PYROTECHNIC HAZARDS CLASSIFICATION
AND EVALUATION PROGRAM
CONTRACT NAS8-23524
PHASE II, SEGMENT 3 FINAL REPORT
TEST PLAN FOR DETERMINING HAZARDS ASSOCIATED
WITH PYROTECHNIC MANUFACTURING PROCESSES
JANUARY 29, 1971

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

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Management and Technical Services Department
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FOREWORD

The studies described in this report comprise Segment 3 of Phase II of Edgewood Arsenal's three-phase Pyrotechnic Hazards Classification and Evaluation Program. Segments 1 and 2 of the Phase II program were reported as follows:

- Segment 1 - Records and Experience Analysis - Report Number GE-MTSD-R-045.
- Segment 2 - Operational Survey - Report Number GE-MTSD-R-040.

This report was prepared by the General Electric Company, Management and Technical Services Department (GE-MTSD), Bay Saint Louis, Mississippi, under National Aeronautics and Space Administration (NASA) Contract NAS8-23524 for the Engineering Test and Evaluation Section, Process Technology Branch, Chemical Process Laboratory, Weapons Development and Engineering Laboratory, Edgewood Arsenal, Maryland.
EXECUTIVE SUMMARY

The objectives of the test plan described herein for the conduct of Phase II and III of the Pyrotechnic Hazards Classification and Evaluation 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 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 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.

RATIONALE

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 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.
TEST GEOMETRY

In order to permit meaningful comparison of data from previous tests/studies, the geometry chosen has whenever possible been similar to or identical with that used in Phase I tests of "TNT equivalency". This has the added advantage of being essentially a full scale (end item) simulation. Departures from this approach have been applied only where the bulk of the material and simulation involved were significantly different from the end items.

SIMULATIONS

Several representative simulations are discussed herein, in order of their estimated importance.

During processing the consolidation of end items involves the potential for initiation of the pyrotechnics by all the "classic" stimuli as discussed further herein. The primary areas of concern are:

a. Can the material detonate under the maximum credible conditions that can be postulated?

b. If a detonation is possible, what are the nature and degree of the resultant/fragment/fire/overpressure hazard?

To provide for the worst case simulation, a test device will be built which will approximate the rupture strength of the die/press/ram combinations in the various dimensions.

To further assure "worst case" conditions, the following conditions will be met:

a. The relief provided by the die kickout pin will be disregarded.

b. The relief capability provided by the vent hole at the bottom of the die will be ignored.

c. The void provided between the ram as it enters the die will be deliberately exaggerated until it approximates that percentage of void which gave the maximum reaction in the TNT equivalency tests conducted in Phase I.

d. The ignition stimuli will be provided by a J-2 blasting cap which will far surpass the localized energy available in any conceivable accident.

If under these extreme conditions detonation cannot be achieved, it may be safely said to be impossible under the accident sequences postulated herein. If explosion or detonation sufficient to rupture the test fixture occurs, the resultant data obtained will indicate the nature and degree of protective measures to be applied.

A similar rationale will be applied to the simulation of an accident occurring after consolidation, while the ram is being withdrawn.
REAMING

In the reaming sequence, the most hazardous or severe condition is assumed to be created if an ignition occurs in the granular material being removed by the tool while abnormal force is being applied to hold the end item against the reaming cutter.

This will be simulated by confinement of the material in a container with a cover plate of approximately 50 pounds bearing on the top of the device. An amount of granular material equivalent to the maximum amount removed by reaming will be placed on top of the consolidated item, and it will be initiated by the J-2 cap. The severity of the resultant reaction will be measured and compared to that to be expected from the high explosive under the same conditions.

As outlined more completely in the sections which follow, the mixing and blending simulations will be treated in a similar manner, to make maximum application of the data which will be obtained. Finally, a runup reaction test series will be conducted to evaluate the probability of a small scale ignition creating a dust cloud which becomes progressively more concentrated.

The simulation applied for the runup reaction tests will be as follows:

a. A multi-modular test device, with each module representing 1/6-scale of a typical operating bay, will be conducted.

b. A "dust ignition" will be created in the dust module using a dispersal technique, ignition energies, and dust concentrations representative of 100 percent ignition levels for the materials tested in the Hartmann Apparatus.

c. Successive modules will contain increasing concentrations, terminating in a mixture density equivalent to that obtained by dispersal of 1/6 of the total material permitted in a typical operating bay (in this case, 1/6 of 100 pounds).

It is believed that these tests and simulations represent a cost effective manner of evaluating the hazards to be encountered in pyrotechnic processing operations and the techniques required to protect against them.
ABSTRACT

This report presents a comprehensive test plan for determining the hazards associated with pyrotechnic manufacturing processes. The rationale for each test is based on a systematic analysis of historical accounts of accidents and a detailed study of the characteristics of each manufacturing process.

The most hazardous manufacturing operations have been determined to be pressing, mixing, reaming, and filling. This conclusion is based on a systematic analysis of an operational survey conducted at Pine Bluff Arsenal.

The hazard potential of a given situation is evaluated in terms of the probabilities of initiation, communication, and transition to detonation (ICT). The characteristics which affect the ICT probabilities include the ignition mechanisms which are present either in normal or abnormal operation, the condition and properties of the pyrotechnic material, and the configuration of the processing equipment.

