction. All physical or chemical reactions that occur during a differential thermal analysis are related to the mass of the sample, size of sample, heating rate of the sample, and particle size of the sample. These chemical or physical reactions represent changes that may be related to decomposition, dehydration, crystalline transition, melting, boiling, vaporation, polymerization, oxidation, and reduction of the material under investigation.

2.3.4 PARR BOMB - HEAT OF COMBUSTION

Test samples of the selected materials will be burned in an oxygen filled metal "bomb" submerged in a measured quantity of water. By observing the rise in water temperature resulting from combustion of the sample, a calculation of the number of heat units (calories) liberated will be performed. Standard test methods will be used with ASTM procedure D240-64 "Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter" the prime reference.

2.3.5 DETONATION TEST

Segment 2 of the proposed testing program consists of the testing of bulk materials in accordance with TB 700-2 as modified to enable acquisition of the maximum physical/chemical characteristics. Specific details concerning individual elements of TB 700-2 are presented in subsequent paragraphs. Tests found to provide the maximum information should be performed prior to others of lesser importance with the intent of reducing the overall testing requirements.

A series of tests will be performed to measure the sensitivity of a pyrotechnic sample to the influence of a No. 8 blasting cap. A two-inch cube sample will be placed on top of a perpendicular, 1-1/2 inch (diameter) by 4-inch (long) lead cylinder. The No. 8 blasting cap will be placed perpendicular to and in contact with the top surface of the sample. A 2-inch wood cylinder with a hole drilled through its center will be used to position and support the blasting cap. The cap will be initiated by a suitable electrical surrent. Detonation of the sample will be evidenced by the deformation (mushrooming) of the lead cylinder. This test will be conducted a minimum of five times, or until detonation is evidenced, whichever is less. Test configuration is shown in Figure 2-4.

2.3.6 IGNITION AND UNCONFINED BURNING TEST

Unconfined samples of pyrotechnics will be ignited and burned in order to evaluate the resultant hazards associated with such burning. These tests will be conducted on single and multiple (four) 2-inch cube samples. For Test No. 1 (single sample test), a 2-inch cube sample will be placed on a bed of kerosene soaked sawdust and the sawdust ignited with an electrically initiated matchhead igniter. This test will be conducted a minimum of two times. In Test No. 2 (multiple sample) four 2-inch cube samples will be arranged with end-to-end contact, on a single bed of kerosene soaked sawdust and the sawdust ignited with a matchhead igniter. This test will be conducted a minimum of one time. The Ignition and Unconfined

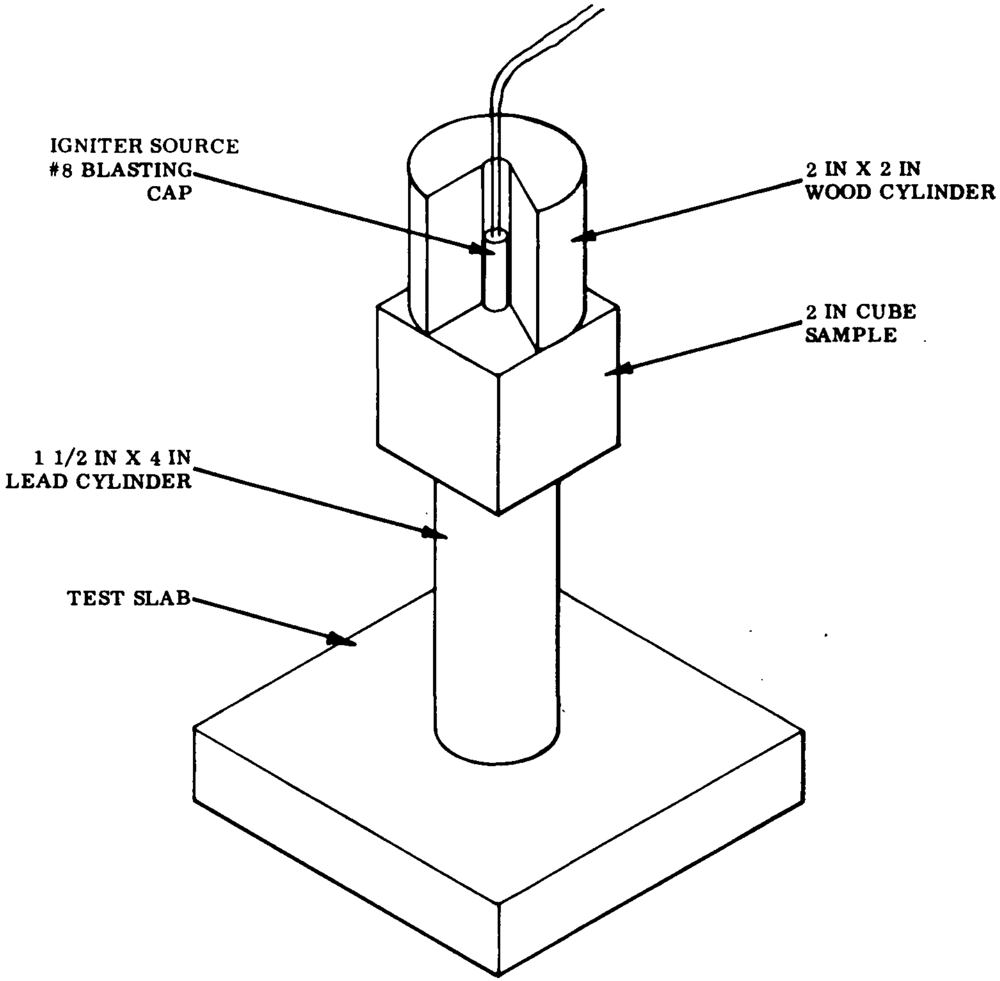


Figure 2-4. Detonation Test Configuration

Burning Test Report will include ignition-deflagration-detonation and burning time data of samples as applicable. Modifications to acquire burn temperatures should be investigated. Test configuration is shown in Figures 2-5 and 2-6.

2.3.7 THERMAL STABILITY TEST

Material samples will be subjected to elevated temperatures to allow the observance of characteristic tendencies to detonate, ignite, decompose or change in configuration. The sample will be placed in an explosion-proof oven, the temperature raised to 75°C (167°F) and maintained at this temperature for a period of 48 hours. Oven temperatures will be continuously recorded throughout the test period. Test configuration is shown in Figure 2-7.

2.3.8 IMPACT SENSITIVITY TEST

A series of tests (20) will be performed to determine the sensitivity of a pyrotechnic sample to mechanical shock (impact). These tests will use the Bureau of Explosives impact test apparatus. A 10-mg sample will be placed in the test cup, the test weight dropped from a predetermined height, striking the sample, and thus imparting the required shock (impact). Modifications to this technique in the form of instrumentation to measure drop weight acceleration, input energy and sensitivity to initiation are suggested. Results of the measurements will enable calculation of dwell time, velocity and time to reaction.

The results of the 20 tests per sample (10 at 3-3/4-inch drop height and 10 at 10-inch drop height) will be reported as the number of trials exhibiting:

- Explosion, flame and noise
- Decomposition, smoke, no noise
- No reaction, no smoke, no noise

Test configuration is shown in Figure 2-8.

2.3.9 FIELD SENSITIVITY TESTING

2.3.9.1 High Explosive (HE) Equivalency Tests

Samples of the PBSM materials will be initiated with an appropriate electro-explosive device. These tests will determine the materials' tendency to transmit from deflagration to detonation and will be instrumented to measure overpressure and impulse at selected distances from the test position. The worst case conditions (total confinement) to which the material could be subjected will be tested during this sequence.

2.3.9.2 Granular Bulk

In this test, the sample will be of a weight and material to simulate the blend existing at the initial mixing phase of the production process. The sample will be subjected to the influence

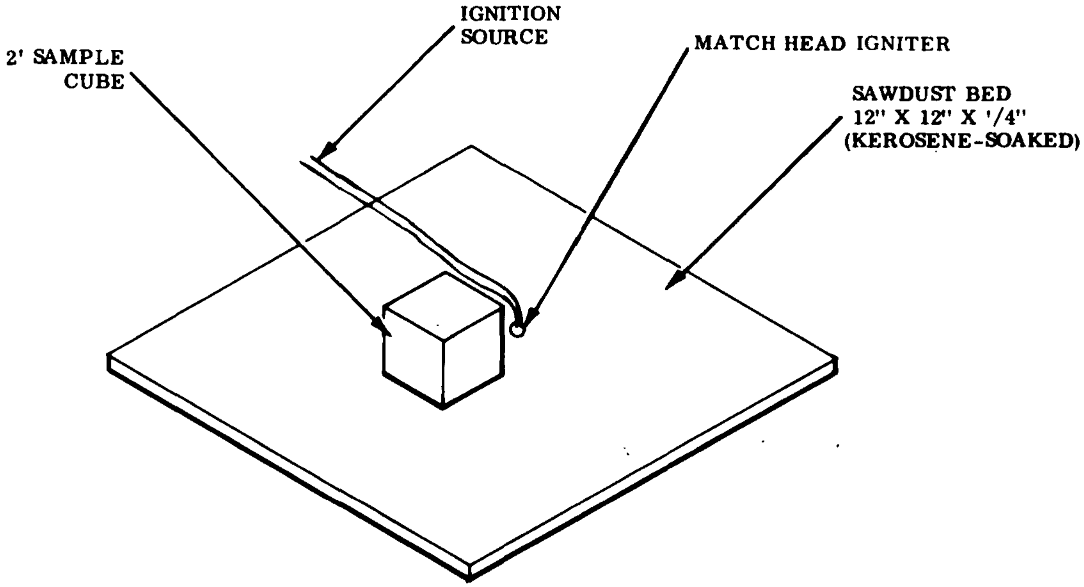


Figure 2-5. Ignition and Unconfined Burning Test No. 1 Configuration

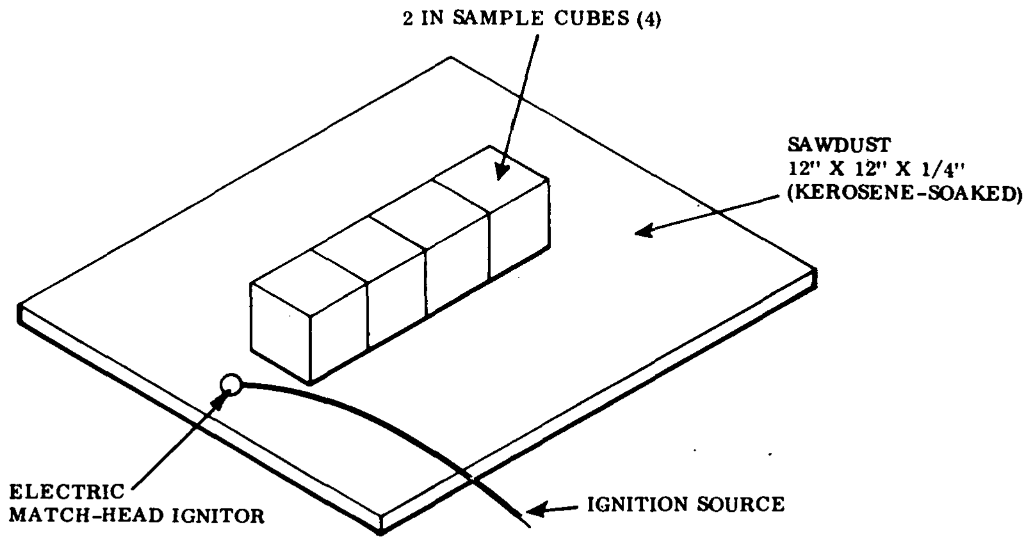


Figure 2-6. Ignition and Unconfined Burning Test No. 2 Configuration

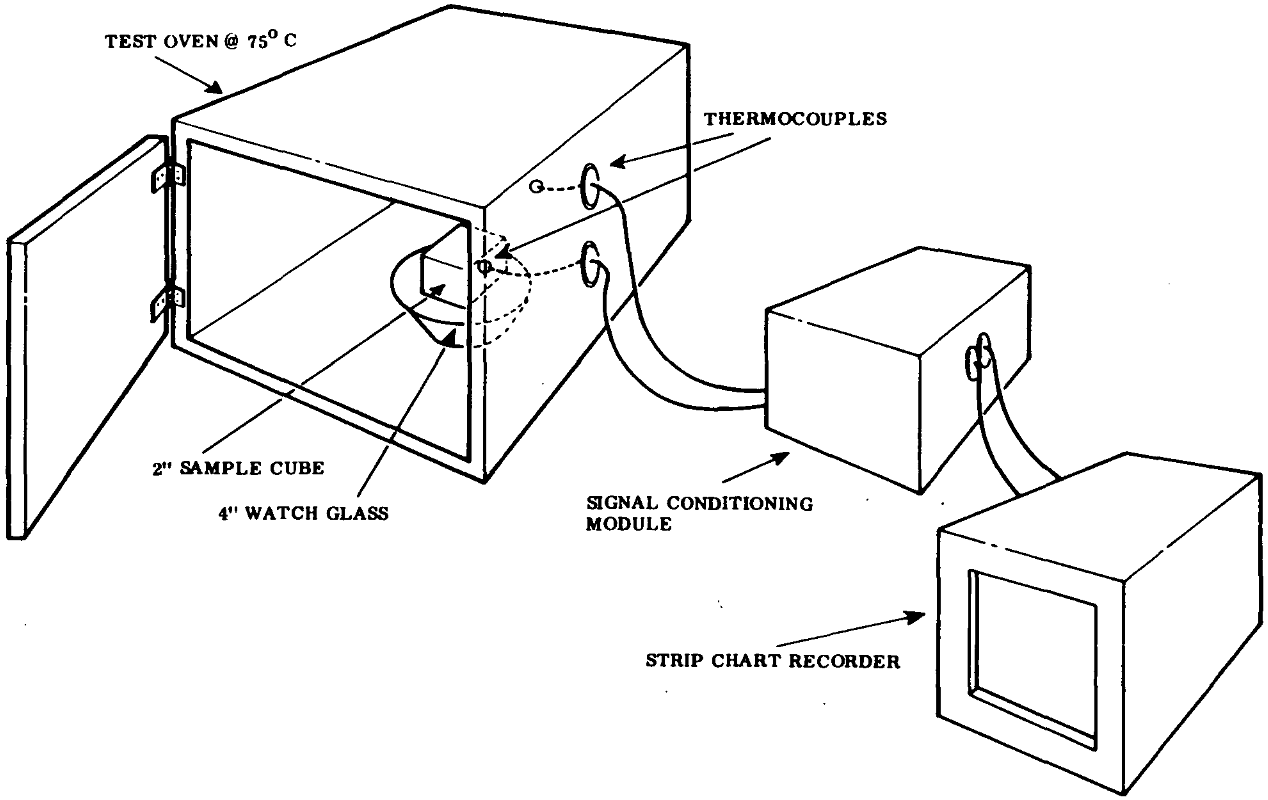


Figure 2-7. Thermal Stability Test Configuration

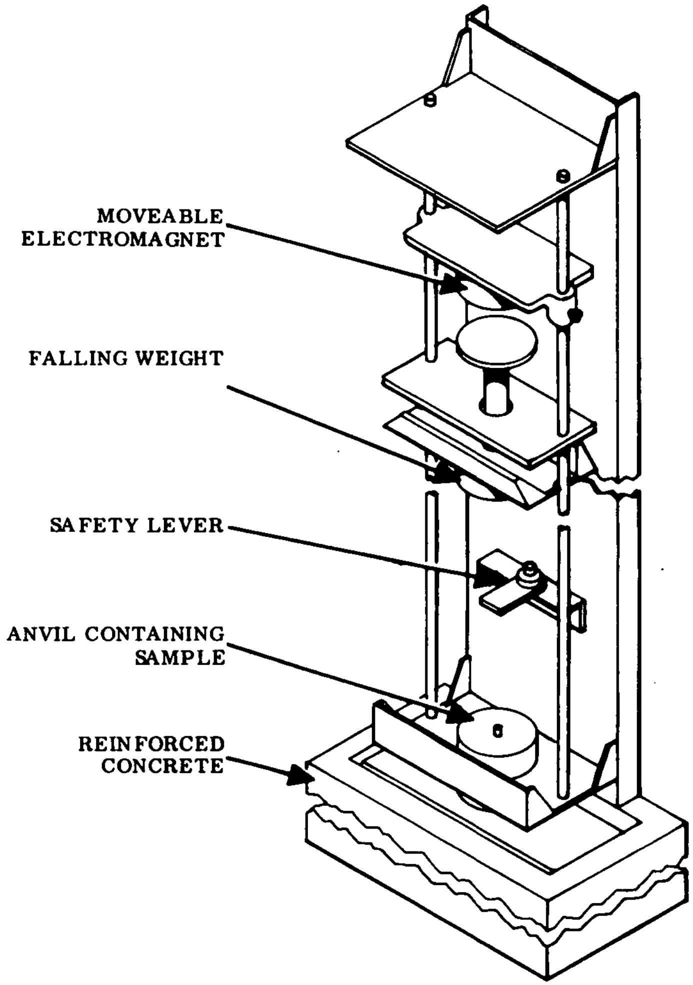


Figure 2-8. Impact Sensitivity Test Configuration

of a suitable ignition source. Blast overpressure gages (used for measuring side-on overpressure) will record the complete pressure time history of the shock wave (if detonation occurs) so that peak pressure and impulse data will be obtained. Calibration runs will be conducted with TNT, C-4 or pentolite of the same measured weight as the sample being tested, and a minimum of three tests will be conducted on each material to assure the validity of data.

2.3.9.3 Preblend Compositions

The samples used in this test will be of such weight and blend and be of such a state, liquid or solid, as to simulate the configuration existing after the consolidation of materials in the second phase of the production process. The sample will be subjected to the influence of a suitable ignition source. Blast overpressure gages (used for measuring side-on overpressure) will record the complete pressure time history of the shock wave (if detonation occurs) so that peak pressure and impulse data will be obtained.

Calibration runs will be conducted with TNT, C-4 or pentolite of the same measured weight as the sample being tested and a minimum of three tests will be conducted on each material to assure the validity of data.

2.3.9.4 Starter Mix Consolidation

If appropriate, the samples used in this test will be processed to simulate the configuration existing at the final stage of the production process. The sample will be subjected to the influence of a suitable ignition source. Blast overpressure gages (used for measuring the side-on overpressure) will record the complete pressure time history of the shock wave (if detonation occurs) so that peak pressure and impulse data will be obtained. Calibration runs will be made with TNT of the same measured (weight) amount as the sample being tested, and a minimum of three tests will be conducted on each material to assure the validity of data.

2.3.10 MIXER SIMULATION TESTS AND RESULTS

As discussed in "systems safety analysis", the mixing operation involving vertical planetary mixers to prepare PBSM formulations has been identified as a primary hazard area. The safety analysis further pointed out that failure modes such as misalignment, impact, or inadequate grounding of the mixer blades and/or mixer bowl are likely to cause ignition by friction within the bulk of the materials. When ignition is induced below the surface, the material supplies a significant pressure head which allows a transient pressure buildup caused by the temporary confinement of reaction by-products.

Previous testing demonstrated that the pressure-time curve of a confined material closely resembles that of a detonating explosive. Thus, a potentially hazardous situation exists during the mixing operation because of the possibility of simultaneous ignition and confinement in a localized region near the bottom of the mixing bowl.

Self confinement simulation tests were designed to provide data to evaluate a potentially hazardous situation. In line with the concept of "worst case" testing, the location and type of ignition source in all cases are chosen to maximize the likelihood of inducing a detonation (according to guidelines established by previous experimental results) while maintaining a credible simulation of an actual mixing operation.

The objectives of this test program are to determine the following criteria:

- Bulk mix and mixing bowl influence on the reaction rate.
- Extent of the pressure buildup.
- Probability of communication to loose mix inadvertently scattered in the vicinity of the mixing operation.
- Scaling laws to predict the outcome of an actual incident.

To accomplish these objectives, a single self-confinement simulation test series is to be performed.

A typical self-confinement test and the results are shown in Appendix D.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

3.1 SIGNIFICANT OBSERVATIONS

3.1.1 GENERAL OBSERVATION AND SIGNIFICANT FINDINGS

The process flow, the ingredients involved and the test program as outlined were oriented toward examination of the hazardous characteristics of the plastic bonded starter mix under different degrees of confinement, stimuli and environment.

The following paragraphs are intended only to relay significant observations by operation sequence and not to correlate to any particular material being processed.

3.1.1.1 Liquid Preblend Preparation

Caution should be taken to avoid accidental loss of material during this process since a change in the weights of material could cause a considerable change in the effectiveness of the PBSM. A variance at this point could effect the ignition, burn rate, and heat output of the PBSM.

3.1.1.2 Solid Preblend Preparation

Mesh size and maximum drying of the solid materials are the two areas in this stage of the process requiring close observation. From information researched, there is some question regarding the proper mesh screen to be used in preparation of the potassium chlorate. One source sites a 325-mesh screen and the other a 60-mesh screen. Since particle size has an effect on the output and, therefore, the hazard potential of the final product, this disagreement should be examined further.

The effect of moisture has been previously discussed; however, its effect in the PBSM should be examined further.

3.1.1.3 Final Blending

The presence of objectional vapor could affect the operator judgement and technique, and the need for extreme caution at this time is deemed mandatory. The mixing time requirements and the odor could cause excessive haste and result in an undesirable accident. The liquid constituents are normally non-flammable while flammability of the off-gassing vapors is unknown, but would be researched in a follow-on program. On the basis of such studies, the presence of a vapor detector and warning system should the vapors exceed desirable limits would be advisable.