Analytic expressions are derived which describe the physical conditions of the system, thus permitting a variety of processes to be evaluated in terms of a small number of experiments.
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SECTION 1
INTRODUCTION AND SUMMARY

1.1 GENERAL

In accordance with the requirements of Contract NAS8-23524, Amendment 4, Phase II, Segment 3, GE-MTSD has prepared the following test plan for Phase II, Segment 4 of the Pyrotechnic Hazards Classification and Evaluation Program.

The following manufacturing processes are considered the areas of primary concern based on a systematic analysis (as given in Appendix A) of the findings from operational surveys, plant tours, and inspections conducted at Pine Bluff Arsenal:

- Pressing and consolidation of pyrotechnic mixtures in the grenade and canister body (Figure 1-1).
- Blending and mixing of pyrotechnic smokes and starter mixes (Figure 1-2).
- Reaming of the filled and pressed grenades or canisters to remove excess pyrotechnic mix (Figure 1-3).
- Filling of grenades and canisters (Figure 1-4).

Secondary hazards were evidenced in areas where settled or suspended dust and vapor accumulations could conceivably result in combustion propagation to large concentrations of the pyrotechnic with its ultimate detonation.

In view of these areas of concern, data is required to furnish a basis for discrete safety assessments and design recommendations. The function of this test plan is to propose an experimental program to develop data specifically to substantiate these recommendations. This concept is illustrated in Figure 1-5.

1.2 APPROACH

For ease of understanding, the test plan is summarized graphically in Figures 1-6 through 1-8. The development of the test plan is divided into three phases of evaluation: initiation, communication and transition, and incident severity. Each of the phases relates the material properties, environment, and protection of the four critical manufacturing processes, i.e., pressing, mixing, reaming, and filling, to the proposed test.

1.2.1 INITIATION EVALUATION

The proposed initiation tests, as illustrated in Figure 1-6, are designed to determine the minimum electrical and mechanical energy required to induce ignition of pyrotechnic materials. The
Figure 1-1. Typical Pressing Operation
Figure 1-2. Typical Mixing Operation
Figure 1-3. Typical Reaming Operation
Figure 1-4. Typical Filling Operation
Figure 1-5. Fundamental Elements Affecting Pyrotechnic Hazards
Figure 1-6. Initiation Evaluation
Figure 1-7. Communication and Transition Evaluation
Figure 1-8. Incident Severity Evaluation
initiation mechanisms for the critical manufacturing processes are:

- Pressure
- Friction
- Heat transfer (from frictionally heated component)
- Electrostatic discharge

The initiation tests will supply data to determine the probability of initiation of a pyrotechnic by normal or abnormal operation of a given manufacturing process. The relevancy of the proposed tests is detailed in Section 3.

1.2.2 COMMUNICATION AND TRANSITION

Once initiation has occurred, the reacting material communicates with the adjacent nonreacting material providing a mechanism for propagation of the reaction front. The reaction may be such that the reaction front velocity is accelerated until it exceeds the velocity of sound. This occurrence is referred to as a transition from deflagration to detonation.

The reaction front velocity in a material is a function of the material's reaction rate--its chemical properties, its dispersal, pressures, and temperatures. In general, the more exothermic the reaction and the larger the exposed surface-to-volume ratio, the higher the rate of reaction. Likewise, the smaller the difference between the initiation temperature and the ambient temperature, the easier it is for the reaction to propagate. High ambient temperature and pressure reduce this difference.

All parameters except the chemical properties are considerably affected by the degree of confinement of the material. Thus, the experimental investigations shown in Figure 1-7 are designed to determine the effect of degree and type of confinement. These test configurations include:

- Unconfined Material
- Vessel Confinement - Pyrotechnic material in a closed, rigid chamber. This investigation includes determining whether the blast overpressure released is a characteristic of the deflagrating/detonating pyrotechnic or is a result of pneumatic rupture of the vessel caused by static buildup of pressure during burning.
- Self Confinement - Large mass alone as its own confining medium.

The pyrotechnic material may be dispersed as a dust suspended in air. The communication properties of this distribution may readily lead to a transition to detonation. Variations in dust density may be required to induce a transition. Such a condition is referred to as inducing a runup reaction. The terminal element in a runup chain may be a concentration of pyrotechnic
powder which, if able to maintain the detonation through its bulk, would result in a violent explosion. Simulation of the runup conditions and study of the results is a proposed test.

Communication between adjacent or separated concentrations of pyrotechnic materials or items may provide a means of propagating a local accident to many surrounding locations, resulting in a major incident. A complete study of communication probability in this situation is beyond the scope of this investigation, but a limited study is proposed which would determine the communication characteristics between concentrations occurring in one or two situations during manufacture.

1.2.3 INCIDENT SEVERITY EVALUATION

Tests are proposed, as shown in Figure 1-8, to determine the severity of the incidents resulting from the potential hazards outlined and to determine the criteria necessary to minimize these effects. The proposed test program will determine the characteristics of the following in the appropriate accident simulations:

- Fragments
- Fireball/Afterburning
- Pyrotechnic Material Dispersion
- Blast Overpressure

The severity of the hazard to personnel and equipment is a function of these parameters. The analysis of these data will provide criteria for implementation in existing pyrotechnic manufacturing processes and in the design of future equipment.

1.3 PLANNING

The test plan and method of approach selected were based on the extension of the planning projected for the total Phase II effort as shown in Figure 1-9. The preliminary planning for the accomplishment of this segment necessitated a detailed review of its objectives and the establishment of a projected approach to successfully complete the objectives.

The physical characteristics of the manufacturing processes are functionally related. For maximal efficiency and generality, the approach to the test plan (diagrammed in Figure 1-10) is to test the common functional characteristics of the manufacturing processes which may affect their hazard potentials. Tests are designed to provide appropriate initiation stimuli and to study the conditions for communication into a hazardous situation due to a transition into detonation. These data can then be applied to a specific manufacturing process by adequately describing the corresponding conditions which occur during either its normal or abnormal operation. This concept is reflected in the modified approach to Segment 4 shown in Figure 1-11. The rationale for and description of the specific tests shown are developed in the remainder of the report.
Figure 1-9. Phase II Logic Diagram
Figure 1-10. Phase II, Segment 3 Logic Diagram
Figure 1-11. Phase II, Segment 4 Logic Diagram
SECTION 2
INITIATION, COMMUNICATION, TRANSITION

2.1 GENERAL

This section presents, with amplifications, the following physical/chemical phenomena, some or all of which normally occur sequentially during the reaction development from initiation to detonation when a pyrotechnic mixture (solids and dusts) is ignited:

- Initiation at a localized region.
- Communication to adjacent material by a subsonic burning process (deflagration).
- Transition from deflagration to detonation.
- Propagation of detonation.

Although it is not an objective of the current program to express results in terms of damage to a human body, a discussion of body vulnerability is included to facilitate better understanding of the rationale of this study as it ultimately relates to the vulnerability of the human body and the applicability of the data.

This section is intended to briefly summarize the results of recent investigations rather than to fully describe the kinetics of chemical reactions of pyrotechnic mixes.

2.2 INITIATION

That explosions are thermal in origin is widely accepted. According to the "hot spot theory," energy must be transformed into heat to give a "hot spot" of suitable size and temperature to support growth. At a microscopic scale, ignition of a reactable granular material is caused by:

- Adiabatic compression of trapped air pockets
- Intergranular friction
- Granular-container wall and intragranular friction
- Heat injection

Any of these mechanisms is capable of generating a "hot spot" inducing a chemical reaction. If the reaction is exothermic and the energy in the "hot spot" is above a critical threshold level, the reaction will be self-sustaining, thus initiating the material.

One or more of the microscopic ignition mechanisms may be stimulated by the mechanical/electrical effects induced during manufacturing processes. These macroscopic initiating mechanisms include:

- Pressure
• Friction
• Heat transfer
• Electrostatic discharge

The magnitude of the contributions of these effects is dependent upon the manufacturing process involved and whether it is operating under normal or abnormal conditions.

2.3 COMMUNICATION

The reaction front communicates with the adjacent unreacted material propagating the reaction. In some materials, an increase in reaction rate accompanies the propagation of the reaction front. For a significant increase of the reaction rate to occur, the heat generated by the chemical reaction must be liberated at a greater rate than is necessary to sustain the combustion and to balance the conductive heat losses.

From experimental investigations, the following factors have been postulated as influencing the burning rate of pyrotechnics:

• Degree of confinement
• Surrounding gas pressure
• Density
• Temperature
• Cross-sectional area of combustion zone
• Nature of chemical reaction process
• Rate of heat loss

2.4 TRANSITION FROM DEFLAGRATION TO DETONATION

A number of investigators have noted that the culminating action of a deflagration process, whose reaction front propagates with monotonically increasing pressure and temperature, is its transformation into a shock wave. It is during transition that the reaction front transforms from a subsonic to a supersonic wave. Thus the reaction undergoes a transition from deflagration (burning) to detonation, forming a shock wave reaction front.

It has not been determined, experimentally, whether the mechanisms required to transform deflagration into detonation are the same for pyrotechnics and explosives.

2.5 PROPAGATION OF DETONATION

In a general sense, the ability of a solid to maintain a reacting compression wave is referred to as its ability to support propagation. High speed photographic studies by several investigators on thin films of azides and fulminates have shown that the following processes contribute
to propagation of detonation:

- Creation of a dust-like atmosphere by the action of the shock front breaking up the solid into fine particles, thereby increasing the material's surface-to-volume ratio and, consequently, the reaction rate.

- Shock initiation whereby gas pockets ahead of the reaction zone are compressed and serve as ignition sources to maintain the shock wave. In some materials, intercrystalline friction can also result in providing hot spots ahead of the reaction zone.

A thorough literature survey revealed that by no means are the events leading from initiation to detonation completely understood, and it only points out the need to expand the state-of-the-art in this field.

2.6 INCIDENT SEVERITY CONSIDERATIONS

There are three primary categories of hazards to the human body associated with an explosion; namely, blast, thermal, and fragmentation.

- Blast - Blast injuries are classified as being either direct or indirect. White and Richmond (reference Bibliography, Doc. 250) have reported that three parameters of the blast wave affect the extent of the direct injuries to the body: (1) the rate of pressure rise at the blast wave front, (2) the peak overpressure attained, and (3) the duration of the positive phase of the overpressure. Indirect blast injuries are associated with the impact of missiles, either penetrating or non-penetrating, and the physical displacement of the body as a whole.

- Thermal - Thermal injuries may result through either radiation or direct contact with pyrotechnics being sprayed or dispersed.