From the information presently available, the quantity of material being handled is in the neighborhood of 30 pounds,and this could effectively reduce the potential incident severity.

3.1.2 TEST PROGRAM

The test program outlined in Section 2 is oriented towards examination of those stimuli readily recognizable as being present during the manufacturing, transportation, and storage processes. There are many other applicable tests and chemical/physical characteristics analyses which could be performed concurrent with the proposed tests. A few of the basic critical parameters are contained in Appendix E.

3.1.3 DATA EVALUATION AND SIMULATION

The process of system safety analysis, test data evaluation, and hazard identification are readily applied to a simulation technique whereby the physical/chemical characteristic can be matrixed to the test result and hazard identification to form a predictive model of all the parameters. By this application, significant differences in levels of risk between processes can be assessed and the maximum theoretical, maximum credible, and maximum probable incidents involving the PBSM can be prepared and then compared with other similar materials. The application of this technique is by nature dependent on the performance of a test program as outlined and would be appropriate for the follow-on program.

3.2 RECOMMENDATIONS

Based on the scope of this study, it is recommended that the test program as outlined be implemented and such modifications made to the test methods as to allow for maximum acquisition of physical/chemical characteristics of the PBSM under the particular test environment.

It is also recommended that an in-depth review of the production process as finalized be undertaken with the intent of isolating those potential hazardous areas beyond the scope of those identified in this study. An actual plant survey with specific interest in determining those areas where potential hazards exist as single incident, dual incident or multiple incident situations and whether the situations anticipated could cause communication from deflagration to a detonation reaction in the PBSM would be advisable.

APPENDIX A
BIBLIOGRAPHY

SPECIFIC SOURCES

Explosives Accident/Incident Abstracts, September 1961 through June 1967. Armed Services Explosives Safety Board. AD 660 020.

Fedowitz, F., Jr. "Sensitivity of Explosives and Propellants to Impact and Friction". N67-15987.

Freeman, E. S. and Rudloff, W. K. "The Catalytic Reactivity of Metal Oxides on the Thermal Decomposition of Potassium Chlorate". AD 467 442.

Markowitz, M. M., Bonita, D. A., and Stewart, H., Jr. *J. Phys. Chem.* *68* (8) 2282 (1964).

McLain, J. H. and McClure, M. D. "Effect of Phase Change in Solid-Solid Reactions". AD 831 733.

Miravet, M. and Rocchiccioli, C. *C. Mikrochim. Acta* (1961).

Olson, Carl M. *J. Electrochem Soc.*, Vol. 116, 1969, 33C-35C.

Rudloff, W. K. and Freeman, E. S. *J. Phys. Chem.* *73* (5) 1209 (1969)

Tanner, Herbert G. *J. Chem. Educ*. 36 (2) 58 (1959).

Taradoire, F. Bull. *Soc. Chem.* 9, 610-20 (1942).

Thikol Company. Longhorn, Texas. AD 642 407.

U. S. Army Technical Bulletin 700-2, "Explosives Hazards Classification Procedures".

THERMAL ANALYSIS SOURCES

Berg, L. G. and Yasnikova, T. E. "Thermographic Determination of Thermal Effects of Polymorphic Transformations", *Russ. J. Inorg. Chem.* *11* (4) 477 (1966).

David, D. J. "Determination of Specific Heat and Heat of Fusion by Differential Thermal Analysis", *Analytical Chemistry* *36* (11) 2162 (1964).

Evans, J. P. and Scrogham, K. G. "Evaluation of Analytical Standards by Differential Thermal Analysis and Differential Scanning Calorimetry" (NASA Contract No. NAS8-20073), 29 April 1968, N68 35618.

EXPLOSIVES SOURCES

Andreyev, K. K., Belyayev, A. F., Goldbinder, A. I., and Gorst, A. G. "Theory of Explosives". Foreign Technology Division, Wright-Patterson AFB, Ohio. 31 January 1964. AD 605 706.

Ascani, Diamond C. "The Literature of Explosives", Advances in Chemistry Series No. 78, 565 (1968).

Blunt, R. M. "Proceedings of First Pyrotechnic Seminar", Denver Research Institute, Denver, Colorado, 1 October 1968. AD 679 911.

Brinkley, Ruth F. and Van Dolah, Robert W. "Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1960", U. S. Bureau of Mines Information Circular 8106, 1962.

Brinkley, Ruth F. and Van Dolah, Robert W. "Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1961", U. S. Bureau of Mines Information Circular 8191, 1963.

Dirmeik, Ivan Daniel. "Anodic Passivation of Metals in Fused Salt Electrolytes", Corrosion 25 (4) 180 (1969).

---------- "Explosive Safety, Executive Lecture Series", TRW Space Technology Laboratories, Cape Kennedy, Florida, June 1965. N67-15981 through N67-15991.

Federoff, Basil T., et.al. Encyclopedia of Explosives and Related Items, Picatinny Arsenal, Dover, New Jersey, 1962.

---------- "Final Technical Report", Amcel Propulsion Company, Asheville, North Carolina, March 1965, AD 474 401.

Gorst, A. G. "Powders and Explosives", Foreign Technology Division, Wright-Patterson AFB, Ohio. 20 September 1963. AD 423 801.

Hoge, K. G. "Friction and Wear of Explosive Materials", Lawrence Radiation Laboratory, University of California, Livermore. UCRL-50134. 1 September 1966.

Jackson, Henry J. "A Study of the Electrical Characteristics of Some Explosives and Explosive Mixtures", Picatinny Arsenal, Dover, New Jersey. October 1963. AD 425 988.

Kristal, Joseph and Kaye, Seymour. "Survey of Sensitivity Characteristics of Typical Delay, Igniter, Flash, and Signal Type Pyrotechnic Compositions." Picatinny Arsenal, Dover, New Jersey. (Department of the Army Proj. 1C 52380/A302) April 1964. AD 439 383.

Nagy, John, Cooper, Austin R., and Dorsett, Henry G., Jr. "Explosibility of Miscellaneous Dusts", Bureau of Mines, Washington, D. C. December 1968. PB 182677.

Parandjuk, Seraphim. "The Theory of Detonation, the Combustion Mechanism, and the Properties of Explosives", Compilation of Abstracts. ATD Report 65-116. 21 December 1965. AD 629 780.

Ridner, Richard M., Wachtell, Stanley, and Saffian, Leon W. "Establishment of Safety Design Criteria for Use in Engineering of Explosive Facilities and Operations", Picatinny Arsenal, Dover, New Jersey, June 1967. AD 818 394.

--------- "Safety Principles for Laboratory and Pilot-Plant Operations with Explosives, Pyrotechnics, and Propellants", Naval Ordnance Laboratory, White Oak, Maryland. 1 July 1964. AD 446 737.

Staff, Explosives Research Center. "Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1964", U. S. Bureau of Mines Information Circular 8272, 1965.

Staff, Explosives Research Laboratory. "Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1962", U. S. Bureau of Mines Information Circular 8218, 1964.

--------- "The Theory of Detonation, the Combustion Mechanism, and the Properties of Explosives", Annotated Bibliography, Aerospace Technology Division, Library of Congress, Washington, D. C. (ATD Work Assignment No. 50C, Report No. 1) AD 460 101.

Zaehringer, Alfred J. "Solid Propellant Bibliography", Jet Propulsion 900, August 1957.

OTHER SOURCES

Doc. 1 Hazard Classification Test Report: Phases I and II. Space Systems Division, United States Air Force Systems Command, Los Angeles 45, California. 26 May 1964.

Doc. 2 Proceedings of the Fifth Symposium of Elextroexplosive Devices. 5EED-67. The Franklin Institute Research Laboratories, Philadelphia, Pennsylvania 19103. 13-14 June 1967.

Doc. 3 Pollard, Frank B. and Arnold, Jack H., Jr., Aerospace Ordnance Handbook. Prentice-Hall, Inc., Englewood Cliffs, New Jersey. 1966.

Doc. 5 Ellern, Dr. Herbert. Military and Civilian Pyrotechnics. Chemical Publishing Company, New York. 1968.

Doc. 6 Fundamentals of Protective Design. Corps of Engineers, Office of the Chief of Engineers. 1946.

Doc. 7 Explosives Series Properties of Explosives of Military Interest. AMCP 706-177. March 1967.

Doc. 8 Theory of Explosives (Russian). Foreign Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. 1963.

Doc. 9 Shidlovskiy, A. A. Foundations of Pyrotechnics. AD 602 687. Foreign Technology Division, Wright-Patterson Air Force Base, Ohio. 30 April 1964.

Doc. 10 Demolition Materials. TM 9-1375-200. Department of the Army. January 1964.

Doc. 11 Military Explosives. TM 9-1300-214 and TO 11A-1-34. Departments of the Army and the Air Force. November 1967.

Doc. 12 Military Pyrotechnics Series, Part One: Theory and Application. AMCP 706-185. April 1967.

Doc. 13 Rindner, Richard M., Wachtell, Standly, and Saffian, Leon W. Establishment of Safety Design Criteria for Use in Engineering of Explosive Facilities and Operation. Ammunition Engineering Directorate, Picatinny Arsenal, Dover, New Jersey. June 1967.

Doc. 14 The Theory of Detonation, the Combustion Mechanism, and the Properties of Explosives. ATD Report 64-88. Aerospace Technology Division, Library of Congress. 11 August 1964.

Doc. 15 Explosives Accident/Incident Abstracts. AD 660 020. Armed Services Explosives Safety Board. October 1967.

Doc. 16 Detection Techniques for Hazardous Vapors of Elemental Propellants. Technical Documentary Report No. ASD-TDR-63-294. AD 414 947. Directorate of Aeromechanics, Aeronautical Systems Division, Air Force System Command, Wright-Patterson Air Force Base, Ohio. July 1963.

Doc. 17 Berlad, A. L. and Buley, C. R. Radiative Effects on Explosive Instability. AFRPL-TR-67-24. AD 807 548. Defense Research Corporation, Air Force Rocket Propulsion Laboratory, Air Force Systems Command, Edwards, California. January 1967.

Doc. 18 Safety Principles for Laboratory and Pilot Plant Operations with Explosives, Pyrotechnics, and Propellants. AD 446 737. The Naval Ordnance Laboratory, White Oak, Maryland. July 1964.

Doc. 19 Explosives Safety Manual. AFM No. 32-6. Department of the Air Force. 1 November 1961.

Doc. 21 Altman, F. D. Model Studies of Explosive Storage Cubicles. U. S. Naval Weapons Laboratory, Dahlgren, Virginia. May 1964.

Doc. 22 Coulter, George A. Dynamic Calibration of Pressure Transducers at the BRL Shock Tube Facility. AD 654 508. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. May 1967.

Doc. 23 Military Pyrotechnics Series, Part Two: Safety, Procedures and Glossary. AMCP 706-186. October 1963.

Doc. 24 Cohen, Edward and Dobbs, Narval. Minutes of the Ninth Explosives Safety Seminar: Cost Effectiveness Studies of Facilities for High-Hazard Explosive Material, p. 427. Ammann and Whitney, Consulting Engineers, New York, New York.

Doc. 25 Roth, Milton. Process Control Methods for Determining Small Amounts of Moisture in Pyrotechnics, I. Electrolyic Hygrometer. Technical Report 3239. AD 463 060 or 1.

Doc. 26 McLain, Joseph H. and McClure, Michael D. Effect of Phase Change in Solid-Solid Reactions. AD 831 733. Department of the Army, Edgewood Arsenal Research Laboratories, Chemical Research Laboratory, Edgewood Arsenal, Maryland. Prepared by Department of Chemistry, Washington College, Chestertown, Maryland.

Doc. 27 Kholevo, N. A. New Data on the Sensitivity of Condensed Explosives to Mechanical Shock. AD 834 333. Picatinny Arsenal, Dover, New Jersey. May 1968.

Doc. 28 Bowden, F. P., et al. Growth of Burning to Detonation in Liquids and Solids. AD 667 216. Cambridge University, Cambridge, England. December 1967.

Doc. 29 Methodology for Assessing the Hazard of Electromagnetic Radiation to Ordnance: Final Report for the Contract Period 23 July 1965 through 23 October 1966. Research Report SU-238/6. Electromagnetic Hazards Division, U. S. Naval Weapons Laboratory, Dahlgren, Virginia. 23 November 1966.

Doc. 30 Clear, Arthur J. Standard Laboratory Procedures for Determining Sensitivity, Brisance, and Stability of Explosives. Technical Report 3278. Feltman Research Laboratories, Picatinny Arsenal, Dover, New Jersey. December 1965. (Revision of Technical Report FRL-TR-25 dated January 1961.)

Doc. 31 Cleaver, Harry E. Instrumentation of a Standard Dropweight Tester for Liquids. AD 649 510. U. S. Naval Ordnance Laboratory, White Oak, Maryland. 2 February 1967.

Doc. 32 Collection and Destruction Standards for Ammunition and Explosive Material.

Doc. 33 Mississippi Test Facility Safety Manual.

Doc. 34 Comparative Test of Propellants by Peak Side on Overpressure and Side on Impulse. Report HS-148. U. S. Army Missile Command. October 1967.

Doc. 35 Napodensky, H. S. Sensitivity of Solid Propellants to Impact. Technical Report AFRPL-TR-67-145. AD 816 625. Air Force Rocket Propulsion Laboratory, Edwards, California 93523. April 1967.

Doc. 36 Ammunition Series: Section 4, Design for Projection. AMCP 706-247. July 1964.

Doc. 37 Elwell, R. B., Irwin, O. R., and Vail, R. W., Jr. Project SOPHY - Solid Propellant Hazards Program. AD 819 299. Aerojet Corporation. August 1967.

Doc. 38 Engineering Design Handbook, Explosive Series, Explosive Trains. Headquarters, U. S. Army Material Command. AMCP 706-179. March 1965.

Doc. 39 Laing, Edward B. Design of Ammunition Maintenance Facility for Conventional and Advanced Weapons. Ammann and Whitney, Consulting Engineers, New York, New York. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 40 Goff, Charles R. Processing of Initiating Explosives. Day and Zimmermann, Inc., Lone Star Army Ammunition Plant, Texarkana, Texas. 1 November 1967.

Doc. 41 Kaplan, Kenneth. The Meaning of Simultaneity of Detonation with Respect to the Application of Quantity-Distance Regulations. URS Corporation, Burlingam, California. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 42 Rindner, R. M. Supporting Studies to Establish Safety Design Criteria for Storage and Processing of Explosive Materials. AD 828 638. Quarterly Report No. 21. Ammunition Engineering Directorate, Ammunition Production and Maintenance Engineering Division, Picatinny Arsenal, Dover, New Jersey. 1 October 1967 - 31 December 1967.

Doc. 43 Same as above-dated 1 October 1966 - 31 December 1966.

Doc. 44 Woolfolk, R. W. and Amster, A. B. Low Velocity Detonations. AD 827 748. Stanford Research Institute, Menlo Park, California. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 45 Buschman, E. H. Recent Developments in Flooring for Hazardous Areas. AD 827 756. Naval Ordnance Station, Indian Head, Maryland. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 46 Biron, J. E. Explosive Accident/Incident Information Report Systems Briefing. AD 827 742. Naval Weapons Laboratory, Dahlgren, Virginia. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 47 Liddiard, T. P., Jr. Low Amplitude Shock Initiation of Burning in High Explosives. AD 827 739. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland. 1 November 1967.

Doc. 48 Mason, Charles M., Van Dolak, Robert W., and Weiss, Milton L. Dropweight Testing of Explosive Liquids. 6799. United States Department of the Interior, Bureau of Mines. 1966.

Doc. 49 Singer, Irwing A. and Smith, Maynard E. Atmospheric Dispersion at Brookhaven National Laboratory. AD 414 401. Brookhaven National Laboratory, Upton, Long Island, New York. (Air and Water Pollution Int., J. Pergamon, President.) 1966.

Doc. 50 McCay, W. C. Safety in Pyrotechnic Manufacture. AD 827 758. Longhorn Army Ammunition Plant, Marshall, Texas. (Originally published in the Minutes of the Ninth Explosives Safety Seminar, Naval Training Center, San Diego, California, 15-17 August 1967, 1 November 1967 (AD 824 044).)

Doc. 51 Environmental Criteria for Pyrotechnic Storage and Handling. MIL-STD-5272C or MIL-STD-81D. AD 815 967.

Doc. 52 Glossary of Sensitivity Terms. AD 832 344. ICRPG Committee on Sensitivity of New Materials, Chemical Propulsion Information Agency. April 1968.

Doc. 53 Carrazza, James A., Jr. and Kaye, Seymour M. Compilation of Sensitivity Characteristics of Pyrotechnic Compositions. Picatinny Arsenal, Dover, New Jersey. February 1968.

Doc. 54 Augsthalns, Valdis A. and Blissel, John J. Characteristics of Polymers for Use in Pyrotechnic Fuels. AD 811 443. Edgewood Arsenal, Maryland 21010. March 1967.

Doc. 55 Engineering Actuated Handbook. AMCP 706-270. U. S. Army Material Command.

Doc. 56 Rindner, R. M. Supporting Studies to Establish Safety Design Criteria for Storage and Processing of Explosive Materials. Ammunition Engineering Directorate, Ammunition Production and Maintenance Engineering Division, Picatinny Arsenal, Dover, New Jersey. 1 July 1967 - 30 September 1967.

Doc. 57 Johnson, E. G. Propellant Hazard Research Facility. Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama. October 1967.

Doc. 58 Afanas, G. T., et al. Sensitivity of Explosives to Mechanical Effects and Methods of Increasing Their Stability. AD 630 026. The John Hopkins University, Silver Spring, Maryland. 20 May 1965.

Doc. 59 Bowden, F. P., et al. Growth of Burning to Detonation in Liquids and Solids. AD 647 392. University of Cambridge, Cambridge, England. December 1966.

Doc. 60 Rindner, Richard M. Response of Explosive to Fragment Impact. AD 644 461. Picatinny Arsenal, Dover, New Jersey. December 1966.

Doc. 61 Cohen, E. and Dobbs, N. Supporting Studies to Establish Safety Design Criteria for Storage and Processing of Explosive Materials. AD 617 614. Ammann and Whitney, New York, New York. (Contract Da-28-017-AMC-42 (A) for Picatinny Arsenal, Dover, New Jersey.) June 1965.

Doc. 62 Historical Summary - Safety Data Pertinent to Manufacture and Loading of Solid Propellant. AD 642 407. Thiokol Chemical Corporation, Longhorn Army Ammunition Plant, May 1964.

Doc. 63 Investigation of Hazards in the Processing of Pyrotechnic Mixtures for Chemical Agent Munitions. Final Technical Report, 1 July 1964 through 1 December 1964. AD 474 401. Edgewood Arsenal, Maryland. March 1965.

Doc. 64 Andreyer, K. K., et al. Theory of Explosive Substances. AD 643 597. Foreign Technology Division, Wright-Patterson Air Force Base, Ohio. 7 October 1966.

Doc. 65 Weals, F. H. and Wilson, C. H. High Explosive Equivalency Tests of Rocket Motors. U. S. Naval Ordnance Test Station, China Lake, California. November 1965.

Doc. 66 Kingery, C. N. and Pannill, B. F. Peak Overpressure versus Scaled Distance for TNT Surface Bursts (Hemispherical Charges). Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. April 1964.

Doc. 67 Price, Donna and Liddiard, T. P., Jr. The Small Scale Gap Test: Calibration and Comparison with the Large Scale Gap Test. AD 487 353. U. S. Naval Ordnance Laboratory, White Oak, Maryland. 7 July 1966.

Doc. 68 Project SOPHY - Solid Propellant Hazards Program. Downy Plant Research Division. September 1966.

Doc. 69 Goodman, H. J. Compiled Tree-Air Blast Data on Bare Spherical Pentolite. Report No. 1092. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. February 1960.

Doc. 70 Kingery, C. N. and Pannill, B. F. Parametric Analysis of the Regular Reflection of Air Blast. Ballistics Research Laboratories, Aberdeen Proving Grounds, Maryland. June 1964.

Doc. 71 Feroroff, Basil T. Encyclopedia of Explosives and Related Items, I, II, and III. AD 257 189. Picatinny Arsenal, Dover, New Jersey. 1960.

Doc. 72 Feroroff, Basil T., et al. Encyclopedia of Explosives and Related Items, II. AD 422 747. Picatinny Arsenal, Dover, New Jersey. 1962.

Doc. 73 Feroroff, Basil T. Encyclopedia of Explosives and Related Items, III. AD 653 029. Picatinny Arsenal, Dover, New Jersey. 1966.

Doc. 74 Wershkowitz, Joseph. The Action of an Explosive on Surrounding Non-Reacting Metal Dust. AD 150 486. Picatinny Arsenal.

Doc. 75 Determination of the Effect on Certain Structures of the Blast Wave from Five Ton Hemispherical Charges. AD 247 013. Suffield Experimental Station, Ralston, Alberta. 28 October 1960.

Doc. 76 Gross, Russell W. Engineering Evaluation Test of Cartridge, Photoflash, XM143. AD 246 074. Picatinny Arsenal, TPR TS-9.

Doc. 77 DOD Contractors' Safety Manual for Ammunition, Explosives, and Related Dangerous Material. Department of Defense, Office of the Assistant Secretary of Defense (Installations and Logistics). October 1968.

Doc. 78 Electromagnetic Hazards to Electroexplosives Subsystems. Technical Report AFAL-TR-66-354. Air Force Avionics Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. January 1967.