- Fragmentation - Fragmentation injuries are possible if high velocity fragments result. The relationship between fragment mass, velocity, and density that will cause injury upon impact with the body are indeterminate. It has been generally concluded that any wound causing a serious cavity in the body can be considered lethal. The threshold for such an injury can be taken to be almost 100 feet per second for a 10-gram fragment. For smaller fragments, the threshold velocity is, of course, higher.
SECTION 3
RECOMMENDED TEST PROGRAM

3.1 GENERAL

This section presents the recommended Phase II, Segment 4 test plan, including a brief process analysis of the rationale used to develop the plan as well as the proposed tests germane to the establishment of ICT criteria.

3.2 PROCESS ANALYSIS

It is the intent of this process analysis to establish and identify the primary ignition areas based upon locations of high mechanically induced stresses and to identify environmental characteristics which would affect the reaction severity and the hazard potential.

3.2.1 PRESSING

3.2.1.1 Description

Pressing is a forming process in which pyrotechnic bulk materials are compressed by the application of pressure in order to achieve an increased density. The pressure required for consolidation is expressed in terms of the bulk modulus of the material (see Appendix B, paragraph B.9). The most probable locations of the various ignition sources during the pressing process are identified in Figure 3-1.

The pressing process sequence may be described as follows. Initially, as the ram is descending, work is expended by collapsing or driving out the air pockets between the powder particles, resulting in heat rise by adiabatic compression of the air bubbles. Next, backward extrusion takes place accompanied by dust formation as the powder or mix is carried upwards between the walls of the die and the ram by the air flow from the escaping air pockets. Friction between granules of powder, friction between the surface of the containing wall and grit particles, and electrostatic charge buildup by triboelectric effects are generated by the descending ram. Stress (and ultimately intergranular friction) is concentrated at the outer edge of the ram tip due to biaxial loading of the ram tip by the material entrapped between the ram and wall of the die and material underneath the ram. Finally, after the air is driven out of the pyrotechnic material, the now highly compressed material becomes plastically deformed by intercrystalline strain as the ram continues to descend.

It should be noted that the greatest potential for spark initiation occurs between the ram and the die just as the ram starts its initial downward travel. This high potential is due to the very small air gap between the die and ram permitting a spark discharge at a relatively low voltage.
Figure 3-1. Sequence of Functional Events During the Pressing Operation
and the low electrostatic ignition energy of the dust cloud (generated by the turbulent action of
the escaping air pocket).

In summary, the following potential initiation mechanisms occur during press forming:

- Adiabatic compression of air pockets
- Friction concentration by biaxial stress
- Electrostatic ignition between ram and die
- Plastic deformation by intercrystalline strain
- Both intergranular and granule-wall friction

3.2.1.2 Theory

This paragraph develops the mathematical formalism describing the mechanically induced
temperature rise of a material subjected to a pressing operation. The material is assumed
chemically inert below ignition temperature so that all energy imparted to the system is accumu­
lated as heat, and the temperature rise is related to the heat absorbed per unit mass by the
specific heat, \( C = \frac{dQ}{dT} \). The applied pressure, in general, includes shear components
(particularly near the periphery of the piston) and is non-isotropically distributed. The analysis
can be simplified by assuming that only an isotropic pressure, \( P \), occurs. This assumption is
valid in any case if the material under pressure is characterized as a low viscosity fluid.

The mechanical work performed is homogenously distributed as heat over the bulk of the mate­
rial. The energy increase per unit mass is

\[
\Delta Q = J \int \frac{P \Delta \rho}{\rho} \, dX
\]

(Equation 3-1)

where \( J \) is the mechanical equivalent of heat, and \( dX \) is the relative volume compression
\( (dX = dV/V, \text{where } V \text{ is the volume}) \) induced by the application of a pressure \( (P) \) to a material
of density \( \rho \). From the definition of specific heat \( (C) \) and bulk modulus \( (\beta) \) (see paragraph
B.9), the increase in temperature is

\[
\Delta T = J \int \frac{\beta P \rho}{C \rho} \, dP
\]

(Equation 3-2)

If the specific heat is independent of applied pressure, Equation 3-2 can be rewritten as

\[
T_f (\text{final temperature}) = \alpha \Delta Q + \gamma
\]

\[
\alpha = \frac{1}{C}, \quad \gamma = T_i (\text{initial temperature})
\]
Note that in the pressing operation $P = \frac{F}{A}$ where $F$ is the force exerted by the press piston and $A$ is the piston face area, as illustrated in Figure 3-2.

3.2.2 REAMING

3.2.2.1 Description

Reaming is a machining process in which the size, shape, or surface properties of a part are changed by removing the excess material. Specifically, machining is accomplished by locally straining the material to fracture through the relative motion of the tool and work piece.

Datsko asserts that most of the heat generated during machining is carried away with the chips and a small amount is conducted to the work piece. The most likely ignition mechanism during a normal reaming operation is, therefore, thermal contact of a frictionally heated tool cutting edge with the pyrotechnic material. If the tool temperature at any point exceeds the material's ignition temperature, then ignition is possible.

3.2.2.2 Theory

A determination of maximum tool temperature is complicated by an ignorance of the fraction of energy transferred to the tool and the thermal characteristics of the tool. An estimate can be made by making appropriate assumptions.

The power output of the reamer is

$$P = \omega \tau$$

where $\omega$ is the angular velocity of reaming tool and $\tau$ is the torque on the tool induced by the work piece.

Some of this power is dissipated in imparting kinetic energy to the chips and some is lost to sound, but a fraction $\kappa$ is dissipated via friction into heat. Only a fraction $\kappa'$ of $\kappa P$ is absorbed through the tool surface, so the rate of heat transfer to the tool is

$$P_T = \kappa \kappa' \omega \tau$$

If the heat transfer properties were ideal, allowing no temperature gradients, and the tool was thermally isolated, then the temperature rise would become

$$\Delta T = \frac{1}{C_m} \int_{t_1}^{t_2} P_T dt$$

in the period of time $\Delta t$.

Even though ideal thermal conditions are not met, this approximation can be made by defining $C_m$ as the effective heat capacity for the tool, where $m$ is the effective mass of the bit tip.

Thus the final temperature becomes

$$T_f = \int \frac{\kappa \kappa' \tau \omega dt}{C_m} + T_i.$$
Figure 3-2. Functional Operation of Reaming
Defining the heat transferred to the tool per unit mass as

\[ Q_T = \frac{1}{\eta} \int \kappa \kappa' r \omega \, dt, \]

then

\[ T_f = \frac{Q_T}{C} + T_i \]

(Equation 3-3)

Equation 3-3 can then be rewritten into the same form as obtained in the pressing operation:

\[ T = \alpha Q_T + \gamma \]

\[ \alpha = \frac{1}{C}, \gamma = T_i \]

The torque \( \tau \) and speed \( \omega \) necessary for ignition of pyrotechnic materials have been measured under MIL-STD-1234. As described under MIL-STD-1234, a rotary friction apparatus uses a drill bit to deliver energy to a pyrotechnic sample of material in an insulated cup. (Rotary friction apparatus tests are further detailed in paragraph 3.3.1.2.)

3.2.3 MIXING/BLENDING

Mixing refers to an operation where components of pyrotechnic materials are combined into a homogenous compound. The actual process of mixing is accomplished by a kneading of mix between beaters and hopper. As shown in Figure 3-3, the forces acting at any point along the arc of contact between the hopper and beaters are a radial force, \( F_r \), and a frictional (or viscous) force, \( F_f \). The force of friction is given by

\[ F_f = \mu F_r, \]

where \( \mu \) is the coefficient of friction.

Electrostatic charge buildup and friction between crystals of powder, the surface of the hopper, and grit particles are generated by the beaters moving at a relative velocity, \( V_f \), through the mix. Microscopic triboelectric effects within the mix and between the mix and beaters/hopper result in charge separation. If electric fields within the mix exceed its dielectric strength, an electrostatic discharge (spark) will occur. If the discharged energy is above a critical level, ignition of the mix will result.

Charge separation will decay with time with a time constant proportional to the mix's bulk resistivity, which acts as a normal conductive path if the resistivity is low. Thus, the maximal electric field is determined by the rate of generation of charge separation and the decay rate and is a potential initiation source only if critical conditions are exceeded. Mechanical stress
SYMBOL

$V_i$, speed of blade
$t_f$, distance of closest approach
$q$, coefficient of friction
$F_r$, radial force
$F_f$, force of friction

1. plastic deformation area
2. beater mix rubbing area
3. hopper mix rubbing
4. electrostatic discharge area

Figure 3-3. Functional Effects in Mixing/Blending Operations
and friction are maximal directly underneath the beater (along the line AB shown in Figure 3-3).

To summarize, the following potential ignition mechanisms may occur in normal mixing operations:

- Plastic deformation by intercrystalline stress
- Friction heating between beater and mix
- Friction heating between hopper and mix
- Electrostatic discharge between beater and hopper

3.2.4 FILLING

Gravitational filling is performed by a dumping operation, and, as a result, a loose powder is deposited in a heap inside a metal container. Whenever a loosely compacted material is transported through the air or agitated, a dust cloud is likely to result from the mechanical interaction with the air. During the filling of an open top vessel, an updraft is created by air being displaced by the powder. The interaction of the flowing air and powder may disperse a dust cloud into the surrounding environment of the filling operation. Without proper ventilation, gravitational settling of the dust cloud and spillage will result in a gallery type situation, consequently, providing a system with increased probability of runup.

As shown in Figure 3-4, the following conditions are present in filling operations:

- Triboelectric effects between air and falling dust cause electrostatic charge transfer between air and dust during free fall.
- Dust particles impinge against the sides of the vessel, effecting a charge transfer between the dust and vessel.
- Significant concentrations of electrostatic charge and heat may accumulate in the bottom of the vessel.
- Displaced air updraft disperses a dust cloud (increasing the potential hazards associated with filling).

3.3 PROPOSED TESTS

As stated previously, the results of the proposed tests will contribute to the requirement to establish hazard criteria to apply to manufacturing processes. The tests are presented in the following paragraphs in the generic groups: initiation, communication and transition, and scale tests.
Figure 3-4. Functional Effects in Filling Operations

1. Viscous Flow
2. Free Fall Impingement
3. Electrostatic Change and Heat Buildup
4. Dust Cloud Draft
5. Gravitational Settling Area
The object of this report is to develop a test plan for Segment 4. While establishing a logical approach to meeting this requirement, several tests which would contribute to development of ICT criteria have been determined which either would be more applicable to other phases or segments of the program or are beyond its scope (or budget).