Doc. 80 Explosives Accident/Incident: Abstracts - July 1967 through 1968. AD 673 013. Armed Services Explosives Safety Board. July 1968.

Doc. 81 Eden, H. F., Bowden, M., Felsenthal, P., and Meyer, S. Pyrotechnic Materials: Their Resistivity, Charge Generation, and Sensitivity to Spark Discharge. Weapons Development Engineering Laboratories, Edgewood Arsenal, Maryland. July 1968.

Doc. 82 Medenica, Walter V. Blast Shields Testing. NASA, George C. Marshall Space Flight Center, Huntsville, Alabama. NASA TN D-4894.

Doc. 83 Nusbaum, M. S. Munitions Filling Development for New and Standard Agents. AD 479 253. Chemical Process Laboratory, Weapons Development and Engineering Laboratories, Edgewood Arsenal, Maryland 21010. March 1966.

Doc. 84 Nusbaum, M. S. Munitions Filling Development for New and Standard Agents. AD 817 999. Chemical Process Laboratory, Weapons Development and Engineering Laboratories, Edgewood Arsenal, Maryland 21010. June 1967.

Doc. 85 Nusbaum, M. S. Munitions Filling Development for New and Standard Agents. AD 831 240. Department of the Army, Edgewood Arsenal, Weapons Development and Engineering Laboratories, Chemical Process Laboratory, Edgewood Arsenal, Maryland 21010. April 1968.

Doc. 86 Kirby, Richard B. Quick-Mix Laboratory Mixing Techniques. AD 848 514. U. S. Naval Ammunition Depot, Crane, Indiana. 3 January 1969.

Doc. 87 McKinney, C. Dana, Parkhurst, Robert F., and Torpley, William B. Feasibility of Ultrasonic Deseration and Compaction of Pyrotechnic Powders. Report No. 66-77. AD 818 260. Chemical Process Laboratory, Weapons Development and Engineering Laboratories, Edgewood Arsenal, Maryland 21010. July 1967.

Doc. 88 System Safety Program for Systems and Associated Subsystems and Equipment: Requirements for: MIL-STD-882. Department of Defense. 15 July 1969.

Doc. 89 Nusbaum, M. S. Munitions Filling Development for New and Standard Agents. ITT Research Institute, 10 W. 35th Street, Chicago, Illinois 60616. Prepared for Chemical Process Laboratory, Edgewood Arsenal, Maryland, September 1966.

Doc. 90 Poppoff, I. G. Research Studies on the Dissemination of Solid and Liquid Agents. Edgewood Arsenal, Maryland. 7 October 1964.

Doc. 91 Ribovich, John, Watson, Richard W. and Gibson, Frank C. Instrumented Card Gap Test. AIAA Journal. **6**, 1260 (July 1968).

Doc. 92 Aluminum Powder, Flaked, Grained, and Atomized. MIL-A-512A. Department of Defense. 22 May 1961.

Doc. 93 Charcoal (For Use in Munitions). JAN-C-178A. Army Number 50-11-420. Navy Number 51C51A. 31 January 1945.

Doc. 94 Dye, Benzathrone. MIL-D-0050074C (MU). 9 May 1968.

Doc. 95 Chemical Corps Purchase Description Chemical Agent, TK-Dried and Ground. 196-131-776. 15 December 1961.

Doc. 96 Dye, Solvent Green 3 (For Green Smoke Mixtures). MIL-D-3277A. 23 August 1950.

Doc. 97 Dye, Vat Yellow 4. MIL-D-50029B. 18 July 1960.

Doc. 98 Hexachloroethane, Technical. MIL-H-235B. Military Specification. 13 March 1968.

Doc. 99 Magnesium Carbonate. MIL-M-11361B. 14 August 1953.

Doc. 100 Nitrocellulose. MIL-N-244A. 30 April 1964.

Doc. 101 Potassium Chlorate, Technical. MIL-P-150B. 19 July 1956.

Doc. 102 Federal Specification: Sugar, Refined and Brown, Beet or Cane. JJJ-S-791h. 25 April 1968.

Doc. 103 Sulfur, Ground (For Use in Ammunition). MIL-S-487B. 7 August 1947.

Doc. 104 Federal Specification: Acetone, Technical. O-A-51d. 23 April 1956.

Doc. 105 Canisters, Smoke, HC, 155MM Shell, M1 and M2. MIL-C-3120D(MU). March 1964.

Doc. 106 Explosive: Sampling, Inspection and Testing. MIL-STD-650. August 1962.

Doc. 107 TNT. MIL-T-248A. October 1963.

Doc. 108 Tetranitrocarbazole (TNC) (For Ordnance Use). MIL-T-13723A. October 1954.

Doc. 109 Explosive Composition HTA-3. MIL-E-46495A (MU). February 1961.

Doc. 110 Grenade, Rifle, Smoke, Colored, M22A2 Assembling, Marking, and Packing. MIL-G-20473A. December 1951.

Doc. 111 Grenade, Rifle, Smoke, M22A2: Chemical Loading Assembly. MIL-G-13590A. August 1954.

Doc. 112 Shell, Illuminating, M314 for 105 MM Howitzers, M2 and M4 Loading, Assembling, and Packing. MIL-S-20399A. April 1965.

Doc. 113 Grenade, Rifle, Smoke, M23A1: Chemical Loading Assembly. MIL-G-13598A. 24 August 1954.

Doc. 114 Static Acceptance Test for Light Output of Flash Munitions. MIL-STD-277. 6 June 1956.

Doc. 115 Pyrotechnics: Sampling, Inspection, and Testing. MIL-STD-1234. 30 March 1967.

Doc. 116 Cartridge, 105MM, Smoke (HC and Colored), BE, M84B1, and M84E1. MIL-C-20418A (MU). Assembling, Marking, and Packing. 4 December 1951.

Doc. 117 Canisters, Smoke, M3 and M4, for 155MM Shell. MIL-C-003297B(MU). 6 December 1955.

Doc. 118 Canisters, Smoke, HC and Colored, for 105 MM Shell, M1 and M2. MIL-C-003298D. March 1964.

Doc. 119 Grenade, Hand, Smoke, M18. MIL-G-12326F (MU). 30 June 1965.

Doc. 120 Schuman, William J., Jr. . The Response of Cylindrical Shells to External Blast Loading. Memorandum Report No. 1461. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. March 1963.

Doc. 121 Land Mines. TM 9-1345-200. Department of the Army. 8 June 1964.

Doc. 122 Berning, Warren W. Investigation of the Propagation of Blast Waves Over Relatively Large Distances and the Damaging Possibilities of Such Propagation. Report No. 675. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. 8 July 1948.

Doc. 123 Nagy, John, Cooper, Austin R. and Dorsett, Henry G., Jr. Explosibility of Miscellaneous Dusts. Report of Investigation 7208. United States Department of the Interior, Bureau of Mines. December 1968.

Doc. 124 Zabetakis, Michael G. Flammability Characteristics of Combustible Gases and Vapors. Bulletin 627. United States Department of the Interior, Bureau of Mines. 1965.

Doc. 125 Shear, R. E. and Day, B. D. Tables of the Thermodynamic and Shock Front Parameters for Air. Memorandum Report No. 1206. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. May 1959.

Doc. 126 Index of Technical Manuals, Technical Bulletins, Supply Manuals (Types 7, 8, and 9), Supply Bulletins, and Lubrication Orders PAM 310-4. Department of the Army. 21 October 1969.

Doc. 127 Large Solid Propellant Boosters Explosive Hazards Study Program, Project SOPHY. AD 468 775. May 1965.

Doc. 128 Walker, F. J. Liquid Oxygen Detonation Tests. Report No. 57AGT187. Component Development Unit, General Electric. 27 February 1957.

Doc. 129 Couch, Gerald. Hazard Classification Testing of Solid Propellants. United Technology Center, Sunnyvale, California.

Doc. 130 Military Publication. 310-4. Department of the Army. June 1969.

Doc. 131 Bertrand, Brian P. Measurements of the Speed of a Rarefaction Wave Behind a Normally Reflected Shock Wave. BRL MR 1634. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. January 1965.

Doc. 132 Ammonium Perchlorate: Sensitivity Increased/Decreased By Impartities. AD 6A2A07. Longhorn.

Doc. 133 Dunn, Dennis J., Schlueter, S. Donald, and King, Paul V. Ballistic Investigation of Frangible Protective Structures for Space Vehicles - Potential Application of Frangible Construction. U.S.A. Ballistic Research Laboratories. July 1967.

Doc. 134 Military Aspects of Radiological Defense. ST 3-156. U.S. Army Chemical Corps School, U.S. Army Chemical Corps Training Command. December 1961.

Doc. 135 CBR Defense and Material. -800. United States Army Chemical Corps School, Fort McClellan, Alabama. January 1963.

Doc. 136 CBR Training Guide. U.S. Army Chemical Corps School. April 1963.

Doc. 137 Employment of Chemical and Biological Agents. FM 3-10, NW1P36-2, AFM 355-4, FMFM11-3. Departments of the Army, the Navy, and the Air Force. March 1966.

Doc. 138 Field Behavior of Chemical, Biological, and Radiological Agents, TM-3-240, AFM 105-7. Departments of the Army and the Air Force. May 1963.

Doc. 139 Military Chemistry and Chemical Agents. Departments of the Army and the Air Force. December 1963.

Doc. 140 Cramer, H. E., Hamilton, H. L., Jr., and DeSanto, G. M. Atmospheric Transport of Rocket Motor Combustion By-Products. Prepared for Commander, Pacific Missile Hanger, Point Mugee, California. December 1965. (Volume I - Data Analysis and Prediction Technique; Volume II - Experimental Designs and Field Installation; and Volume III - Data Supplement.)

Doc. 141 Gurney, R. W. The Initial Velocities of Fragments from Bombs, Shells, and Grenades. REP 405. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. September 1943.

Doc. 142 Cowan, G. R. and Willis, F. M. Barricading Against Explosions. Eastern Laboratory, Explosives Department, E. T. du Pont De Nemour and Company, Inc., Gibbstown, New Jersey.

Doc. 143 Sterne, Theodore E. A Note on the Initial Velocities of Fragments from Warheads. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. September 1947.

Doc. 144 Investigation of Hazards in the Processing of Pyrotechnic Mixtures for Chemical Agent Munitions. U.S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Maryland. March 1965.

Doc. 145 Pyrotechnic Hazards Evaluation and Classification Program. Safety Management Plan. General Electric - MTSD. February 1969.

Doc. 146 Military Standard: Systems Safety Program for Systems and Associated Subsystems and Equipment: Requirements for MIL-STD-882.

Doc. 147 Safety Requirements for Manufacturing and Processing Military Pyrotechnics. AMCR 385 225. Headquarters, U.S. Army Material Command. July 1965.

Doc. 148 Baker, Wilfred E., Silverman, Sandor, and Dunham, Tom D. Study of Explosions in the NASA-MSC Vibration and Acoustic Test Facility (VATF). Prepared for NASA, Manned Spacecraft Center, Houston, Texas. March 1968.

Doc. 149 Silverman, Sandor, Baker, Wilfred E., and Young, Dana. Response of Blast Door on PV-2 Cell. Southwest Research Institute, San Antonio, Texas. Prepared for Union Carbide, Nuclear Division, Oak Ridge, Tennessee. August 1967.

Doc. 150 Ewing, W. O. and Hanna, J. W. A Cantilever for Measuring Air Blast. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. August 1967.

Doc. 151 Gayle, John B., Blakewood, Charles H., Bronsford, James W., Swindell, William H., and High, Richard W. Preliminary Investigation of Blast Hazards of RP-1/LOX and LH_2/LOX Propellant Combinations. NASA, George C. Marshall Space Flight Center, Huntsville, Alabama. April 1965.

Doc. 152 Perkins, Beauregard, Jr., Lorrain, Paul H., and Townsend, William H. Forecasting the Focus of Air Blasts Due to Meteorological Conditions in the Lower Atmosphere. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. October 1960.

Doc. 153 Liquid Propellant Explosive Hazards. Prepared for Air Force Rocket Propulsion Laboratory. December 1968. Project Pyro. URS Research Co.

Doc. 154 Ballistics Series: Interior Ballistics of Guns. AMCP 706-150. February 1965.

Doc. 155 Ammunition Series: Section 4, Design for Projection. AMCP 706-247. July 1964.

Doc. 156 Safety Requirements for Manufacturing and Processing Military Pyrotechnics. AMCP 706-177. July 1965.

Doc. 157 McGill, Russell. Explosives, Propellants, and Pyrotechnic Safety Covering Laboratory Pilot Plant and Production Operations. AD 272 424. U.S. Naval Ordnance Laboratory, White Oak, Maryland. October 1961.

Doc. 158 Watson, Richard W. Gauge for Determining Shock Pressures. Explosives Research Center, Bureau of Mines, U.S. Department of the Interior, Pittsburg, Pennsylvania. 20 January 1967.

Doc. 159 Armour, Carl. The Invention of a New Type of Friction Sensitivity Apparatus. AD 618 382. Research and Development Department, U.S. Naval Ammunition Depot, Crane, Indiana. 11 June 1965.

Doc. 160 Watkins, T. F., Cackett, J. C., and Hall, R. G. Chemical Warfare, Pyrotechnics and the Fireworks Industry. Pergamon Press Ltd. 1968.

Doc. 161 Jack, W. H., Jr., and Armendy, B. F., Jr. Measurements of Normally Reflected Shock Parameters from Explosive Charges Under Simulated High Altitude Conditions. AD 469 014. U.S. Army Material Command, Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. April 1965.

Doc. 162 Richey, C. M. Project Pyro: Dynamic Pressure Accuracy Evaluation. Air Force Rocket Propulsion Laboratory, AFSC, United States Air Force, Edwards, California.

Doc. 163 Cartridge, 4.2 Inch, Smoke, WP, M328A1, W/Fuze, PD, M521. Loading, Assembling, and Packing. MIL-C-46411B(MU). 31 May 1963.

Doc. 164 Cartridge, 4.2 Inch, Smoke, WP, M328A1, W/Fuze, PD, M521. Loading, Assembling, and Packing. MIL-C-46411B(MU).

Doc. 165 Canisters, CS Filled Components for. MIL-C-51307A(MU).

Doc. 166 Canisters, CS Filled Components for. MIL-C-51307A(MU). 19 April 1968.

Doc. 167 Chemical Agent CS. MIL-C-51029(cm1C). 30 June 1960.

Doc. 168 Research Test of Fragment Penetration of Building Panels, Ballistic Evaluation. Aberdeen Proving Grounds, Maryland. 8 March 1966.

Doc. 169 Method to Evaluate Propagation from Secondary Missiles. Mason and Hanger - Silas Mason Co., Inc., Amarillo, Texas. August 1964.

Doc. 170 Tell, George D. Blast Patterns in Large Model Tunnel Systems - Project 1.2 Operation Snow Ball. AD 471 823. U.S. Army Material Command, Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland.

Doc. 171 Willoughby, A. B., Wilton, C. Goodale, L., and Mansfield, J. Study of Liquid Propellant Blast Hazards. Technical Documentary Report No. AFRPL-TR-65-144. URS Corporation, Burlingame, California. June 1965.

Doc. 172 Proceedings for the National Academy of Science -- U.S. Coast Guard Advisory Committee on Hazardous Material. Conference on Barge Transformation of Chemicals. Charleston, West Virginia. 28-29 July 1965.

Doc. 173 Rice, Thomas K. and Cole, James B., Jr. Liquid Monopropellants - Progress Report No. 3, Burning Rate of Nitromethane. Navord 2885. U.S. Naval Ordnance Laboratory, White Oak, Maryland. 1 June 1953.

Doc. 174 Soroka, Bernard and Wenig, Jacob. An Electrometer Amplifier for Piezoelectric Gages. Uniterm 4089. Department of the Army Project No. 503-04-002. Ballistic Research Laboratory, Aberdeen Proving Grounds, Maryland. April 1962.

Doc. 175 Mason, C. M. and Cooper, J. C. Liquid Phase Combustion of Nitromethane Mixtures. Report No. S-4108. Safety Research Center, Bureau of Mines, Pittsburg, Pennsylvania. April 1, 1969 to September 30, 1969.

Doc. 176 Irwin, O. R. and Waddell, J. L. Study of Detonation Induction in Solid Propellants by Liquid Propellants Explosions. Final Report on Contract No. NAS8-11043. Aerojet-General Corporation, Research and Engineering Division, 11711 Woodruff Avenue, Downey, California. 8 April 1965.

Doc. 177 The Invention of a New Type of Friction Sensitivity Apparatus. AD 617 382. U.S. Naval Ammunition Depot, Crane, Indiana.

Doc. 178 Lewy, Hans. Asymptotic Integration of Fragment Trajectories. Ballistic Research Laboratories Report No. 559. Aberdeen Proving Grounds, Maryland. 13 July 1945.

Doc. 179 Kisselstein, Charles F. Explosion-Proof Enclosures Designs, Tests, and Maintenance. Product Engineering Manager, Crouse-Hinds Company. Syracuse, New York.

Doc. 180 Gurney, Ronald W. and Sarmousakis, James N. The Mass Distribution of Fragments from Bombs, Shells, and Grenades. Report No. 448. Aberdeen Proving Grounds, Maryland.

Doc. 181 Gurney, Ronald W. Fragmentation of Bombs, Shells, and Grenades. BRL Report No. 635. Aberdeen Proving Grounds, Maryland.

Doc. 182 Smith, R. and Wise, R. C. Charts of Maximum Horizontal Range for Fragments. Technical Note No. 496. Aberdeen Proving Grounds, Maryland.

Doc. 183 Bonner, Earl C. Velocities of Fragments Cut from Pressurized Tanks by Line Shaped Charges (U). Technical Note No. 1520. Aberdeen Proving Grounds, Maryland.

Doc. 184 Stubbs, Ian R. Blast and Impact Exposure of Existing Structural Fire Protection Schemes. AD 625 040. T.Y. Lin and Associates, Van Nuys, California. June 1965.

Doc. 185 Eberhard, Robert A. and Kingery, Charles N. A Coefficient of Reflection Over a Concrete Surface. BRL Report No. 860. Aberdeen Proving Grounds, Maryland.

Doc. 186 Dunn, Dennis F. and Schlueter, Donald S. Subsonic Fragment Range Tables. BRL Report No. 1851. Aberdeen Proving Grounds, Maryland. June 1967.

Doc. 187 Fuze, Point Detonating, M48A3, Loading, Assembling, and Packing. MIL-F-60349 (MU). November 1966.

Doc. 188 Fuse, Point Detonating, M521, Metal Parts for. MIL-F-60336 (MU). 3 May 1965.

Doc. 189 Fuze, Point Detonating, M48A3, Loading, Assembling, and Packing. MIL-F-60349 (MU). 15 September 1967.

Doc. 190 Burster, Projectile, M35, Parts for Loading, Assembling, and Packing. MIL-B-46415B (MU). 5 May 1966.

Doc. 191 Fuse, Point Detonating, M521, Loading, Assembling, and Packing. MIL-F-12641B (MU). 14 May 1965.

Doc. 192 Rosenfield, M. J. The Development of Damage Indexes to Structures Due to Liquid Propellant Explosions. Phase I Feasibility Study. Department of the Army, Ohio River Division Laboratories, Corps of Engineers, Cincinnati, Ohio. April 1966.

Doc. 193 Farber, E. A., Dr., Klement, F. W., Prof., and Bonzon, C. F. Prediction of Explosive Yield and Other Characteristics of Liquid Propellant Rocket Explosions. Contract No. NAS10-1255. Engineering and Industrial Experiment Station, College of Engineering, University of Florida, Gainesville, Florida. October 31, 1968.

Doc. 194 Farber, E. A., Dr. Feasibility Study to Explore the Explosive Effects of Liquid Propellants to Define the Mathematical Behavior of Physical Processes Involved. Contract No. NAS10-1255. Engineering and Industrial Experiments Station, Department of Mechanical Engineering, Gainesville, Florida. February 27, 1962.

Doc. 195 Statistical Analysis of Project Pyro Explosion Data. February 25, 1968.

Doc. 196 Standard Operating Procedure for the Conduct of Field Firing Programs as Revised. Ballistic Research Laboratories. February 15, 1955.

Doc. 198 The Study of Missiles Resulting from Accidental Explosions. Safety and Fire Protection Bulletin. March 1966.

Doc. 199 Gorst, A. G. Effects of an Explosion on Its Surroundings. Armed Services Technical Information Agency, Arlington Hall Station, Arlington 12, Virginia. December 1961.

Doc. 200 A Method to Evaluate Propagation from Secondary Missiles. Mason and Hanger, Amarillo, Texas. August 1964.

Doc. 201 Wilhold, G. A., Jones, J., and Guest, S. Environmental Hazards of Acoustics Energy. Aerospace Medical Research Laboratories (AMD), Wright-Patterson Air Force Base, Ohio.

Doc. 203 High Explosive Equivalents, Solid Propellant Motors, IRMGSG, Document 207-63. December 1963.

Doc. 204 Development and Qualification Program for the Electrostatically Insensitive X248 A6/A10 Igniter. AD 462 980. U.S. Naval Propellant Plant, Indian Head, Maryland. 19 February 1965.

Doc. 207 Guided Missile Propulsion Systems Hazards of Electromagnetic Radiation to Ordnance (HERO); RF Characteristics of Electro-Explosive Devices. Task NOL-443. AD 470 466. U.S. Naval Ordnance Laboratory. 1 July - 30 September 1964.

Doc. 208 Tetryl Trinitrophenylmethylnitramine. MIL-T-00339A (MU). 4 November 1965.

Doc. 209 Chemical Agent, Plasticized White Phosphorous (PWP). MIL-C-337B. 7 June 1962.

Doc. 210 Physics of Explosives and Propellants. TM 9-1300-214/TO 11A-1-34.

Doc. 211 Firing Record. Aberdeen Proving Grounds, Maryland. March 8, 1966.

Doc. 212 Rindner, R. M., and Schwartz, H. A. Establishment of Safety Design Criteria for Use in Engineering of Explosive Facilities and Operations. Report No. 5. Picatinny Arsenal, Dover, New Jersey. June 1965.

Doc. 213 Soldier's Handbook for Chemical and Biological Operations and Nuclear Warfare. Department of the Army. April 1963.

Doc. 214 Handbook of Ordnance Material. U.S. Army Ordnance School, Aberdeen Proving Grounds, Maryland. July 1962.

Doc. 216 Explosives Safety Regulations and Procedures. Pamphlet No. 20-85-2. Department of the Army.

Doc. 217 Signals, Illumination, Aircraft, Double-Star AN-M37A2 to AN-M42A2. MIL-S-1398A. Loading, Assembling, and Packing. 27 July 1956.

Doc. 218 Grenade, Hand, Irritant. MIL-G-10124 (Cml C). CD-DM, M6. 7 February 1950.

Doc. 219 Grenade, Hand, Riot Control. MIL-G-45401A (MU). CN-DM, M6A1. 15 July 1963.

Doc. 220 Grenade, Hand, Riot, MIL-G-60087B (MU). CS, M7A3. 3 March 1967.

Doc. 221 Grenade, Hand, Riot, MIL-G-46969 (MU). CS. ABC-M7A2. 17 April 1964.

Doc. 222 Amendment I. Grenade, Hand, Tear, CN or CS, MIL-G-11968B (MU). M7A1. 20 March 1967.

Doc. 223 Grenade, Hand, Tear, CN, M7. MIL-G-13961 (Cml C). 4 February 1955.

Doc. 224 Cartridge, 4.2 inch, CS Smoke, XM 630, Loading, Assembling, and Packing. MIL-C-60413. 16 November 1966.

Doc. 225 Military Explosives. OASMS Study Guide.

Doc. 226 Proposal to Perform an Investigation of Electrostatic Vulnerability of E-8 and XM-15/XM-165 Clusters. U.S. Army Chemical Process Laboratory. March 20, 1970.

Doc. 228 Tooele Army Depot. Basic Plan (U). Appendix B. (CBR Defense Plan) to Annex G to TAD-BP.

Doc. 229 Transportation Corps Reference Data. FM 55-15. Department of the Army. July 1960.

Doc. 230 Small Unit Procedures in Atomic, Biological, and Chemical Warfare. Department of the Army. FM 21-40. November 1958.

Doc. 231 Training Exercises and Integrated Training in Chemical, Biological and Nuclear Warfare. FM 21-48. Department of the Army. August 1960.

Doc. 232 Ammunition General. TM 9-1900 to 11A-1-20. Department of the Army and Air Force. June 1956.

Doc. 233 Prediction of Fallout and Radiological Monitoring and Survey. Department of the Army. 9 December 1958.

Doc. 234 Prediction of Fallout and Radiological Monitoring and Survey. Department of the Army. 14 June 1960.

Doc. 239 Fundamentals of Ballistics. Ordnance Subcourse Number 4, U.S. Army Ordnance School. 10 September 1959.

Doc. 243 Ordnance Installations and Activities in the Zone of Interior. U.S. Army. ST 9-175. Aberdeen Proving Grounds, Maryland. June 1959.

Doc. 244 Infantry Reference Data. U.S. Army Infantry School, Fort Benning, Georgia. March 1961.

Doc. 249 Defense Traffic Management Handbook. DSAH 4500.1, FM 38-9, MCO P 4600.13. Defense Supply Agency. March 1964.

Doc. 250 The Effects of Nuclear Weapons. No. 39-3. Department of the Army. April 1962.

Doc. 251 Radiological Laboratory Manual. U.S. Army Chemical Corps School, Fort McClellan, Alabama. 1963.

Doc. 252 Fallout Prediction. TM 3-210. Department of the Army. May 1962.

Doc. 253 Dorsett, H. G., Jr., Jacobson, M., Nagy, J. and William, P. Laboratory Equipment and Test Procedures for Evaluating Explosibility of Dust. RI Bureau of Mines 5624. U.S. Department of the Interior.

Doc. 254 Operational Aspects of Radiological Defense. FM 3-12. Department of the Army. January 1963.

Doc. 255 Nuclear Weapons Employment. No. 39-1. Department of the Army. May 1959.

Doc. 256 Fundamentals of Ballistics. U.S. Army Ordnance School, ST 9-153. Aberdeen Proving Grounds, Maryland. April 1959.

Doc. 258 Ordnance Ammunition Material. Subcourse No. 28, U.S. Army Ordnance School. 7 June 1960.

Doc. 259 Ordnance Service Fundamentals. Subcourse No. 20, U.S. Army Ordnance School. 5 April 1954.

Doc. 261 Dust Explosibility of Chemicals, Drugs, Dyes, and Pesticides. Bureau of Mines. RI 7132. May 1968.

Doc. 262 Hartmann, Irving. Recent Research on the Explosibility of Dust Dispersion.

Doc. 263 Pyrotechnics: Sampling, Inspection, and Testing. MIL-STD-1234. 18 December 1965.

Doc. 264 Pyrotechnics: Sampling, Inspection, and Testing. MIL-STD-1234. 22 June 1962.

Doc. 265 Datsko, Joseph. Material Properties and Manufacturing Processes. 671 D26. John Wiley and Sons, Inc., New York, 1966.

Doc. 266 Irani, Riyad R., and Callis, Clayton F. Particle Size: Measurement and Interpretation and Application. 541.345 IR1. John Wiley and Sons, Inc., New York. 1963.

Doc. 267 Penner, S. S. and Mullins, B. P. Explosions, Detonations, Flammability, and Ignition. 541.36 P38. Pergamon Press, New York. 1959.

Doc. 268 Williams, Forman A. Combustion Theory. 541.36 W6T. Addison-Wesley Publishing Co., Inc. 1965.

Doc. 269 Sutton, George P. Rocket Propulsion Elements. John Wiley and Sons. 1956

Doc. 270 Baker, Wilfred E. Plastic Response of Thin Spherical Shells to Axisymmetric Transient Loading. Technical Report No. 2, Project No. 02-1635 (IR). Southwest Research Institute. October 1965.

Doc. 271 Baker, Wilfred E. Recent Experimental and Analytical Studies of Safety of Nuclear Reactor Outer Containment Structures. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland.

Doc. 272 Baker, W. E. The Elastic-Plastic Response of Thin Spherical Shells to Internal Blast Loading. Paper No. 59-A-95.

Doc. 273 Elastic Response of Thin Spherical Shells to Exisymmetric Blast Loading. Paper No. 66-APM-EE.

Doc. 274 Hanna, J. W., Ewing, W. O., and Baker, W. E. The Elastic Response to Internal Blast Loading of Models of Outer Containment Structures for Nuclear Reactors. 9 March 1959.

Doc. 275 Adams, Channing L., Sarmousakis, James N., and Sperrazza, Joseph. Comparison of the Blast from Explosive Charges of Different Shapes. BRL Report No. 681. January 1949.

Doc. 276 Packaging and Handling of Dangerous Materials for Transportation By Military Aircraft. AFM 71-4. DSAM 4145.3, TM 38-250, NAVWEPS 15-03-500, MCO P403. 19. Departments of the Air Force, the Navy, the Army, and Defense Supply Agency. 15 November 1965.

Doc. 277 Soroka, Bernard, Wenig, Jacob. A Precision Charge Calibration Circuit for Piezo-Gage Recording. BRL Tech. Note 1229. November 1958.

Doc. 278 Transmittal of Explosives Accident Reports. Armed Services Explosives Safety Board. 1 August 1969.

Doc. 279 NASA USAF Liquid Propellant Blast Hazards Program. Project Pyro Quarterly Progress Report for Period Ending 30 September 1967.

Doc. 280 Gayla, J. B. and Bransfor, J. W. Size and Duration of Fireballs from Propellant Explosions. NASA TM X-53314. 4 August 1965.

Doc. 281 Canister Cluster Assembly, Chemical Agent: XM165 and Canister Cluster, Chemical Agent: XM15. DTM 3-1325-231-12. Edgewood Arsenal, Maryland. May 1969.

Doc. 282 Durge, G. W. System Effects on Propellant Storability and Vehicle Performance. Technical Report No. AFRPL-TR-66-17.

Doc. 283 Solid Rocket/Propellant Processing, Handling, Storage, and Transportation. Volume II. Jannaf Propulsion Committee. May 1970.

Doc. 284 Liquid Propellant Handling, Storage and Transportation. Volume III. Jannaf Propulsion Committee. May 1970.

Doc. 285 Seiden, Lester, Cucchiara, Orlando, and Goodman, Phillip. Development of a Hazardous Vapor Detection System for Advanced Aircraft. Technical Report AFAPL-TR-67-123. October 1967.

Doc. 286 A Guide for the Design of Shock Isolation Systems for Underground Protection Structures. Technical Documentary Report No. AFSWC-TDR-62-64. December 1962.

Doc. 287 Operation Distant Plain Preliminary Report. Volume III. DASA 1876-3. Dasiac Special Report 53-3. January 1968.

Doc. 288 A Study of Transportation of Hazardous Materials. National Academy of Science, National Research Council, Washington, D.C. May 7-9, 1969.

Doc. 289 The New Generation Small Caliber Ammunition Production Equipment Concept. Volume I. Frankford Arsenal, Philadelphia, Pennsylvania. 15 April 1969.

Doc. 290 Farber, Erich A. Characteristics of Liquid Rocket Propellant Explosion Phenomena. Technical Paper No. 396. November 1967.

Doc. 291 Operation Distant Plain Symposium. Volume I(U). DASA 1947-1. DASA Information and Analysis Center, General Electric, TEMPO. September 1967.

Doc. 292 Goodman, Henry J. Directional Effect of Charge Motion on Shock Formation at a Spherical Pentolite Charge. BRL Report No. 1206. June 1963.

Doc. 293 Hazards Tests and Studies, MTF. P. V. King, Mgr., Safety, MTSD. General Electric. September 1967.

Doc. 294 Ammunition and Special Weapons. General Specification for. MIL-A-2550A. 29 September 1961.

Doc. 295 Ammunition and Special Weapons. General Sepcification for. MIL-A-2550A. 27 February 1969.

Doc. 296 Dinsdale, V. T. Proposed Program for Development of Theory and Laboratory Techniques for Determining Detonation Properties of Propellants Using Subcritical Diameter Laboratory Samples. TWR 803, EDR 64-39. Thiokol Chemical Corporation.

Doc. 297 Malick, Donald. The Calibration of Wallboard for the Determination of Particle Speed. BRL Tech. Report No. 61. May 1966.

Doc. 298 Heppner, L. D. Fragmentation Test Design, Collection, Reduction and Analysis of Data. APG Miscellaneous Report 306. September 1959.

Doc. 299 System Safety. AFSC Design Handbook. DH 1-6 Series 1-0.

Doc. 300 Safety: Safety Criteria for Processing, Handling, and Decontamination of Agent CS. AMCR 385-104. U.S. Army Material Command. December 1968.

Doc. 301 Calculator, Downwind Toxic Vapor Hazard, Point Source, ABC-M2. TB CML 83. Department of the Army. 11 February 1963.

Doc. 302 Characteristics of Riot Control Agent CS. EASP 600-1. Department of the Army. October 1967.

Doc. 303 Riot Control Agent CS Decontamination. Professional Standards Division, International Association of Chiefs of Police.

Doc. 304 Grenades and Pyrotechnics. FM 23-30. Department of the Army. October 1959.

Doc. 305 Pyrotechnic Hazards Classification and Evaluation Program. Phase I, Final Report, Contract NAS8-23524. May 1970.

Doc. 306 Military Specification Discharges, Aircraft, Electrostatic General Specification for. MIL-D-9129B. 8 November 1967.

Doc. 307 Cormack, C. M. Recent Progress on the Development of Insensitive EEDs. Naval Air Systems Command. Washington, D.C. AD 824 044.

Doc. 308 Burger, Joseph P. and Rost, D. L. Preliminary Report of the Initiation of Various Types of Electroexplosives by Induced Lighting. AD 827 746.

Doc. 309 Eulitz, E. W. and Jones, R. H. Lightning Detection Warning Systems on Saturn Launch Complexes 34, 37, and 39. TR-107-1. December 18, 1964.

Doc. 310 Faschler, Anthony F. and Kaye, Seymour, M. Electrostatic Sensitivity of 95/5 HMX/Titanium, 95/5 RDX/Titanium, 95/5 PETN/Titanium, and Colloidal Leak Azide. AD No. 249 984. FRL-TN-9. January 1961.

Doc. 311 Cohen, Edward E., and Dobbs, Norval. Cost Effectiveness Studies of Facilities for High Hazard Explosive Material. Ammann and Whitney, Consulting Engineers, New York.

Doc. 312 BRL Technical Notes. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland.

Doc. 313 BRL Publications. Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. 1956-1960.

Doc. 314 Savitt, Jacob. New Explosives Evaluation Technique. ANL-TFR-64-18. Centhoe Explosiform, Inc., Park Forest, Illinois. (Confidential.)

Doc. 315 Bowden, F. P. and Yoffe, A. D. Fast Reactions in Solids. Butterworths Scientific Publications, London, England. 1958.

Doc. 316 Donaldson, Paul A., and Wirieth, Alvin D. Safety Tests of Explosives Transport Trucks. NWC TP 4738. Naval Center, China Lake, California. July 1969.

Doc. 317 Pitt, D. A. Synthesis and Formulation of Explosives. AFAL-TR-67-85. Mining (Minnesota) and Manufacturing. (Confidential.)

Doc. 318 Cap, Blasting, Electric, M6 Assembly and Packing. MIL-C-45468A(MU) Amendment 5. Military Specification. December 1967.

Doc. 319 Datsko, Joseph. Material Properties and Manufacturing Processes. John Wiley and Sons, Inc. 1966.

Doc. 320 Pyrotechnic Mix Formulary and End Item Information. Weapons Development and Engineering Laboratories, Chemical Process Laboratory, Edgewood Arsenal, Maryland. December 1969.

Doc. 321 Rolph, P. J. The Explosive Effects of Pyrotechnic Compositions: The Sympathetic Initiation of Compositions SR 580 and SR 812. Ministry of Defense Royal Armament Research and Development Establishment, Trials, and Instrumentation Division, RARDE. Memorandum 55/69. December 1969.

Doc. 322 Rolph, P. J. The Explosive Effects of Pyrotechnic Compositions: Measurements of Air Blast, Flame Zone and Fragmentation Effects for Certain Compositions. Ministry of Defense Royal Armament Research and Development Establishment, Trials and Instrumentation Division, RARDE. Memorandum 55/69. December 1969.

Doc. 323 Cohen, Edward, Consulting Editor. Prevention of and Protection Against Accidental Explosion of Munitions, Fuels, and Other Hazardous Mixtures. Annals of the New York Academy of Sciences. 152, 1-913.

Doc. 324 Jackson, Willis F. Air Blast from the Static Detonation of the M55 Rocket. Terminal Ballistics Laboratory, Ballistic Research Laboratories, Aberdeen Proving Grounds, Maryland. October 1970.

Doc. 325 Lewis, Bernard, and von Elbe, Guenther. Combustion, Flames and Explosions of Gases. Second Edition. Academic Press, Inc., New York and London. 1961.

Doc. 326 Evans, Marjorie W., and Ablow, C. M. Theories of Detonation. Stanford Research Institute, Menlo Park, California. 16 May 1960.

Doc. 327 Dunn, Robert G., and Wolfson, Bernard T. Single Generalized Chart of Detonation Parameters for Gaseous Mixtures. Journal of Chemical and Engineering Data. 4, 124 (April 1959).

Doc. 328 Stoner, Richard G., and Bleakney, Walker. The Attenuation of Spherical Shock Waves in Air. Journal of Applied Physics. 19, 670 (July 1948).

Doc. 329 Thomas, L. H. Note on Becker's Theory of the Shock Front. The Journal of Chemical Physics. 12, 449 (November 1944).

Doc. 330 Edwards, D. H., Williams, G. T., and Breeze, J. C. Pressure and Velocity Measurements on Detonation Waves in Hydrogen-Oxygen Mixtures. Journal of Fluid Mechanics. 6, 497

Doc. 331 Cowan, George R., and Hornig, Donald F. The Experimental Determination of the Thickness of a Shock Front in a Gas. The Journal of Chemical Physics. 18, 1008 (August 1950).

Doc. 332 Hartmann, Irving, and Nagy, John. Vending Dust Explosions. Industrial and Engineering Chemistry. 49, 1734 (October 1957).

Doc. 333 Parlin, Ransom B., and Giddings, J. Calvin. Application of Probability Theory to Explosive-Ignition Phenomena. The Journal of Chemical Physics. 25, 1161 (December 1956).

Doc. 334 Hartmann, Irving. Recent Findings on Dust Explosions. Chemical Engineering Progress. 53, 107-M (March 1957).

Doc. 335 Kerker, Milton, Cox, Lucile A., and Shoenberg, Melvin D. Maximum Particle Sizes in Polydispersed Aerosols. Journal of Colloid Science. 10, 413 (1955).

Doc. 336 Hartmann, Irving. Recent Research on the Explosibility of Dust Dispersions. Industrial Engineering Chemistry. 40, 752 (1948).

Doc. 337 Zemansky, Mark W. Heat and Thermodynamics. Fourth Edition. McGraw-Hill Book Company, Inc., New York, New York. 1957.

Doc. 338 Roark, Raymond J. Formulas for Stress and Strain. Fourth Edition. McGraw-Hill Book Company, Inc., New York, New York. 1965.

Doc. 339 Smith, D., and Richardson, R. H. Interpretation of Impact Sensitivity Test Data. Contract No. SP-64110(FBM). Allengany. Ballistics Laboratory. Presented at the Combustion Institute-Western States Section Meeting, Santa Barbara, California, 25-26 October 1965.

APPENDIX B

SAFETY ANALYSIS - METHODOLOGY AND CONCEPTS

B. 1 RESULTS OF OPERATIONAL SURVEY

It has been concluded from Operational Survey, based on the degree of hazards associated with pyrotechnic materials, the findings from the Operational Survey, the plant tour, and the system analysis efforts, that the primary hazard areas, as listed according to order of importance, are:

- Pressing and consolidation of pyrotechnic mixtures in the grenade and canister body.
- Reaming of the filled-and-pressed grenade or canister to remove excess pyrotechnic mix.
- Blending and mixing of pyrotechnic smokes and starter mixes.
- Filling/screening operation of grenade and canisters.

Results of the Phase II, Segment 2 Operational Survey based on Pine Bluff Arsenal accident reports for the period from January 1, 1968, to December 31, 1969, are given in Table B-1, Accident/Incident Analysis. As noted in the table, pressing has the largest failure rate (40 percent), followed by reaming (27 percent), then filling (13 percent), and finally blending/mixing (10 percent).

Table B-1. Accident/Incident Analysis

	Station					
Process	Blending/ Mixing	Filling	Pressing	Reaming	Miscellaneous	Total
M18 Grenades	-	-	2	-	-	2
155mm Canisters	1	-	9	11	-	21
Other Canisters	-	-	5	2	1	8
XM675 Cartridges	-	-	-	-	1	1
XM176 Launchers	-	-	-	-	1	1
M126 Bomblets	2	6	4	-	1	13
Starter Mix	2	-	-	-	-	2
Total	5	6	20	13	4	48
	(10%)	(13%)	(40%)	(27%)	(10%)	(100%)

Tables B-2 through B-5 present the System Safety Engineering Quantitative Hazard Analysis. This systematic approach was taken to identify all possible failure modes and actual test requirements for four critical processes:

- Pressing
- Reaming
- Blending/Mixing
- Filling

The technique of analysis used to compile the Quantitative Hazard Analysis Matrix was based in particular on the description of the "corrective actions" given in the Pine Bluff Accident Report. Examining the accident description of the report revealed that in most of the accidents the ignition source was concealed or not in direct view of the operator. This leads to the conclusion that the inherent shortcoming of any type of systems safety analysis is that the "corrective actions" (ultimately the failure modes) are a judgement of what the operator or safety engineer on the scene of the accident believes to have caused an accident.

Finally, for many of the individual accidents, two corrective actions were employed to prevent recurrence of an accident. For example, the corrective action after a small fire on the green smoke press line was to check the press and die for proper alignment and reinstruct employees to clean the die/mold thoroughly. Consequently, for this accident there were two possible modes of failure: Misalignment, and improper procedure during cleaning (resulting in mix still remaining in die). Accidents with possible multiple corrective actions were seldom correlatable. Consequently, for ease of interpretation, they were classified as having unknown failure modes.

Therefore, the failure modes were assigned based on the corrective actions listed in the accident report, and the validity of these results is limited by the accuracy of the accident reports. In addition, for the sake of completeness, all future possible failure modes are given in the matrix.

Referring to the Quantitative Hazard Analysis Matrix, the number of accidents per failure mode is given merely to assign a value of the relative importance of a particular failure mode.

B. 2 CONCLUSIONS

Tables B-2 through B-5 present a fairly comprehensive program for identifying process conditions under which ignition can occur. In order to cover the results of these findings and indicate their relevancy to specific process ignition mechanisms, a fault tree analysis (Figures B-1 through B-4) is presented for each of the processes which have been identified as a critical area.