Therefore, for completeness and in order to present a consistent development, all tests germane to the establishment of ICT criteria are presented. The proposed phase and segment are indicated in the title of each test. If the test is beyond the scope of the current program, it is labeled "follow-on." Each group of tests is detailed to the extent necessary to give the basic general hardware, instrumentation, and data requirements for the specific tests under consideration.

3.3.1 INITIATION TESTS

The proposed initiation tests are designed to determine the energy required to initiate pyrotechnic mixtures. As previously mentioned, the mechanisms of initiation include pressure, friction, electrostatic discharge, and heat transfer. In turn, these mechanisms have been related to specific manufacturing processes. Therefore, an analysis of the maximum heat generation by the manufacturing processes can be compared to the threshold ignition energies of the mechanism common to that process to determine the ignition probability.

Analysis will include both normal and abnormal operations of the manufacturing process. Abnormal operation of a manufacturing process refers to those situations in which the designed range of operating conditions is exceeded. Examples of abnormal operations include misalignment of the press ram, fracture of the reamer blade, excessive material in the press die, excessive material in the vicinity of the filling operation, and improper alignment of the beater blades in a mixing vessel.

The tests will evaluate a complete range of parameters affecting the ignition threshold sensitivity of the pyrotechnic mixture. These parameters include the moisture content (affected by environmental conditions, particularly humidity, temperature, and length of exposure to its environment), the kinds and concentrations of contamination, and the relative concentration of the components of the mixture which would occur in normal and abnormal manufacturing.

As an example, the ignition threshold evaluation of the class of pyrotechnics which use as a vehicle a mixture of potassium chlorate (KClO$_3$) and sulfur (S) will be considered. The stoichiometric ratio of KClO$_3$ to S is 2.55:1. An evaluation of KClO$_3$-S ratios of 2:1 to 3:1 includes the leanest to the richest ratios encountered during normal processing. If the sensitivity is observed to increase towards one (or both) extremes, then the range tested should be expanded to include ratios which could occur during abnormal operation.
The inclusion of other ingredients with the basic mixture may also affect the ignition threshold and will be tested in both normal and abnormal concentrations; likewise, the effect of contamination and moisture content will be studied.

The proposed ignition sensitivity tests are designed to determine the sensitivity of the four mechanisms of heat production: pressure, friction, electrostatics, and direct application of heat.

3.3.1.1 Pressure Induced Reaction Sensitivity (Follow-on)

Reviewing the analysis of pressing, mixing/blending, and reaming, pyrotechnic mixtures are subjected to pressures in excess of 15,000 psi. In order to determine the ignition sensitivity of pyrotechnic compositions to pressure, a program of evaluation testing will determine the pressure sensitivity of initiation.

To meet the objectives of pressure-induced ignition testing, a hydraulic press will be used which is capable of exceeding by 50 percent the pressure encountered during normal operations at Pine Bluff Arsenal. The test procedure consists of placing the pyrotechnic material inside a thermally insulated die block and subjecting the material to increasing pressure until either ignition occurs or normal operating pressures are exceeded by 50 percent.

Data analysis consists of experimentally determining the linear relationship of temperature versus the work done on the system. The rate of work done (during consolidation) will be varied by using different rates of pressure application.

Presented in Figure 3-5 is a theoretical plot of Equation 3-4, temperature versus work; i.e.,

$$T_f = \frac{E}{C} + T_i$$

(Equation 3-4)

where \( E \), work done = \( \int F dx \).

The effect of a spurious occurrence may follow the abnormal process curve into an ignition condition as shown in Figure 3-5. In order to measure these relationships, the instrumentation and data package will consist of:

- A transducer to measure force applied by the ram during consolidation of mix.
- A linear position transducer to measure distance of ram travel.
- Three to four thermocouples placed in the mix, ram, and die areas to determine temperature profiles.
Figure 3-5. Hypothetical Plot of Temperature Versus Applied Energy

\[ \beta = \gamma \]

NORMAL PROCESS

ABNORMAL PROCESS

AMBIENT TEMPERATURE = \( T_1 \)

DECOMPOSITION/IGNITION TEMPERATURE

ENERGY \( E \)

TEMPERATURE

SLOPE = \( \alpha \)
3.3.1.2 Friction Induced Reaction Sensitivity (Follow-on)

Friction has been determined to be one of the most common causes of explosions and fires in the manufacture of pyrotechnics. Frictional effects associated with a particular manufacturing process cannot be quantitatively assessed in view of the difficulty of establishing its relationship and degree of involvement with the manufacturing process stimuli. What can be determined is the relative sensitivity of the compound or composition to various types of frictional stimuli.

An important consideration in frictional effects is whether the melting temperature is less than the ignition temperature. For example, if a material melts before ignition occurs, the melted material acts as a lubricant, lowering the coefficient of friction and, hence, the rate of heat formation.

For a full technical discussion of friction, reference should be made to reports and articles listed in the Bibliography which deal with pyrotechnic materials' sensitivity to friction as tested with various apparatuses:

- Fiber Shoe Friction Apparatus
- Steel Shoe Friction Apparatus
- Rotary Friction Apparatus

3.3.1.3 Electrostatic Discharge

To determine the ignition sensitivity of pyrotechnics to electrostatic discharge, a program of evaluation testing will determine the ignition sensitivity of pyrotechnic dust clouds (dust suspensions in a gas) and pyrotechnic powders. (Spark energy is discussed in paragraph B.14.)