Working across from left to right, a net is constructed of all events which contribute to the hazardous condition. The OR - gate represents a situation where one or more events will result in the occurrence of the resultant condition. The AND - gate represents a situation in which the occurrence of all input events must take place simultaneously before the output event will occur.

Table B-2. System Safety Engineering Quantitative Hazard Analysis Matrix for Pressing

(Based on total of 20 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Die, Ram and Mix	Molding of pyrotechnic mix under controlled pressure conditions in metal containers	1. Misalignment	Jamming of ram in die	Friction: generation of excessive heat concentration by excessive pressure	4 6	Fire Explosion	Check ram and die tolerances and replace steel ram tip with brass ram tip
		2. Impact	Jamming of ram in die	Friction: generation of excessive heat concentration by excessive pressure	None	Possible explosion due to heat buildup as a result of excessive heat and pressure	Check hydraulic pressures in system
		3. Contamination	Misalignment - in addition, mix not of uniform density	Possibly sensitize mixture and result in lowering of the threshold ignition energy	Unknown	Possible explosion due to heat buildup as a result of excessive heat and pressure Possible substandard performance of pyrotechnic device	Check compliance with procedures
		4. Improper procedure, excessive mix	Misalignment	Friction: generation of excessive heat concentration by excessive pressure	6 0	Fire Explosion	Have personnel ensure that dies have been thoroughly cleaned and inspect for excessive mix

Table B-2. System Safety Engineering Quantitative Hazard Analysis Matrix for Pressing (cont'd)

(Based on total of 20 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Die, Ram and Mix (cont'd)		**5. Ungrounded die and ram.**	**Shorting between ground leads**	**Charge buildup between die and ram and eventually charge transfer**	1	**Fire**	**Check grounds**
					0	**Explosion**	
		6. Unknown			1	**Fire**	**Stop operation**
					1	**Explosion**	
Press Room	**Self-explanatory**	**1. Dust/vapor atmosphere of room**	**Toxic atmosphere and poor visibility**	**Highly susceptible to ignitio by electrostatic discharge**		**Possible explosion**	**Improve circulatio and efficiencies at exhaust vents**
		2. Improper heat dissipation from lighting fixtures and surrounding machinery	**Operator error**	**Ignition by hig temperature**		**Possible fire/ explosion**	**Thermal insulation**
Press and Press Stand	**Pressure cylinder which raises and lower ram, and stand which supports cylinder assembly**	**1. Vibration**	**Misalignment**	**Friction: heat generated by excessive pressure**		**Possible fire/ explosion due to heat buildup**	**Vibration dampening**
		2. Excessive pressure	**Exceeded limit of travel of ram causing jamming**	**Friction**	1	**Fire**	**Installed press stops**
					1	**Explosion**	

Table B-2. System Safety Engineering Quantitative Hazard Analysis Matrix for Pressing (cont'd)

(Based on total of 20 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Press and Press Stand (cont'd)		**3. Ungrounded press**	**Shorting between ground leads**	**Charge buildup and transfer**		**Possible fire/ explosion**	**Check grounds**

Table B-3. System Safety Engineering Quantitative Hazard Analysis Matrix for Mixing/Blending

(Based on total of 5 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Hopper, Mix Beater	Mixing of pyro mix slurry under controlled mixing speed in metal container	1. Misalignment	Impact	Friction: generation of excessive heat concentration by excessive pressure	1	Fire	Reinstructed personnel on locking and checking alignment on beaters
		2. Granulation, caked lumps of mix caused friction heating	Misalignment	Friction: generation of excessive heat concentration by excessive pressure	1	Fire	Reinstructed personnel to let acetone and reamed mix to set until softened
		3. Improper procedure - abrading mix or heaters with cleaning paddle	Contamination	Possibly sensitize mixture and result in lowering of threshold ignition energy	1	Fire	Reinstructed personnel on cleaning procedure
		4. Impact (hopper dropped on floor)	Damage to hopper which if unnoticed could result in misalignment	Friction: generation of excessive heat concentration by excessive pressure	1	Fire	Reinstructed personnel on loading procedure
		5. Excessive mix	Spills	Sensitize mixture and result in lowering of threshold ignition energy		Possible fire/ explosion	Reinstructed personnel on loading procedure

Table B-3. System Safety Engineering Quantitative Hazard Analysis Matrix for Mixing/Blending (cont'd)

(Based on total of 5 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Hopper, Mix Beater (cont'd)		6. Contamination	Misalignment	**Sensitize mixture and result in lowering of threshold ignition energy**		**Possible fire/ explosion**	**Reinstructed personnel on loading procedure**
		7. Charge buildup on beater, hopper	**Shorting** between poorly grounded ground leads	**Electrostatic discharge, resulting in possible fire/ explosion**	1	**Fire**	**Check grounding leads**
Mixer	**Motor drive for beaters and accompanying support stand**	**1. Excessive mixing speed**	**Spills**	**Kneading of mix slurry between beater and hopper**		**Possible fire/ explosion**	**Reinstructed personnel on operating procedure**
Mixing Room	**Self-explanatory**	**1. Dust/vapor atmosphere of room**	**Toxic atmosphere and poor visibility**	**Highly susceptible to ignition by spark initiation**		**Possible explosion**	**Impress circulation and efficiency of exhaust vents**
		2. Improper heat dissipation from lighting fixtures and surfaces surrounding machinery	**Operator error**	**Ignition by high temperature**		**Possible fire/ explosion**	**Thermal insulation**

Table B-4. System Safety Engineering Quantitative Hazard Analysis Matrix for Reaming

(Based on total of 13 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Reamer Mix, Canister	**Mix in canister faced or flattened by bevel**	**1. Improper procedure (placed canister in backwards)**	**Damaged bevel**	**Heat generated by bevel abrading metal canister and mix**	**2**	**Fire**	**Safety instruction on procedures**
		2. Misalignment of reamer chuck	**Jamming of bevel in canister**	**Heat generated by bevel abrading metal canister and mix**	**9**	**Fire**	**Check chuck for misalignment**
		3. Contamination by foreign body - burrs	**Misalignment**	**Heat generated by bevel abrading metal canister and mix**	**2**	**Fire**	**Require 100 percent inspection for conformity**
		4. Impact (canister dropped on floor)	**Damage to canister which could possibly result in misalignment**	**Ignition by high pressure**	**None**		**Safety instruction on procedures**
		5. Charge buildup on bevel canister	**Shorting between grounding leads**	**Electrostatic discharge, resulting in possible fire/explosion**		**Possible fire/explosion**	**Check grounding leads**

Table B-5. System Safety Engineering Quantitative Hazard Analysis Matrix for Filling
(Based on total of 9 accidents during the period January 1, 1968 - December 31, 1969)

COMPONENT LOCATION	FUNCTIONAL DESCRIPTION	FAILURE MODE	SECONDARY FAILURES	FAILURE EFFECT	NUMBER OF ACCIDENTS	CRITICAL EFFECT	CORRECTIVE ACTIONS
Filling	Operator dips stainless steel scoops into pyro mix bucket and fills mold using copper funnel	1. Ungrounded mold, funnel, dipper, and bucket	Arcing between ground leads	Discharge between aluminum bucket and steel scoop in majority of cases	5	Fire	New dipper and new ground wires wire installed on bucket
		2. Abrading mix with scoops and walls of container	Sensitize mixture which could possibly lower threshold ignition energy	Friction causing heat generation	1	Possible fire/ explosion	Replaced stainless steel dipper with brass dipper
		3. Spills: operators walking on mix	Electrostatic ignition	Friction causing heat generation	None	Possible fire/ explosion	Have water constantly running on floor of cubicle to wash away mix

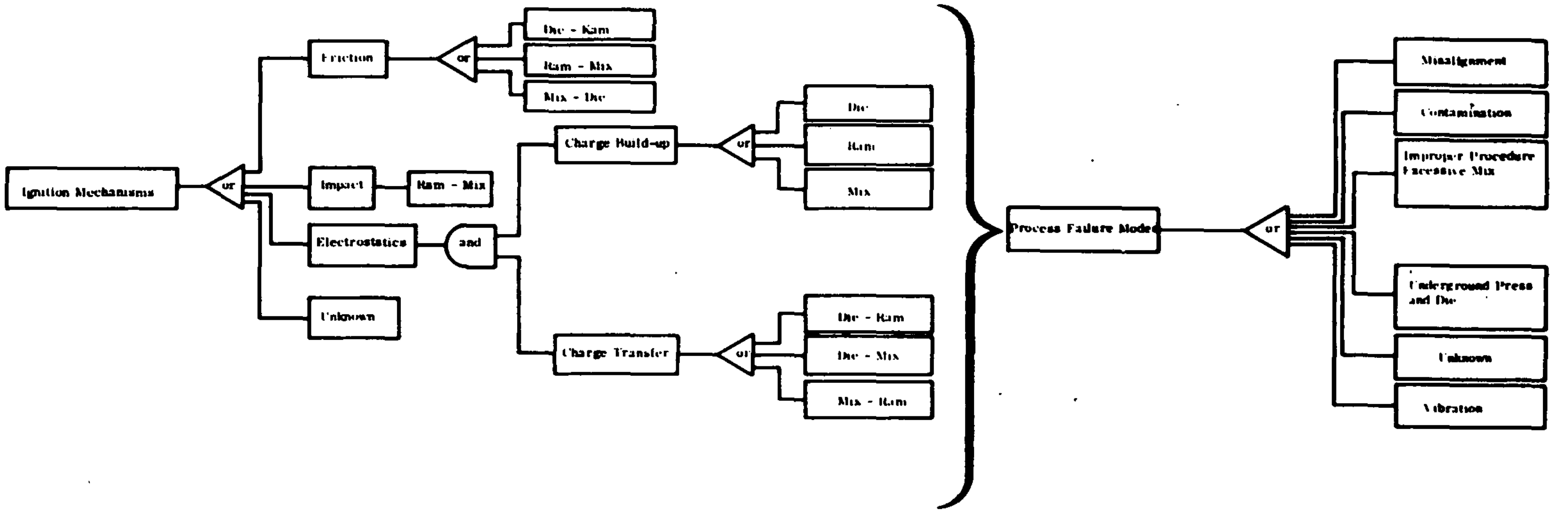


Figure B-1. Fault Tree Analysis of Pressing Operation

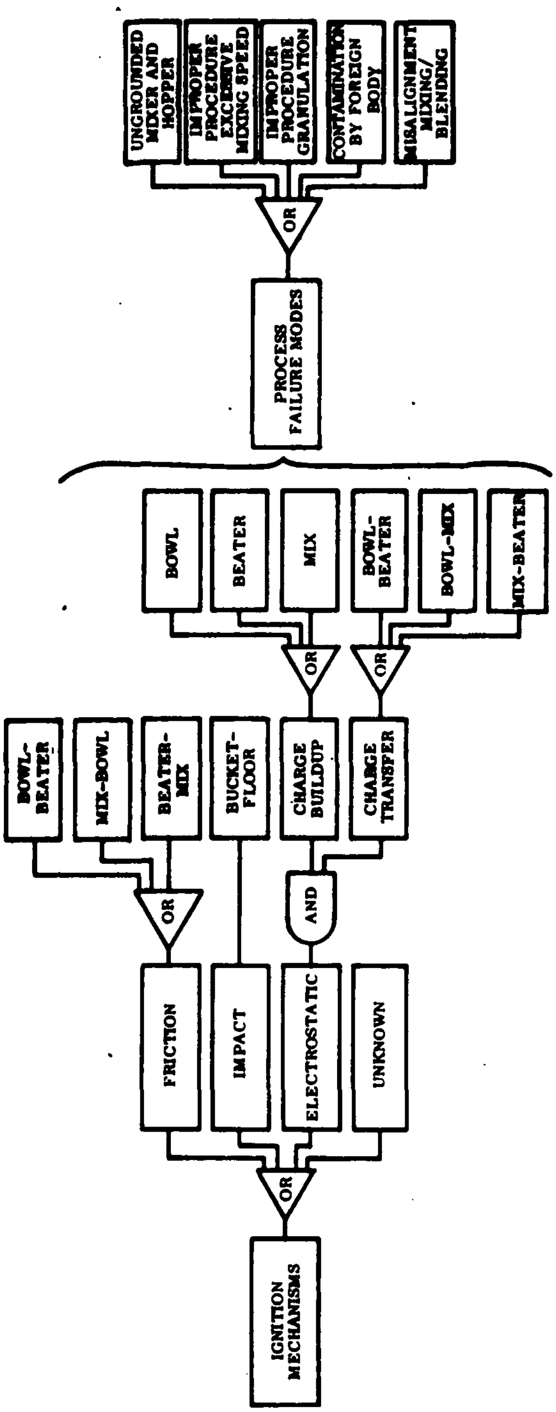


Figure B-2. Fault Tree Analysis of Blending/Mixing Operation

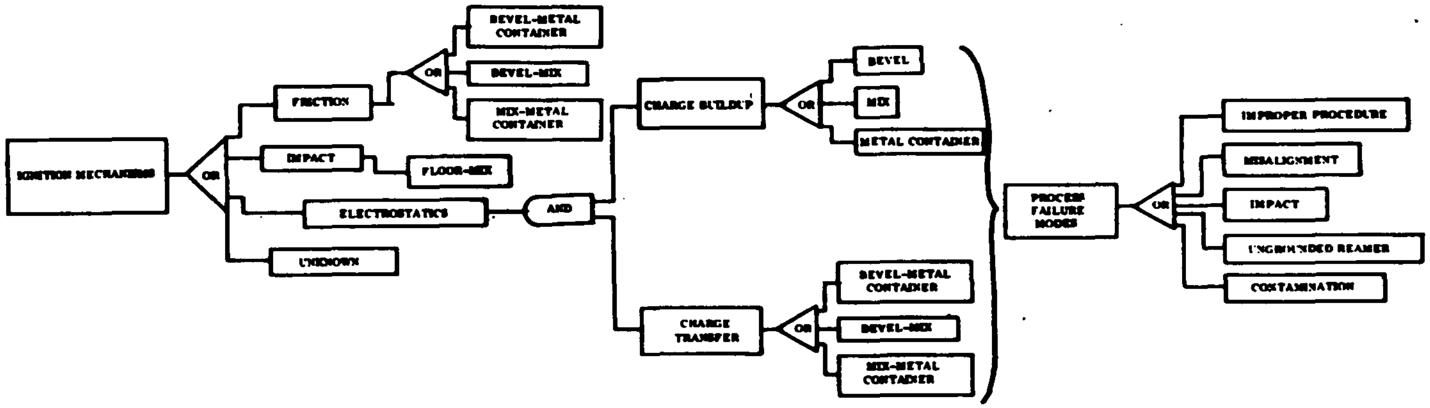


Figure B-3. Fault Tree Analysis of Reaming Operation

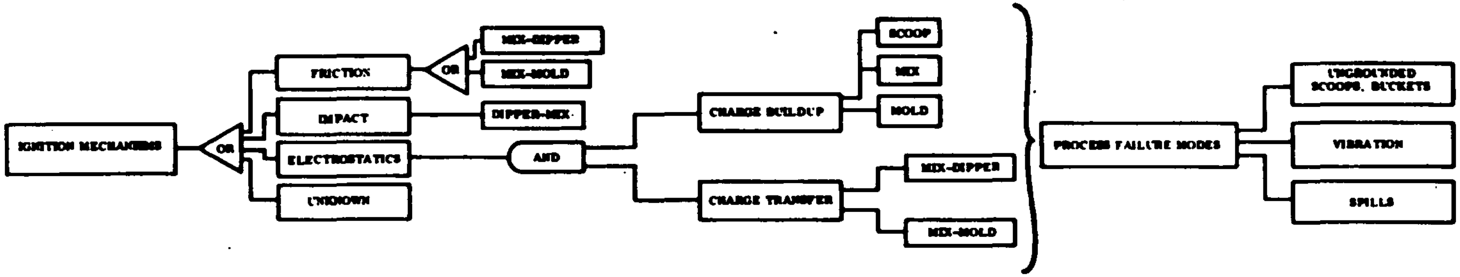


Figure B-4. Fault Tree Analysis of Filling Operation

Characteristic of all the fault trees presented here is that before an incident (fire/explosion) can occur, a procedural or functional failure (i. e., vibration, misalignment, contamination, etc.) must produce an ignition of pyrotechnic material by excessive heat generation (friction, impact and electrostatic).

The following paragraphs are intended only to relay significant observations by operating sequence and not to correlate the observations to the building or material being processed.

B. 2. 1 PRESSING OPERATION

The pressing operation's dependency on the automatic sequences of pallet positioning, pressing, and extracting presents the major hazard potential in this area. The hazards associated with the pressing operations and the application of forces of magnitudes between and 20 and 100 tons should be examined further. Lesser press weights were evidenced on other component operations, but the hazards were not appreciably reduced as evidenced by the Edgewood Safety Reports.

Observations of the pressing sequence and the occurrence of a press malfunction during the plant survey indicate many areas for future hazard evaluation and testing activities. These include but are not limited to:

- Friction
- Impact
- Pinching (Local Pressure)
- Electrostatics

B. 2. 2 BLENDING AND MIXING

Foreign objects represent contaminants which can be a source of ignition for impact/friction type accidents. For example, lack of lock washers or safety wires on the nuts and bolts over the mixing bowl while the mixer is operating presents a potentially hazardous situation. The nuts may work themselves loose, falling in the blending and mixing area, the impact igniting the mix. The possibility exists for friction and the impact between mixer paddles and some of these contaminants. The accumulation of raw materials and blended materials on various pieces of equipment such as mixing paddles was also observed as a potential hazard.

Another potentially hazardous condition exists in the process of reblending of mixes which do not meet the specification burn time requirements. The reblending by addition of various amounts of materials to adjust the burn time constitutes a potential hazard through additional exposure to operating stimuli and contaminants.

B. 2. 3 REAMING

Reaming is accomplished after the operations of fill and press, second fill and press, and, in some cases, an overfill and press. At this station, each canister, grenade, or other end item is reamed to remove excess mix. This process assures consistent dimensions in the end item.

Observations of two separate reaming operations revealed a relatively hazardous condition. A manual operation exhibited what appeared to be approximately a one-out-of-five reject rate because of reamer jamming and misalignment. These occurrences resulted in container damage evidenced by dented surfaces, split-fractures and overreaming.

The rate and nature of these malfunctions suggest further investigation in the areas of friction, impact, and electrostatics.

B. 2.4 FILLING OPERATION

The manual operation of measuring the proper quantity into the prepared palletized container constitutes no great hazard; however, the associated spillage of material caused by rapid motions and proximity of the pressing operation does increase the electrostatics and dust hazard to a level which should be examined in detail.

APPENDIX C

NORMAL STARTER MIX TEST RESULTS

C.1 STARTER MIX II, DRAWING NUMBER B-143-7-5

C.1.1 CHEMICAL COMPOSITION

Starter Mix II had the following chemical composition:

Potassium nitrate	35.0 percent by weight
Charcoal	4.0 percent by weight
Corn starch	26.0 percent by weight
Iron oxide black	22.0 percent by weight
Aluminum, II, C, 4	13.0 percent by weight

C.1.2 TEST RESULTS

Starter Mix II was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - no explosion, average burning time 10 seconds
  - Multiple cube test - no explosion, burn time 12.6 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
  - 3 3/4-inch drop test - no reaction, 10 trials
  - 10-inch drop test - no reaction, 10 trials
- Card gap test - no detonation

C.1.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 2 rating for Starter Mix II, Drawing Number B-143-7-5.

C.2 STARTER MIX III, DRAWING NUMBER B-143-7-6

C.2.1 CHEMICAL COMPOSITION

Starter Mix III had the following chemical composition:

Potassium nitrate	70.5 percent by weight
Charcoal	29.5 percent by weight

C.2.2 TEST RESULTS

Starter Mix III was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - no explosion, average burning time 22.6 seconds
  - Multiple cube test - no explosion, burn time 38.6 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
  - 3 3/4-inch drop test - no reaction, 10 trials
  - 10-inch drop test - no reaction, 10 trials
- Card gap test - no detonation

C.2.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 2 rating for Starter Mix III, Drawing Number B-143-7-6.

C.3 STARTER MIX V, DRAWING NUMBER B-143-7-9

C.3.1 CHEMICAL COMPOSITION

Starter Mix V had the following chemical composition:

Potassium nitrate	54.0 percent by weight
Charcoal	6.0 percent by weight
Corn starch	40.0 percent by weight
Nitrocellulose/acetone 4/96	30/70 percent by weight

C.3.2 TEST RESULTS

Starter Mix V was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - deflagration, average burning time 3.45 seconds
  - Multiple cube test - no explosion, burn time 4.8 seconds
- Thermal stability test - no explosion, ignition, or change in configuration; sample lost 19.5 grams weight
- Impact sensitivity test
  - 3 3/4-inch drop test - no reaction, 10 trials
  - 10-inch drop test - no reaction, 10 trials
- Card gap test - no detonation

C.3.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 2 rating for Starter Mix V, Drawing Number B-143-7-9.