3.3.1.3.1 Dust Suspension (Phase II, Segment 4)

Evaluation of pyrotechnic dust suspensions in terms of initiation, communication, and transition phenomena will be performed. Using a modified Hartmann apparatus for the ignition study of pyrotechnic dusts, measurements will be made to determine the:

- Minimum electrical energy of ignition as a function of dust particle density, humidity, and stoichiometric ratio.
- Maximum reaction-induced pressure and rate of pressure rise as a function of chemical imbalance of stoichiometric ratio.

Figure 3-6 shows the Bureau of Mines Hartmann Apparatus used for measuring the ignition energy, pressure, rate of pressure rise, and temperature of dust explosions. Ignition occurs by discharging a 24-watt continuous spark source; dust dispersion is accomplished by releasing air from a 3-cubic inch (50cc) reservoir at 100 psi. The chamber consists of a 2-3/4-inch diameter steel tube, 12 inches long, that is vertically mounted.
Figure 3-6. Bureau of Mines Hartmann Apparatus
Solid state circuitry has been designed to replace the original Hartmann firing circuit. In view of the requirement for measuring pressure rise developed by dust explosions, biomation transient recorders will be used to record the pressure from transducers located inside the chambers. The technique for interpretation of the data from Hartmann Apparatus testing is presented in Appendix C of this report.

3.3.1.3.2 Dust Layers (Phase III)

The apparatus shown in Figure 3-7 will be used to determine the minimum energy for spark ignition of a dust layer. The electrical energy required for ignition of a layer of pyrotechnic powder is determined by discharging a condenser across a spark gap containing a layer of pyrotechnic material. The test setup consists of connecting the positive terminal of the condenser to a probe and the negative terminal to a 1-inch diameter aluminum platen holding the dust.

3.3.1.4 Heat Transfer (Phase III)

The temperature of all equipment in contact with the pyrotechnic is far below the ignition temperature during normal processing of pyrotechnic materials. During abnormal operation, frictional effects producing hot chips or frictional sparks may result. If these hot elements contact the pyrotechnic material, the local temperature may exceed the ignition temperature. If the heat transferred forms a "hot spot" with heat content above a critical threshold level, then initiation will result. Differential thermal analysis techniques will be used to determine the ignition temperature of the various pyrotechnic materials for comparison with expected temperature excursions. Ignition via frictional spark contact will also be studied by causing frictional sparks to fall on various pyrotechnic materials.

3.3.2 Communication and Transition Tests

The purpose of communication and transition testing is to study the characteristics of a system interacting with its environment which affect the runup potential of the critical system from ignition to detonation. Specifically, the tests are designed to determine the potential of the reacting material for communication (by shock wave, fragmentation, pyrotechnic spray, etc.) to adjacent material, inducing ignition of the entire system. The end result is a much larger critical mass than the initiating mass; consequently, the incident is much more severe and the damage to equipment and personnel is much more extensive.

The effects of confinement are studied in two classes of boundary yield strength: "vessel confinement," in which a rigid walled vessel with non-zero yield strength contains the reacting material; and the less restricting case of "self-confinement." While the yield strength of a self-confinement configuration is essentially zero, the extra material supplies a small ambient pressure, and, because of its inertial mass, the material contains the reaction by-products for a
Figure 3-7. Test Setup of Spark Gap Test Fixture
The characteristics of dust suspension reactions are also of interest, particularly as a runup mechanism. The nature of the reaction of pyrotechnic dust suspensions may be such that certain dust densities or variations in density may run up to transition within the confines of a room, thus providing a severe hazard potential. The reality and importance of this type of simulation are borne out by history. Extensive accidents have occurred in manufacturing installations as a result of runup reactions propagating through dust cloud formations. This class of accident frequently results in severe damage to facilities and equipment and extensive injuries to personnel.

Communication between full scale components is discussed in paragraph 3.3.2.4.

3.3.2.1 Vessel Confinement

When a material deflagrates within an enclosed container, the gases liberated by combustion cannot escape, increasing the internal pressure until either the container ruptures or the reaction is complete. The reaction rate may be an increasing function of pressure, in which case the reaction may run up into detonation. The supersonic shock wave propagated during detonation has a shattering effect on the vessel and has a characteristic wave shape when observed with a transducer. While the shock wave shape is a function of the magnitude, duration, order of reaction, distance from source, and existence of reflected waves, it retains one characteristic feature in all situations. The rise time of the pressure front is always very short in duration as the thickness of this region is only a few mean free molecular path lengths. Thus, it is possible to determine whether a detonation has occurred by its characteristic signatures.

This technique is used in TNT equivalency testing to establish a material's energy output relative to TNT for equal masses. TNT equivalency testing was discussed in the Phase I final report and will be treated in more detail in the Phase III final report.

Although the instrumentation/detector techniques are identical, the testing philosophies of TNT equivalency and vessel confinement differ. Rather than determining material properties, the purpose of vessel confinement is to simulate the conditions of confinement presented in "worst case" manufacturing conditions to determine the runup potential under the worst conceivable conditions.