C.4 STARTER MIX VI, DRAWING NUMBER B-143-7-3

C.4.1 CHEMICAL COMPOSITION

Starter Mix VI had the following chemical composition:

● Potassium chlorate	43.2 percent by weight
● Sulfur	16.8 percent by weight
● Sodium bicarbonate	30.0 percent by weight
● Corn starch	10.0 percent by weight
● Nitrocellulose/acetone 4/96	40/60 percent by weight

C.4.2 TEST RESULTS

Starter Mix VI was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - no explosion, average burning time 17 seconds

  - Multiple cube test - no explosion, burn time 20.1 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
  - 3 3/4-inch drop test - explosion, 6 trials; no reaction, 4 trials
  - 10-inch drop test - explosion, 9 trials; no reaction, 1 trial
- Card gap test - no detonation

C.4.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 7 rating for Starter Mix VI, Drawing Number B-143-7-3.

C.5 STARTER MIX XII, DRAWING NUMBER B-143-7-1

C.5.1 CHEMICAL COMPOSITION

Starter Mix XII had the following chemical composition:

• Potassium nitrate	70.5 percent by weight
• Charcoal	29.5 percent by weight
• Nitrocellulose/acetone 4/96	50/50 percent by weight

C.5.2 TEST RESULTS

Starter Mix XII was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - deflagration (some particles left pan and were scattered unburned), average burning time 0.8 seconds
  - Multiple cube test - deflagration (same as single cube test), burn time 1.6 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
  - 3 3/4-inch drop test - no reaction, 10 trials
  - 10-inch drop test - explosion, 2 trials; decomposition, 5 trials; no reaction, 3 trials
- Card gap test - no detonation

C.5.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 7 rating for Starter Mix XII, Drawing Number B-143-7-1.

C.6 STARTER MIX XXV, DRAWING NUMBER B-143-7-4

C.6.1 CHEMICAL COMPOSITION

Starter Mix XXV had the following chemical composition:

• Potassium nitrate	35.0 percent by weight
• Charcoal	4.0 percent by weight
• Silicone	26.0 percent by weight
• Iron oxide black	22.0 percent by weight
• Aluminum, II, C, 4	13.0 percent by weight
• Nitrocellulose/acetone 4/96	16.7/83.3 percent by weight

C.6.2 TEST RESULTS

Starter Mix XXV was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
  - Single cube test - no explosion, average burning time 5.0 seconds
  - Multiple cube test - no explosion, burn time 5.8 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
  - 3 3/4-inch drop test - no reaction, 10 trials
  - 10-inch drop test - no reaction, 10 trials
- Card gap test - no detonation

C.6.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 2 rating for Starter Mix XXV, Drawing Number B-143-7-4.

C.7 FIRST FIRE VII, DRAWING NUMBER B-143-9-1

C.7.1 CHEMICAL COMPOSITION

First Fire VII had the following chemical composition:

• Silicone	25.0 percent by weight
• Titanium	25.0 percent by weight
• Iron oxide red	25.0 percent by weight
• Red lead	25.0 percent by weight
• Nitrocellulose/acetone 4.50/36.75	9/32 percent by weight

C.7.2 TEST RESULTS

First Aire VII was tested in accordance with TB 700-2, Chapter 3, "Minimum Test Criteria for Bulk Explosive Compositions and Solid Propellant Compositions," with the following results:

- Detonation test - no explosion, burning, or fragmentation
- Ignition and unconfined burning test
    - Single cube test - no explosion, average burning time 5.75 seconds
    - Multiple cube test - no explosion, burn time 7.0 seconds
- Thermal stability test - no explosion, ignition, or change in configuration
- Impact sensitivity test
    - 3 3/4-inch drop test - no reaction, 10 trials
    - 10-inch drop test - no reaction, 10 trials
- Card gap test - no detonation

C.7.3 CLASSIFICATION

Test results, per TB 700-2, paragraph 3-13, indicate a probable military Class 2 rating for First Fire VII, Drawing Number B-143-9-1.

APPENDIX D

MIXER SIMULATION TESTS AND RESULTS

D.1 RATIONALE

As discussed in the Systems Safety Analysis of the Phase II, Segment 3 report (GE-MTSD-R-054), the mixing operation involving the 175-quart, 125-pound batch vertical planetary mixers currently being used to prepare colored smoke formulations has been identified as a primary hazard area (Figure D-1). The safety analysis further pointed out that failure modes such as misalignment, impact, or inadequate grounding of the mixer blades and/or mixer bowl are likely to cause ignition by frictional of electrical spark within the bulk of the pyrotechnic materials. When ignition is induced below the surface, the material above supplies a significant pressure head which allows a transient pressure buildup caused by the temporary confinement of reaction by-products.

Previous testing, as reported in the Phase I final report (GE-MTSD-R-035), demonstrated that the pressure-time curve of a confined pyrotechnic closely resembles that of a detonating explosive. Thus, a potentially hazardous situation exists during the mixing operation because of the possibility of simultaneous ignition and confinement in a localized region near the bottom of the 125-quart mixing bowl.

Self confinement simulation tests of large bulk pyrotechnics were designed to provide data to evaluate a potentially hazardous situation. In line with the concept of "worst case" testing, the location and type of ignition source in all cases were chosen to maximize the likelihood of inducing a detonation (according to guidelines established by previous experimental results) while maintaining a credible simulation of an actual mixing operation involving the 175-quart mixing bowls containing 125-pounds of pyrotechnic smoke composition.

D.2 TECHNICAL APPROACH

D.2.1 OBJECTIVES

The objectives of this test program were to determine the following criteria:

- Bulk mix and mixing bowl influence on the reaction rate.
- Extent of the pressure buildup.
- Probability of communication to loose powder inadvertently scattered in the vicinity of the mixing operation.
- Scaling laws to predict the outcome of an actual incident involving the 175-quart mixers.

To accomplish these objectives, two self-confinement simulation test series were performed. The vessels used to contain the pyrotechnic material were:

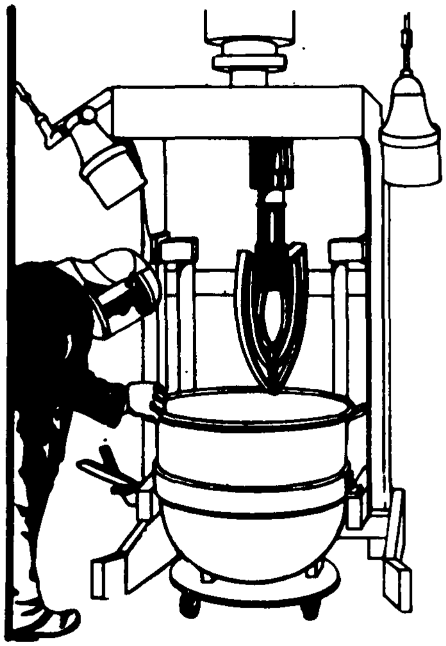


Figure D-1. Typical Mixing Operation

- 6-inch stainless steel pipe.
- 80-quart stainless steel mixing bowl.

D.2.2 MIXER EQUIPMENT SCALING

Testing was based on simulating fully loaded, 175-quart capacity stainless steel mixing bowls containing 125-pounds of pyrotechnic smoke composition (Figure D-2). The height of the composition when 125-pounds were placed into the 175-quart bowl was 16 inches. The bowl was 26 inches in diameter and 24 inches high. The bowl was made of grade 304 stainless steel, 12 gage thickness.

D.2.3 SELF CONFINEMENT SIMULATION USING 6-INCH STAINLESS STEEL PIPE

D.2.3.1 Setup

Pyrotechnic mixes can simultaneously be ignited and confined in a localized region near the bottom of the mixer bowl. The mix and vessel influence on the reaction rate is through boundary effects, thereby enabling a transitory high pressure buildup.

It is assumed that ignition takes place at the bottom of the mixing bowl in an arbitrarily small localized region representing 10 percent of the total bowl area. Therefore, approximately 12.5 pounds of a 125-pound batch (representing a solid cylinder 16 inches high and 7 inches in a diameter) effectively confines the ignition area through boundary effects and enables pressure buildup.

As closely as possible to the dimensions given in the preceding paragraph, a six-inch diameter, 12-gage stainless steel pipe (with a cover plate of the same type of material welded across the bottom) was filled with sulfur yellow smoke composition to a height of 16 inches (See Figures D-3 and D-4). Two types of igniters, hot wire and engineer's special blasting cap, were placed in the bottom of the vessel. To determine the effects of a void on reaction rate, a paper cone was placed over the J-2 blasting cap during one test.

Two pounds of granular sulfur yellow composition were placed within three feet of the vessels to determine the probability of communication to composition inadvertently scattered in the vicinity of the mixer (See Figure D-5).

Additionally, the two-pound tray was covered in several tests to determine if this would affect the probability of communication.

D.2.3.2 Instrumentation

The instrumentation package consisted of the following (Figure D-6):

- Blast overpressure package - 2 locations
- 24 fps documentation - Mitchell cameras
- Thermocouples - 3 locations

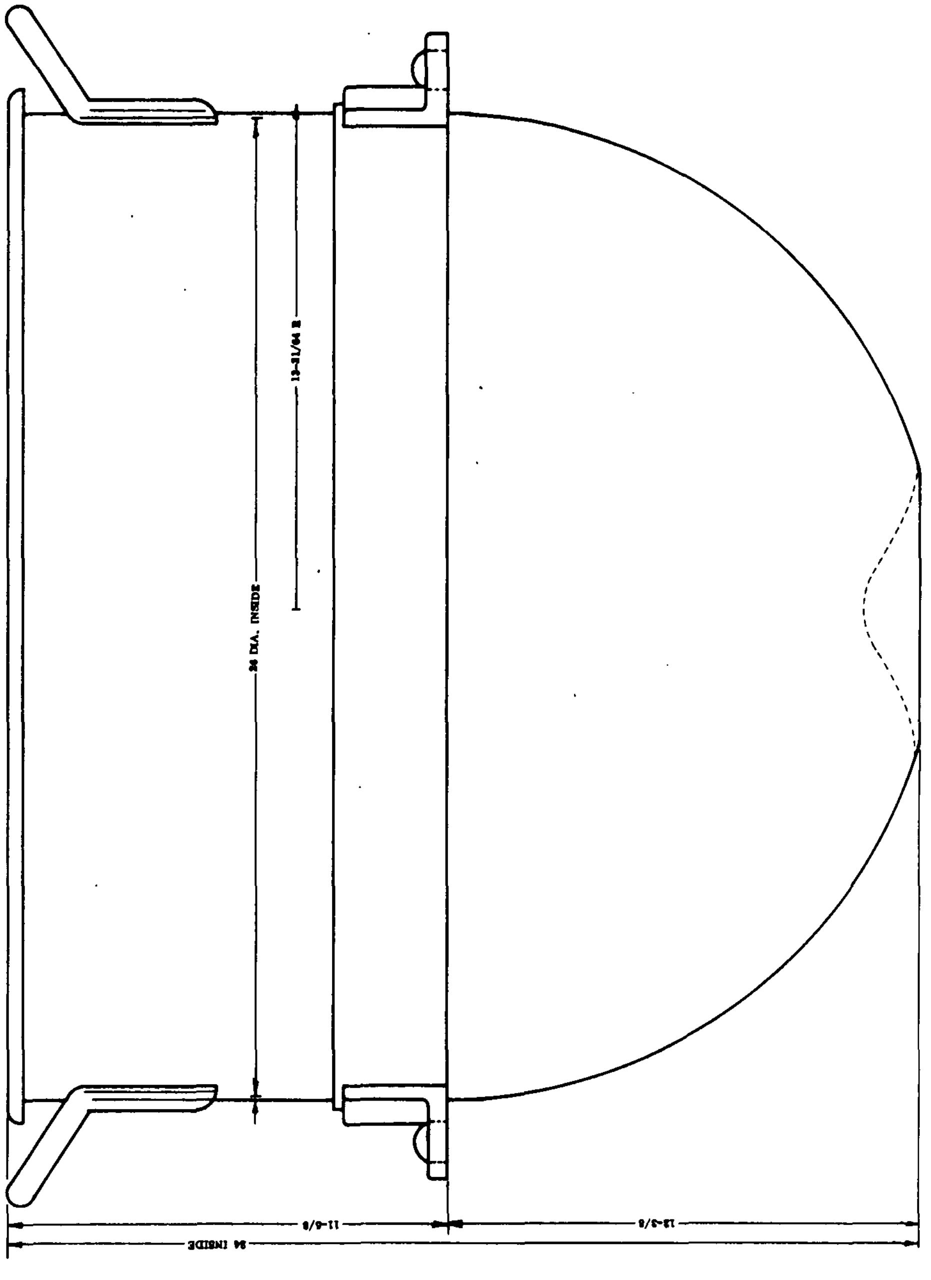


Figure D-2. 175-Qt. Capacity Stainless Steel Mixing Bowl

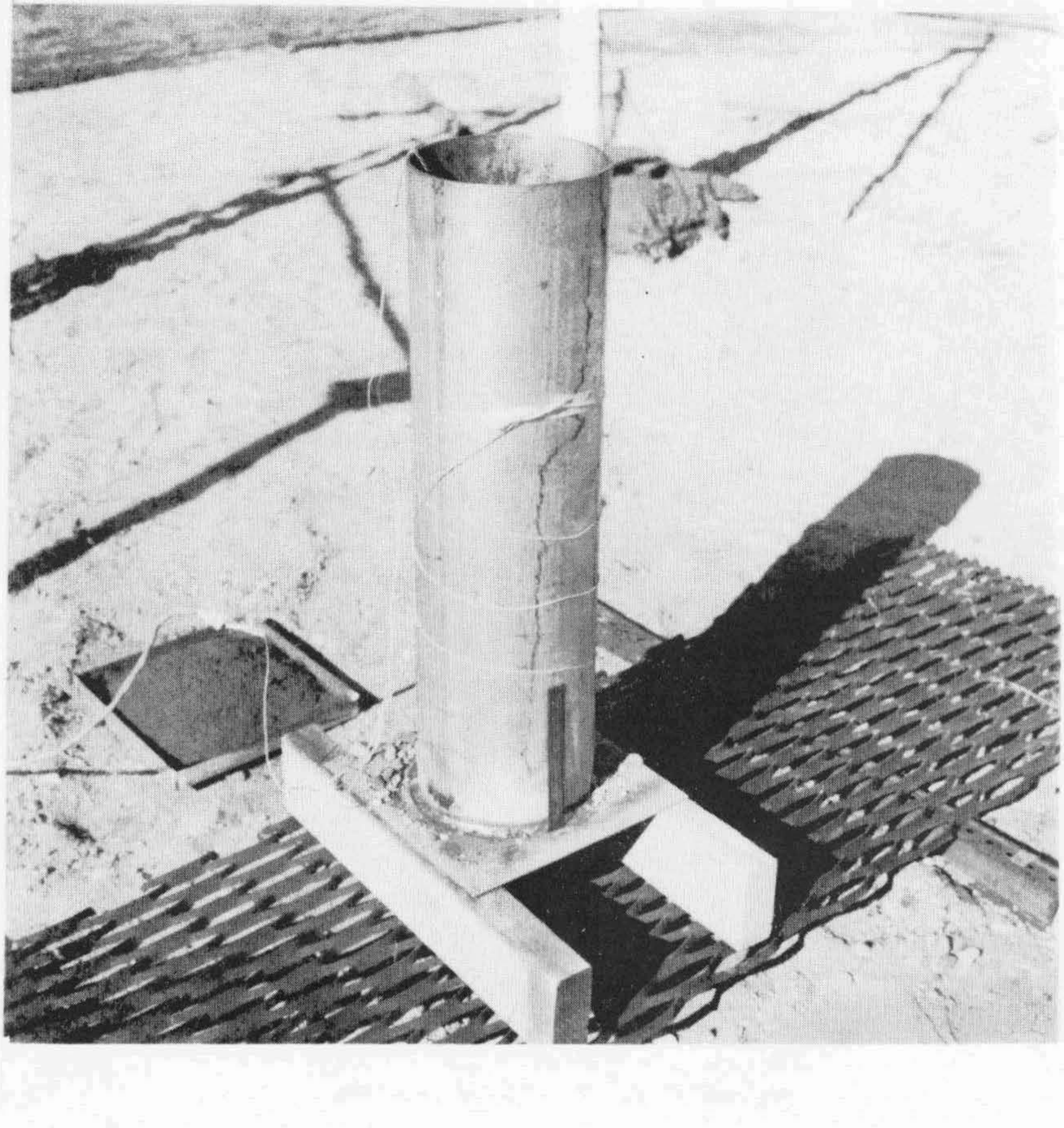
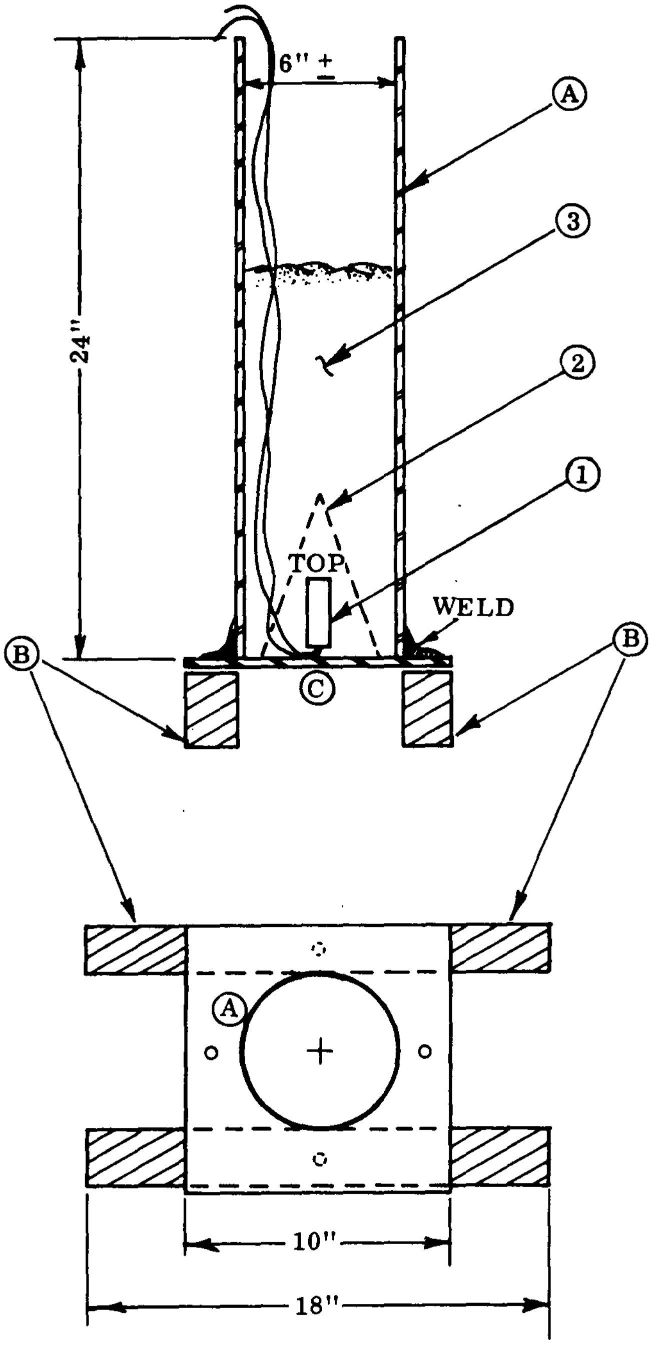


Figure D-3. Six-Inch Diameter 12 Gage Pipe



MATERIALS:

Ⓐ 304 S/S, .1094" ± .02" - PIPE
Ⓑ PINE - 2" x 4"
Ⓒ PLATE, 304 S/S, .125" THK.

① HOT WIRE OR J-2 WITH INSULATED LEADS
② 7" PAPER CONE
③ 12-1/2 LBS. OF SMOKE MIX

TEST VESSEL-MIXING OPERATION

Figure D-4. Six-Inch Test Vessel for Mixing Simulation

NOT REPRODUCIBLE

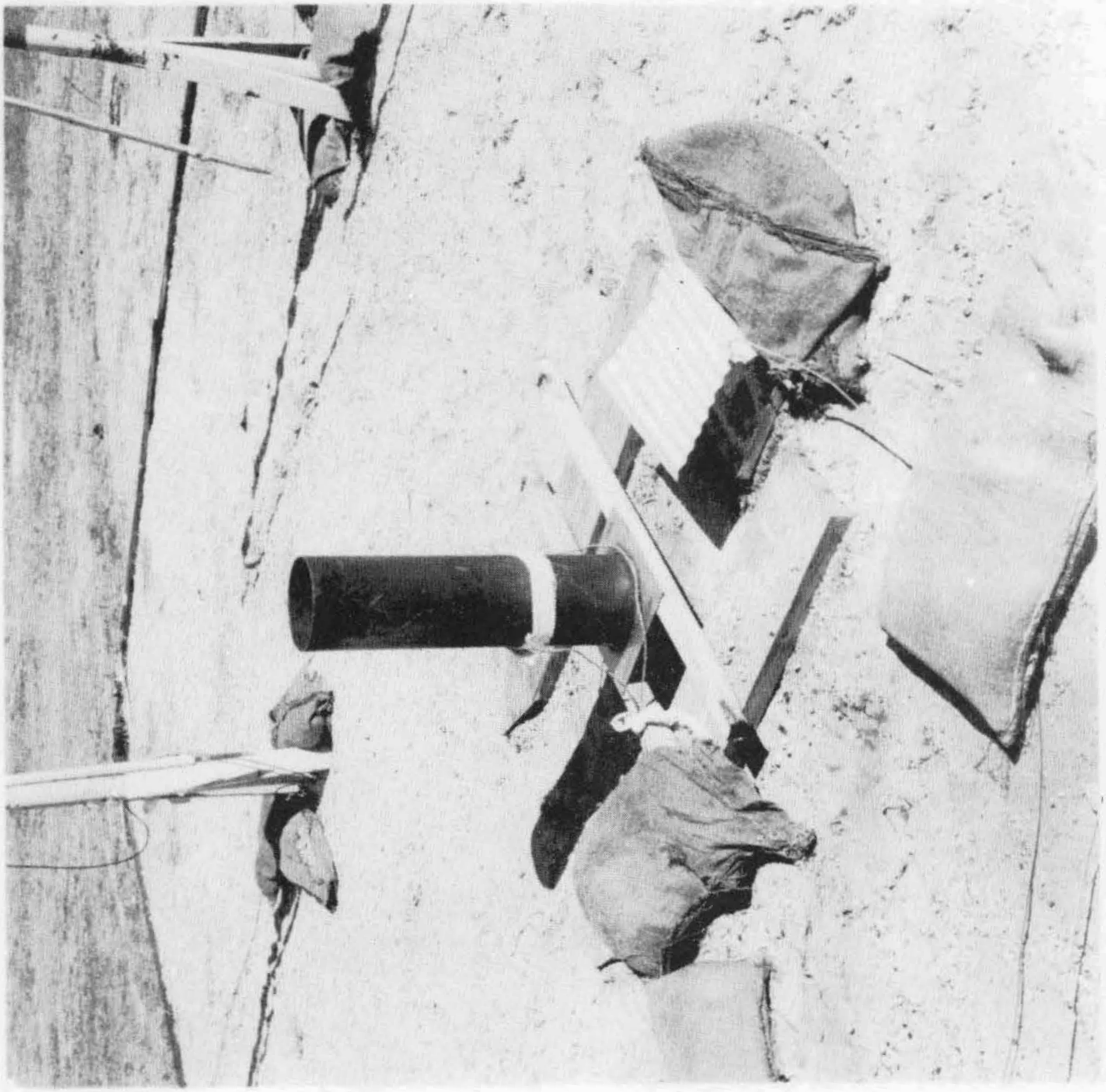
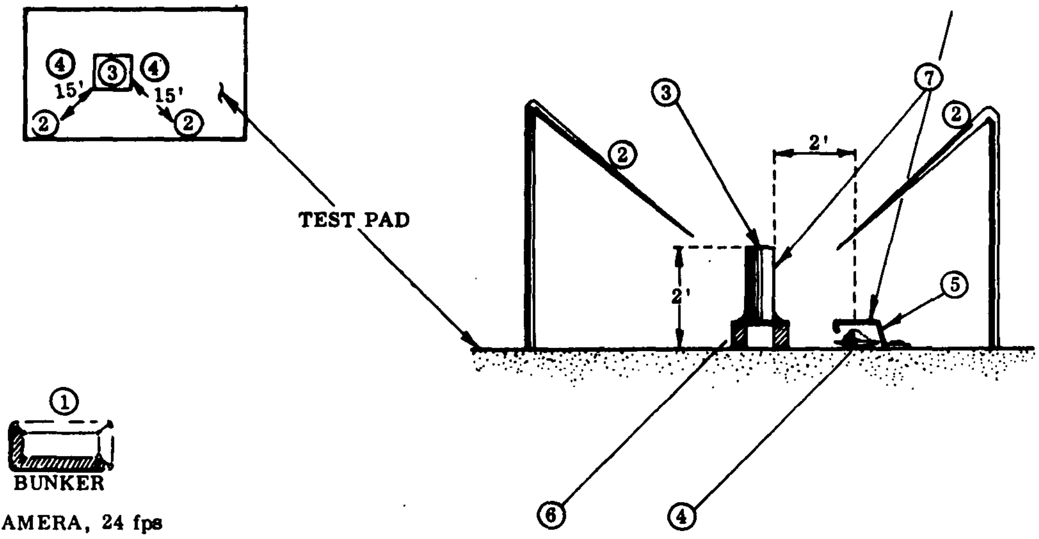


Figure D-5. Test Setup for Six-Inch Pipe Tests



① MITCHELL CAMERA, 24 fps
② TRANSDUCER
③ TEST VESSEL
④ 2 LBS. OF SMOKE MIX WITH METAL TRAY
⑤ PROTECTIVE COVER, METAL
⑥ 2" x 4" PINE
⑦ THERMOCOUPLE, 2 EA.

Figure D-6. Instrumentation Setup for Six-Inch Pipe Tests

D.2.4 SELF CONFINEMENT SIMULATION USING 80-QUART STAINLESS STEEL MIXING BOWL - QUASI FULL SCALE

D.2.4.1 Setup

An 80-quart stainless steel mixing bowl containing 46 pounds of smoke composition was used to determine runup and sympathetic potential of an accident involving a 175-quart vertical mixer (Figure D-7). By using a large scale mixing bowl, the actual severity of reaction can be determined for this particular type of vessel and pyrotechnic composition.

A two-pound loose pile of sulfur yellow smoke powder was placed three feet from the mixing bowl in order to simulate mix inadvertently scattered in the vicinity of the mixer. Additionally, the two-pound trays were covered in several tests to determine if this would effect the probability of communication. A J-2 blasting cap for ignition placed in the bottom of the vessel. This test was repeated to verify the initial data acquired.

D.2.4.2 Instrumentation

The instrumentation package consisted of the following (Figure D-8):

- Blast overpressure package
- 24 fps documentation - Mitchell Cameras
- Thermocouples - three locations

D.3 TEST RESULTS

D.3.1 TEST 1

D.3.1.1 Setup

For test 1, twelve pounds of sulfur green were placed in a six-inch ID, stainless steel pipe. An S-94 squib, placed in the bottom of the pipe, was used for ignition.

D.3.1.2 Chronology of Events

Test 1 occurred as follows:

		TIME
a.	Ignition	0 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around the test vessel containing the burning composition	10 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	35 seconds
d.	Flame extinguished and intense dark smoke.	60 seconds

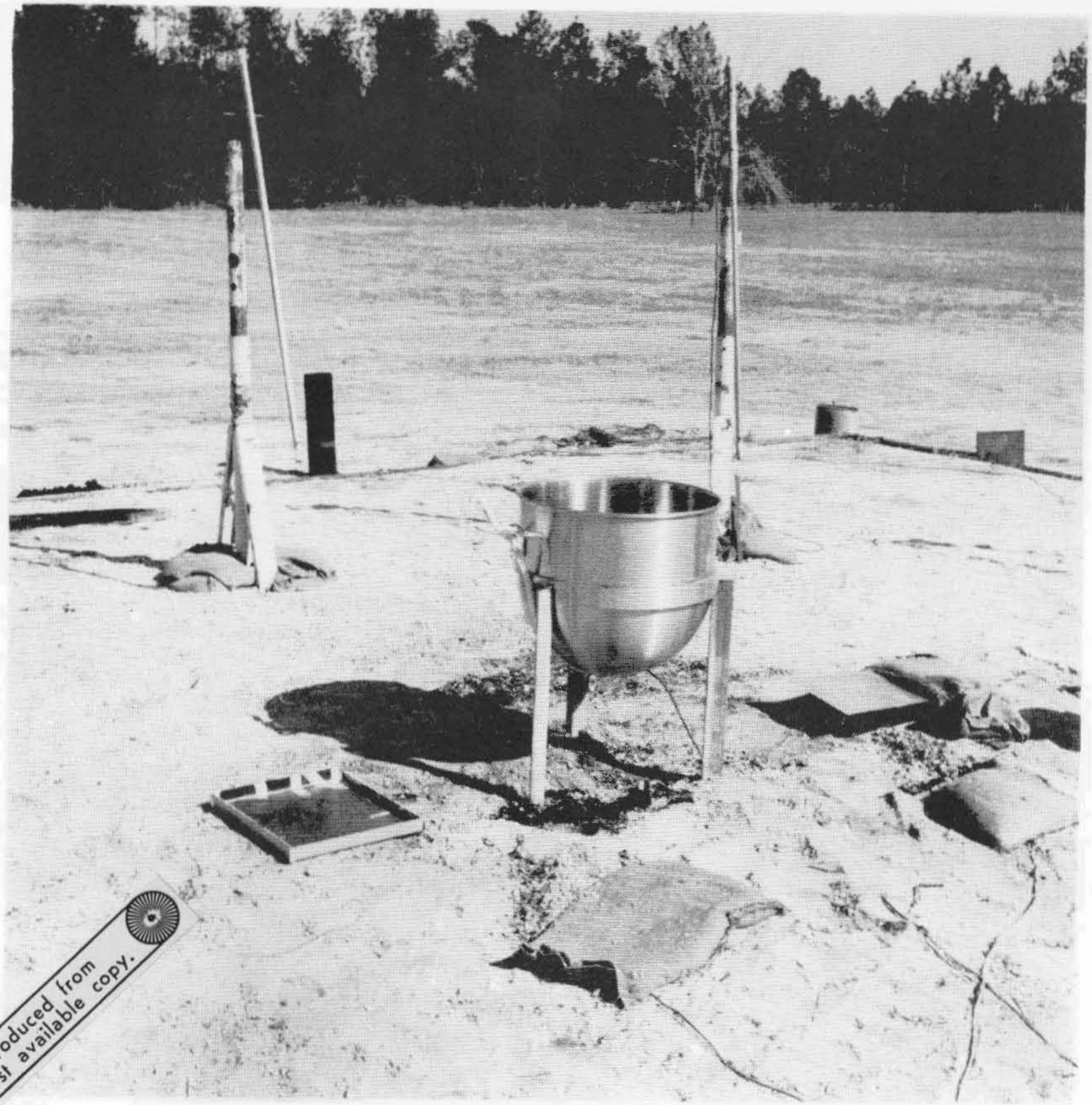
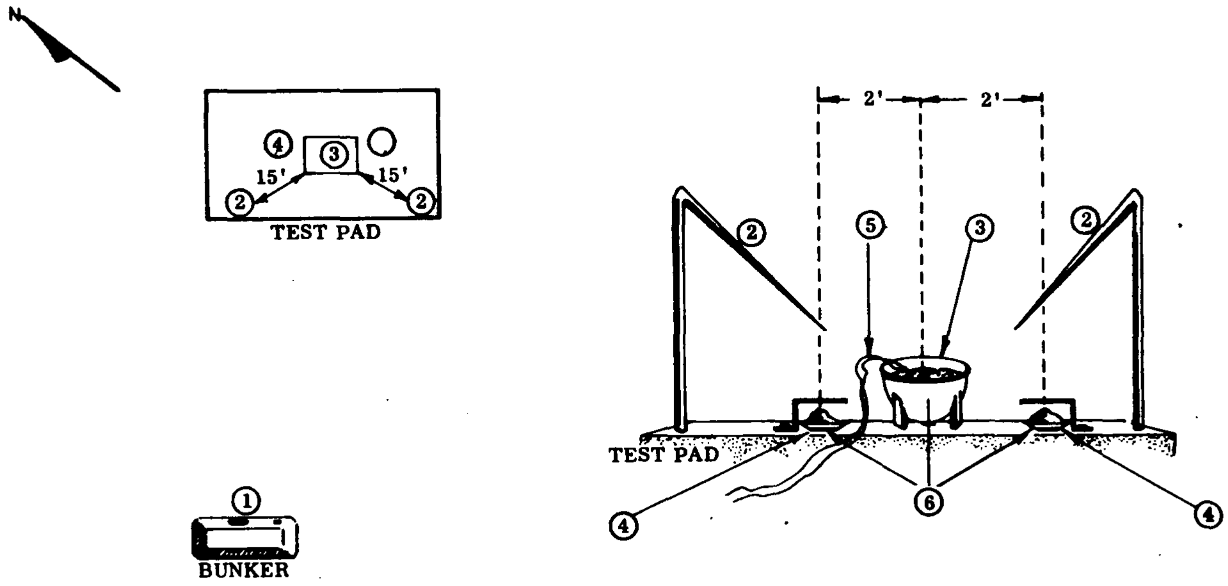


Figure D-7. 80-Quart Stainless Steel Mixing Bowl



① MITCHELL CAMERA, 24 fps.
② TRANSDUCER
③ 80 QT. MIXER BOWL WITH 46 LBS. OF MIX.
④ 1-2 LBS. OF SMOKE WITH METAL TRAY AND PROTECTIVE COVER.
⑤ IGNITION WIRE, INSULATED.
⑥ THERMOCOUPLES, 1 EA.

Figure D-8. Instrumentation Setup for 80-Quart Mixing Bowl Tests

		TIME
e.	Recurrence of flame inside the vessel.	120 seconds
f.	Dark smoke	180 seconds
g.	End of test	8 minutes

D.3.1.3 Observations

All of the sulfur green composition was consumed (Figure D-9).

D.3.1.4 Meteorological Conditions

Meteorological conditions during test 1 were:

- Wind Direction - 130°
- Wind Velocity - 8 knots
- Temperature - 48°F
- Humidity - 23%
- Pressure - 30.40 mm Hg

D.3.2 TEST 2

D.3.2.1 Setup

For test 2, twelve pounds of sulfur violet were placed inside a ID stainless steel pipe, and a hot wire was used as the ignition source.

D.3.2.2 Chronology of Events

Test 2 proceeded as follows:

		TIME
a.	Ignition	0 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around the test vessel containing the burning smoke composition.	5 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	16-20 seconds
d.	Flame extinguished and intense dark smoke.	45 seconds
e.	Smoldering	90 seconds
f.	End of test	8 minutes

Figure D-9. Typical Intense Dark Smoke Cloud 70 Seconds After Ignition, Six-Inch Pipe

D.3.2.3 Observations

All of the sulfur violet composition was consumed.

D.3.2.4 Meteorological Conditions

Meteorological conditions for test 2 were:

- Wind Direction - NE/50°
- Wind Velocity - 4-5 knots
- Temperature - 40°F
- Humidity - 28-30%
- Pressure - 30.47 mm Hg

D.3.3 TEST 3

D.3.3.1 Setup

For test 3, 46 pounds of sulfur violet were placed in an 80-quart mixing bowl. A J-2 blasting cap was used as the ignition source.

D.3.3.2 Chronology of Events

Test 3 events were as follows:

		TIME
a.	Ignition	0 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around the vessel containing the burning smoke composition, characteristized by the entire area being enveloped in flames.	5 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	25 seconds
d.	Dark smoke	70 seconds
e.	End of test	8 minutes

D.3.3.3 Observations (Figures D-10 and D-11)

The sample material was:

- Completely burned
- Still smoldering 25 minutes after ignition
- Spewed approximately 25 feet down wind. Raw material was also scattered.

Figure D-10. Typical Height of Reaction, 80-Quart Mixing Bowl

Figure D-11. 40-Seconds After Ignition, 80-Quart Bowl

D.3.3.4 Meteorological Conditions

Meteorological conditions for test 3 were:

- Wind Direction - SE
- Wind Velocity - 5-7 mph
- Temperature - 50°F
- Humidity - 40%
- Pressure - 29.38 mm Hg

D.3.4 TEST 4

D.3.4.1 Setup

For test 4, twelve pounds of sulfur violet were placed in a six-inch steel pipe. A J-2 blasting cap with a paper cone placed over it was used as a biased ignition source.

D.3.4.2 Chronology of Events

Test 4 proceeded as follows:

		TIME
a.	Ignition	0-5 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around the test vessel containing the burned smoke mix.	30 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	40 seconds
d.	Flame extinguished and intense dark smoke appeared	50 seconds
f.	Smoldering	60 seconds
g.	End of test	8 minutes

D.3.4.3 Observations

During test 4, it was observed that:

- The twelve-pounds of sulfur violet, located down wind from the pipe, was completely consumed.
- There was no apparent difference in the reaction of the material when the paper cone was placed over the J-2 blasting cap.

D.3.4.4 Meteorological Conditions

Meteorological conditions for test 4 were:

- Wind Direction - SE

- Wind Velocity - 5-7 mph
- Temperature - 50°F
- Humidity - 40%
- Pressure - 29.38

D.3.5 TEST 5

D.3.5.1 Description

For test 5, twelve pounds of sulfur violet were placed in the bottom of a six-inch steel pipe. A J-2 blasting cap was used as the ignition source.

D.3.5.2 Chronology of Events

Test 5 proceeded as follows:

		TIME
a.	Ignition	0 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around test vessel containing burned smoke mix	5 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	11 seconds
d.	Flame extinguished and intense dark smoke appeared.	17 seconds
e.	Dark smoke	20 seconds
f.	Smoldering	50 seconds
g.	End of test	8 minutes

D.3.5.3 Observations

The sulfur violet composition was completely burned.

D.3.5.4 Meteorological Conditions

Meteorological conditions during test 5 were:

- Wind Direction - SE
- Wind Velocity - 5 mph
- Temperature - 49°F
- Humidity - 38%

D.3.6 TEST 6

D.3.6.1 Description

For test 6, 46 pounds of sulfur violet were placed in an 80-quart mixing bowl with a J-2 blasting cap used as the ignition source.

D.3.6.2 Chronology of Events

Test 6 proceeded as follows:

		TIME
a.	Ignition	0 seconds
b.	Blow-out of material, fire and smoke in a two-foot diameter circle around the test vessel containing the burning smoke mix.	4 seconds
c.	Maximum reaction and communication to mix in adjacent tray on ground.	4-21 seconds
d.	Dark smoke	21-41 seconds

D.3.6.3 Observations

Violent deflagration, heavy smoke and spewing occurred during test 6. The reaction was such that there were alternations between smoke, spewing of material, and flame, too rapid to time (Figures D-10 and D-11). Propagation to pans apparently took place in this time (exact time was not determined because of the violent reaction). Dense smoke existed for the period from 21 to 41 seconds.

D.3.6.4 Meteorological Conditions

Meteorological conditions during test 6 were:

- Wind Direction - SE
- Wind Velocity - Calm
- Temperature - 48°F
- Humidity - 40%

D.3.7 SUMMARY OF CHRONOLOGY OF EVENTS

The data for each of the six tests is summarized in Table D-1.

D.3.8 SUMMARY OF TEMPERATURE MEASUREMENTS

The data for each of the six tests is summarized in Table D-2.

Table D-1. Summary of Chronology of Events

TEST NUMBER	MATERIAL			IGNITION SOURCE			EVENT			
	12 Lbs. SG	12 Lbs. SY	46 Lbs. SY	S-94	Hot Wire	J-2	Time to Maximum Reaction	Communications to Passive Sensors	Duration of Visible Flame	End of Reaction
1	X			X			35 sec.	< 35 sec.	180 sec.	
2		X			X		16 sec.	< 16 sec.	45 sec.	90 sec.
3			X			X	25 sec.	< 25 sec.		70 sec.
4		X				(w/paper cone)	40 sec.	< 40 sec.	50 sec.	60 sec.
5		X				X	11 sec.	< 11 sec.	17 sec.	50 sec.
6			X			X	4-21 sec.	< 4-21 sec.	21 sec.	41 sec.

Table D-2. Summary of Thermocouple Data

Test Number	Thermocouple Location								
	Container (Six-Inch Pipe or 80 Qt) Temp			Pan Temp.			Cover Temp.		
	1 Ignition Time	Maximum Temp.	2 Temp. Rise Time	1 Ignition Time	Maximum Temp.	2 Temp. Rise Time	1 Ignition Time	Maximum Temp.	2 Temp. Rise Time
1	10 sec.	--	--	35 sec.	--	--	--	(was not used) --	--
2	10 sec.	272°F	4-1/2 min.	60 sec.	780°F	--	10 sec	240°F	3 min.
3	52 sec.	360°F	4-1/4 min.	downwind 20 sec.	424°F	3 min.	(upwind - no ignition)		
4	7 sec.	320°F	4 min.	35 sec.	416°F	2 min.		472°F	1 min.
5	7 sec.	320°F	5-1/2 min	5 sec.	400°F	3 min.	5 sec.	780°F	--
6	64 sec.	352°F	5-1/2 min.	40 sec.	320°F	4 min.	27 sec.	440°F	2-3/4 min.

1 - Ignition Time - Time required for temperature to rise 10°F above ambient temperature

2 - Temperature Rise Time - Time required for Temperature to rise to maximum temperature from functioning of igniter.

D. 4. CONCLUSIONS AND RECOMMENDATIONS

D. 4. 1 CONCLUSIONS

Based on the results of the six tests, the following has been concluded:

- The mixing operation presents a fire hazard in view of the extensive dispersal of fire brands accompanying ignition. In all six tests, at least a fifteen foot mushroom was generated immediately after ignition. This resulted from a blow-out of combustion gases through the mix formulation.

- Even though every attempt was made to protect the passive sensors (which were placed in the vicinity of the bowl in order to measure probability of communication to loose powder incidentently scattered during mixing operation) from the fire brand shower by using protective covers, the passive sensors were ignited eventually by the intense fire brand shower. As shown in Figure D-12 and D-13, the areas of coverage with burning fire brands are as follows:

Amount of Pyro (lbs)	Area
12 pounds	8 sq. ft.
46 pounds	64 sq. ft.
125 pounds	240 sq. ft. (extrapolated)

  In order to obtain a reasonable estimate of the area affected by a full 125 pound batch, the available data is fitted to the function

  $$(\text{Area}) = (\text{Mass})^{B}$$

  As shown in Figure D-14, this equation will pass through the origin (i.e., zero area affected if no mass is expended) with the parametric solutions $A = 0.17$ and $B = 1.55$. Thus the extrapolated area affected by 125 pounds of pyrotechnics is calculated to be approximately 240 square feet. The radius of a 240 square foot circle is approximately 9 feet, which established a minimum safe distance (assuming no wind) in which sympathetic ignition of pyrotechnic material would fail to occur.

- Amplitude of dynamic overpressure was below minimum level required to trigger transient recorders. Additionally, there was no evidence of flexure pressure in the walls of any of the vessels either from dynamic overpressure or thermal expansion.

NOTE

The bottom of both the six-inch and 80-quart bowl were deliberately unsupported so as to simplify the calculation of the rupture strength/pressure.

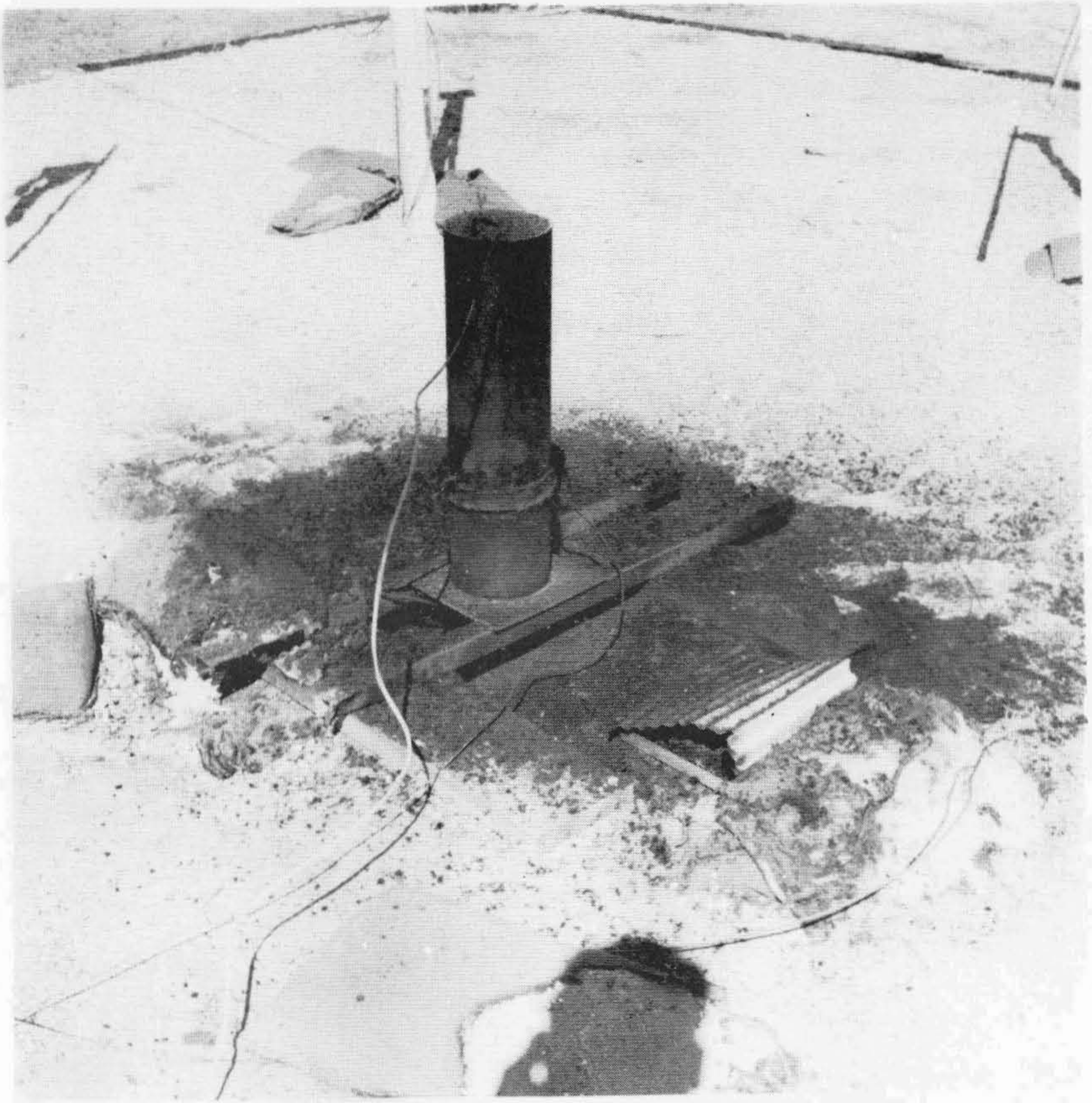


Figure D-12. Result of J-2 Ignition (Approximately 8 Square Feet Covered with Burned Mix)

Figure D-13. Results of 80-Qt. Test Showing Blow-out of Mix (Approximately 64 Square Feet Covered with Burned Mix)

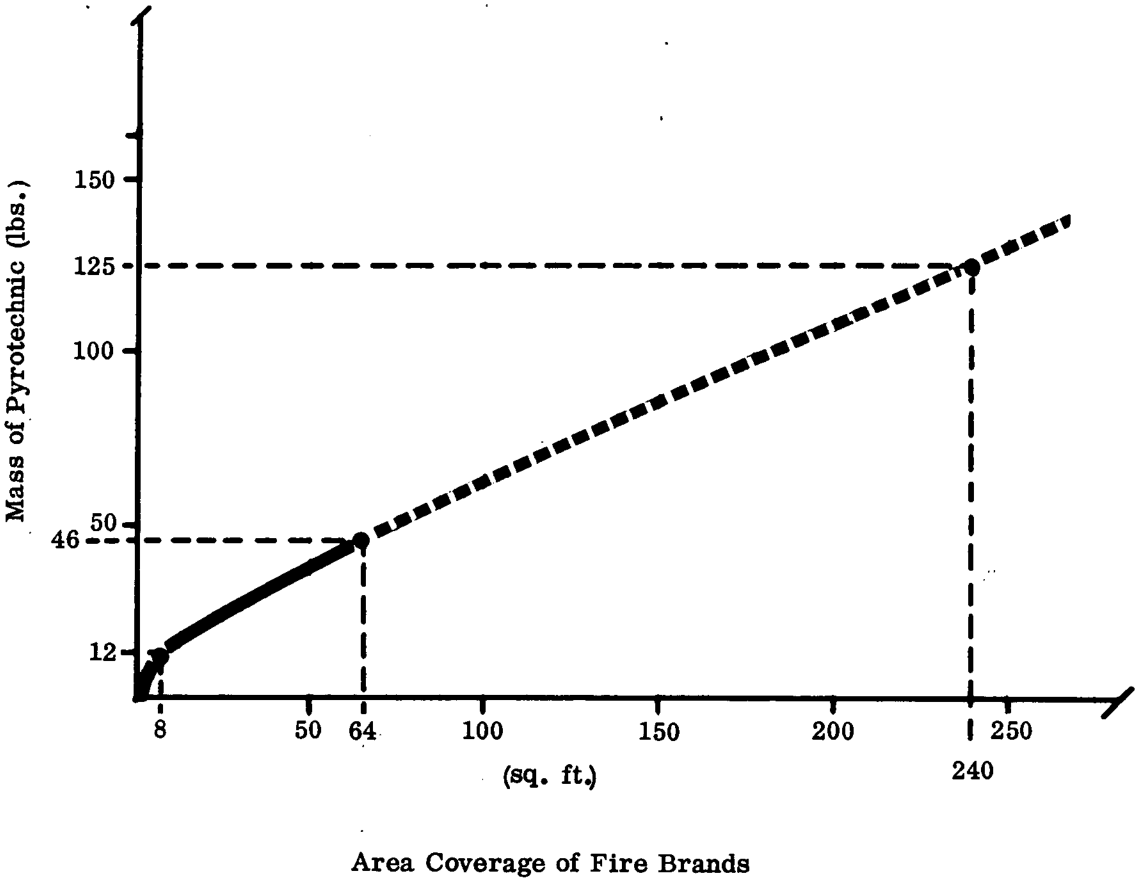


Figure D-14. Fitted Curve for Fire Brand Dispersal

- A greater degree of blow-out of unburned mix for the twelve-pound tests using blasting cap igniters was evidenced as compared to the hot wire or S-94 tests. Consequently, the duration of events (Table D-1) for the blasting cap tests are much shorter than hot wire or S-94 testing.
- As a result of placing the paper cone over the blasting cap in the twelve-pound test less material was blown-out; consequently, the duration of events (Table D-1) for the paper cone blasting cap test was greater than similar tests without the paper cone.
- Comparing the temperature/time plot (Figure D-15) for a J-2 blasting cap and hot wire igniter placed individually in twelve pounds of sulfur violet shows the temperature rise and maximum temperature developed by the J-2 cap configuration to be greater than the hot wire configuration by 18 percent.
- Comparing the temperature/time plot (Figure D-16) for the 46-pounds and 12 pounds of sulfur violet tests both configurations being ignited by a J-2 blasting cap shows the temperature of the twelve-pound configuration increasing sooner than the 46 - pound configuration. In view of the fact that the thermocouple for the twelve-pound test is closer to the igniter source than for the 46-pound test, a longer time is required for the respective thermocouple to register any temperature increase. Additionally, the temperature rate rise and maximum temperature developed by the 46-pound tests are greater than the twelve-pound configuration by 9.7 percent.

D.4.2 RECOMMENDATIONS

It is recommended that good housekeeping be emphasized on all mixing and filling operations. Mixing beater speeds should be carefully maintained to prevent spillage in the immediate vicinity of the mixing operation.

It is recommended that whenever the compositions tested (sulfur violet and sulfur green) are stored in quantity under the minimal "safe distance" (9 foot), precautionary measures such as protective covers be employed to reduce to a minimum the probability of communication.

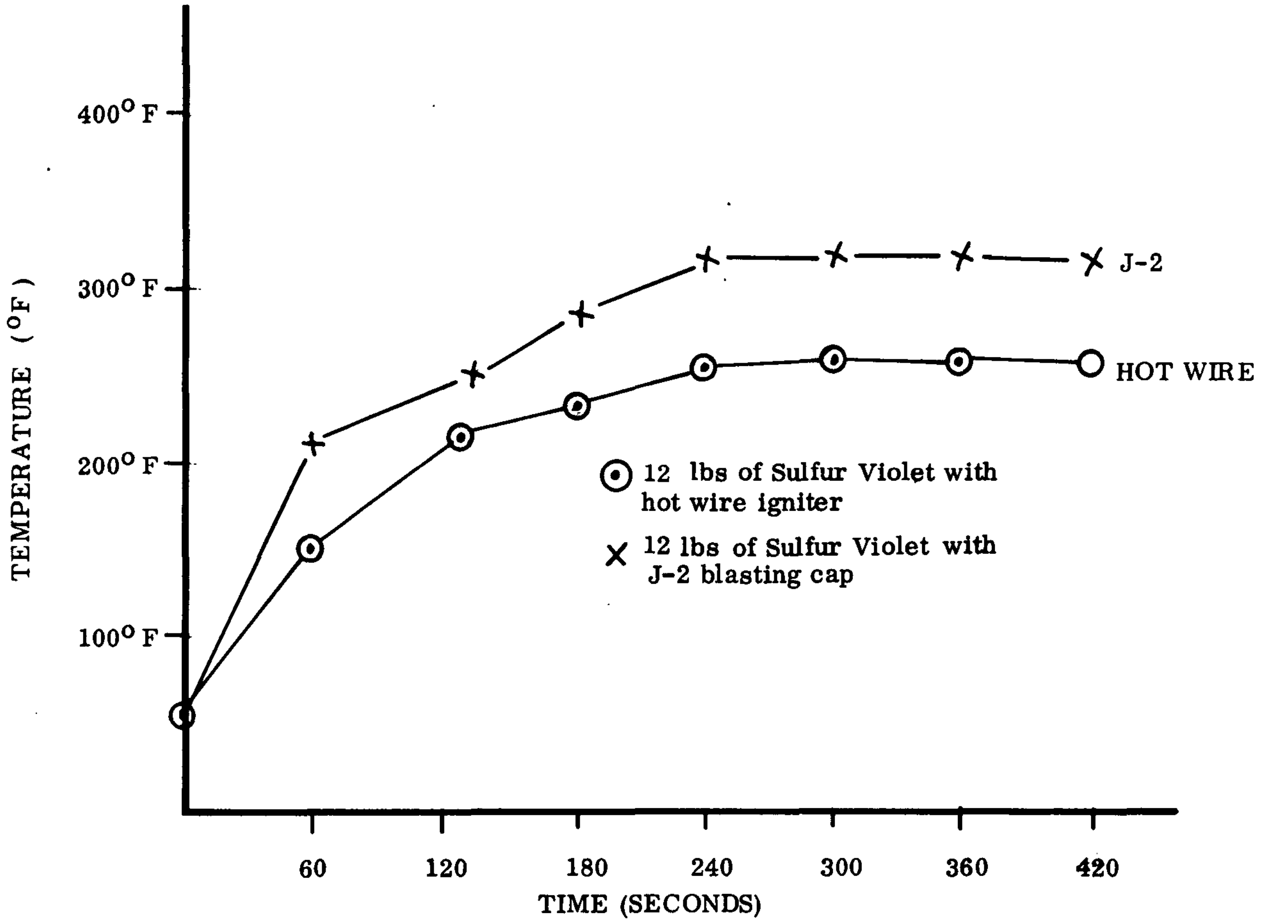


Figure D-15. Temperature/Time Plot for J-2 Blasting Caps and Hot Wire Ignition Tests Individually Placed in 12 lbs of Sulfur Violet

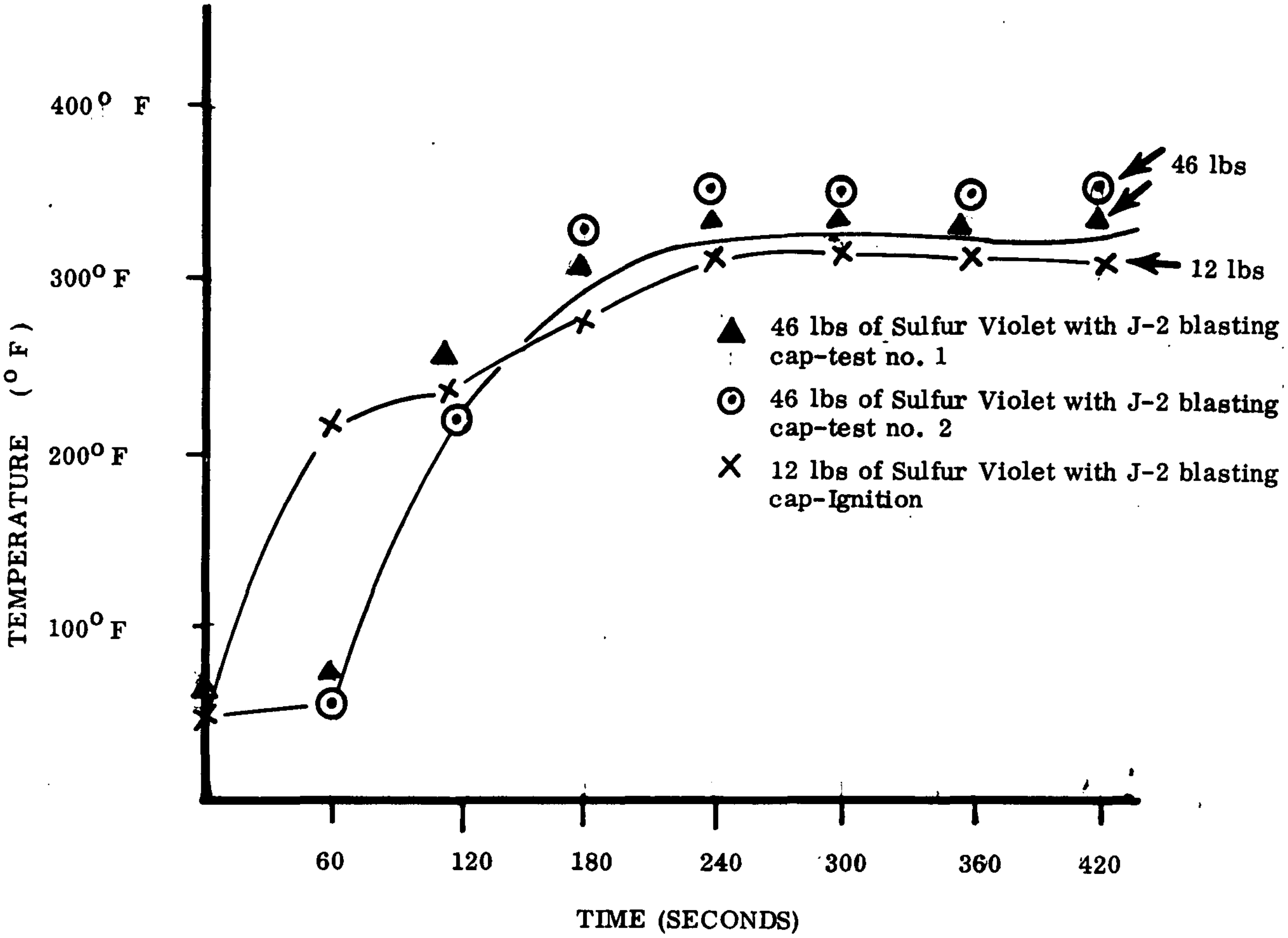


Figure D-16. Temperature/Time Plot for 46 lbs and 12 lbs of Sulfur Violet Simulation Tests both Ignited by J-2 Blasting Caps

APPENDIX E

RELATED MATERIAL PROPERTIES

E. 1 INTRODUCTION

In order to develop a program which has general application to a variety of processes, determination of basic critical parameters, as defined below, are required. These parameters are functionally related to:

- The mechanical and electrical threshold energy for initiation, communication, transition.
- Energy release characteristics to assess the margin of safety of the manufacturing operation.

E. 2 TNT EQUIVALENCY

Mathematical techniques are applied to obtain a relationship between blast overpressure of pyrotechnic materials tested and that of TNT.

E. 3 DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) measurements of a material are used extensively to determine heat content and to detect any exothermic or endothermic changes. Changes which may occur are as follows:

- Decomposition
- Dehydration
- Crystalline Transition
- Melting
- Boiling
- Vaporization
- Polymerization
- Oxidation
- Reduction
- Specific Heat

The functional operation of DTA relies on comparison measurements. The temperature difference between a sample and a chemically inert reference material is compared while both are heated at the same rate. Applying the known heat content of the reference material to the relative temperature measurements provides a complete thermal history.

E. 4 HEAT LIBERATION

A Parr bomb calorimeter is used to determine the thermal energy liberated during combustion of a unit mass of material. The material and its reaction are completely confined inside a vessel (Parr bomb) of known heat capacity. Determination of its average temperature rise or the average temperature rise of the vessel in a bath of known heat content will establish the heat liberated during reaction.

E. 5 SPECIFIC PRESSURE FROM COMBUSTION

The pressure generated as a result of the reaction of a unit mass of material confined to a unit volume can be determined by including a pressure transducer in a high strength confining vessel of known volume; e. g. , a Parr bomb vessel.

E. 6 SPECIFIC GAS LIBERATED VOLUME

The gas liberated during a confined chemical reaction determines the pressure buildup. If the pressure generated is greater than the yield strength of the confining medium (i. e. , die, hopper, canister, self-confinement, etc.), a blast pressure release is likely to result. The volume liberated at standard temperature and pressure can be determined by accurate chemical formulation (ratio of fuel oxidizer) and weighing. Alternatively, the volume liberated can be inferred from the pressure determination (paragraph E. 5), assuming an ideal gas and determination of the gas temperature.

E. 7 THERMAL CONDUCTIVITY

Thermal conductivity is defined as the time rate of transfer of heat by conduction across the unit sample area when subjected to a unit temperature gradient.

E. 8 SPECIFIC HEAT

The specific heat capacity of a material is the heat absorbed in a unit mass to cause a temperature rise of one degree.

E. 9 BULK MODULUS

The modulus, β, of volume elasticity can be expressed as

$$\beta = \frac{dP}{dV} V$$

where dP is a change in pressure on the material and $\frac{dV}{V}$ is the resulting fractional change in volume. The bulk modulus specifies the amount of pressure required to compress a material a given amount.

E. 10 ELECTRICAL CONDUCTIVITY

Electrical conductivity is determined by the current which flows through a unit area when subjected to a unit potential gradient.

E. 11 DIELECTRIC CONSTANT

The dielectric constant of a medium is defined by ϵ in the equation

$$F = \frac{QQ'}{\epsilon r^2}$$

where F is the force of attraction between two charges Q and Q' separated by a distance r and in a uniform medium.

E. 12 DIELECTRIC STRENGTH

Dielectric strength is the minimum electric field to which the dielectric material must be subjected before a disruptive discharge occurs through the sample.

E. 13 TRIBOELECTRICITY

The triboelectric effect refers to charge transfer between dissimilar surfaces upon rubbing together. Triboelectric effects provide a mechanism for spatial charge separation. An electrometer can be employed to measure the electric fields due to charge separation. If the electric field between the separated charge becomes larger than the dielectric strength of the material between the charge, a spark may occur, reducing the electric field. This spark is a potential ignition source (see electrostatic ignition energy, paragraph E. 14).

E. 14 ELECTROSTATIC IGNITION ENERGY

The electrostatic ignition energy of pyrotechnic dusts/powders is the minimum energy in a spark discharge which will ignite the material. Experimentally, the electrostatic energy is stored in a capacitor at a voltage sufficient to exceed the sample's dielectric strength. The energy stored in a capacitor charged to a voltage, V, is

$$E = \frac{1}{2} CV^2$$

where C is the capacitance. When discharged through a spark gap, most of this energy is transferred to the material within the gap. Thus, it is conventional to parameterize the spark by the energy stored in the capacitor.