Reaction characteristics of pyrotechnics may depend on the method of ignition (as occurs with explosives). Ignition by detonation, as supplied by a blasting cap, may induce a reaction which remains supersonic or high velocity subsonic. Ignition by a hot wire, spark, or squib induces initially a low velocity subsonic reaction. Another consideration in the subsequent reaction rate is that some ignition sources induce turbulence of the material in the vicinity of the source. This
local dispersal of material may affect initial runup characteristics (see paragraph 3.3.2.3). Thus, in general, the reaction rate is a function of the method of ignition.

3.3.2.1.1 Confined Pyrotechnic Powder (Phase II, Segment 4)

This test series will simulate the worst case conditions occurring during manufacture. An analysis of manufacturing processes indicates that the worst case vessel confinement occurs during pressing. On the downward stroke of the piston, a condition of vessel confinement exists with very high rupture strength (greater than 50K psi), voids of 20 to 40 percent of the vessel volume, and pyrotechnic material in a loose powder. There are small leaks around the piston, but, for the purpose of establishing a worst possible condition simulation, the test vessel will have no leaks. Phase I TNT equivalency testing results indicated that maximal TNT equivalency resulted with a loosely packed powder in a vessel with 20 to 40 percent voids.

The conditions of vessel confinement, material dispersal, and percentage of voids in all other manufacturing processes are less severe than the conditions to be tested. Thus, a ceiling will be established beyond which no reaction will progress as a result of confinement during manufacture.

3.3.2.1.2 Confined End Items (Phase II, Segment 6)

The scope of Phase I TNT equivalency testing did not include testing of completely compressed pyrotechnics such as occur in most end items. Consequently, it is not known whether conditions of maximal density in which there are no voids and intimate contact between grains (in conditions of maximal consolidation, the grain structure is replaced by a single solid mass) and large internal stress components will run up under confinement. This situation occurs during the pressing operation at the end of the piston's compression stroke. A one or two percent void existing in the relief valve of the press die will be included in simulation.

Again, conditions in all other manufacturing processes are not as extreme as that discussed, so experimental results will provide a ceiling for all situations which include end item vessel confinement.

3.3.2.1.3 Reamer Simulation (Phase II, Segment 6)

During the reaming operation, a combination of end item and loose dust is present. Worst case testing of this environment will be performed by confining an end item with the end cap removed. Loose dust equivalent to that removed during a single reaming operation will be positioned at the exposed end of the end item and all will be confined in a rigid vessel. A worst case void will be included (probably 20 to 40 percent of the volume unoccupied by the end item).
3.3.2.2 Self-Confinement

The confinement of a reaction established by a moveable but massive outer layer of nonreacting material is a function of the area density (mass per unit area) of the confining material. Thus, a maximum credible degree of self-confinement results from concentrated, high pyrotechnic mass configurations. The mixing operation provides a worst case. Because bulks of up to 125 pounds are contained in an open-topped mixing bowl, the material distribution is concentrated in a compact volume and a high mass situation exists. But, in addition, a degree of vessel confinement is established by the mixing bowl.

Instrumentation/detection requirements are the same as those of vessel confinement. It should be noted that all confinement tests fall in the same generic experimental classification; hence, they have the same instrumentation requirements.

3.3.2.2.1 Vertical Section of Mixing Bowl (Phase II, Segment 4)

The mixing bowls used at Pine Bluff Arsenal are large (26-inch diameter by 24-inch depth) and, unfortunately, unavailable. However, simulation of the appropriate parameters affecting runup potential can be maintained without performance of a full scale test. The test configuration will consist of a vertical tube and bottom with rupture characteristics similar to the mixing bowls. The tube will be filled with pyrotechnic mix to a depth equal to the maximum depth of material in a mixing bowl, and ignition will be induced at the bottom of the tube to simulate the maximum credible conditions for runup by self-confinement.

3.3.2.2.2 Large Scale Mixing Bowl (Phase II, Segment 6)

In the limit of one-dimensional propagation of the reaction front, the vertical section test is sufficient to establish runup potential. To establish validity of the previous test, a large scale simulation of the worst case self-confinement afforded by a mixing operation is proposed. Again, ignition will occur at the bottom of the mix to correspond to a maximum credible degree of self-confinement.

3.3.2.2.3 Vertical Section of Dust Box (Phase II, Segment 4)

This test simulates the conditions encountered in the dust box which collects the excess material from the reaming process (see Figure 1-3). Ignition is induced near the exposed surface of the pyrotechnic material as would occur if frictional sparks of ignited material fell into the box. The vessel and instrumentation described in paragraph 3.3.2.2.1 can also be used for this study; but, rather than induce ignition at the bottom of the material, it will be ignited near the top.

3.3.2.3 Reactions in Pyrotechnic Dust Suspensions

Loose pyrotechnic powder is present in almost all manufacturing operations. Dispersal of some of this powder into the air forming a dust suspension provides a situation with a high hazard potential.
Bureau of Mines research indicates that fine particulate suspensions in air capable of supporting combustion can be made to run up into detonation in proper densities and sufficient volume. Because dust suspensions behave as a gas, they can occupy large volumes of a room. They can also interface with any exposed material to provide a means of communication to other components (this aspect of dust cloud reactions is discussed further in paragraph 3.3.2.4.5).

Dust clouds can be formed during normal operations, dispersed as a result of a spill, expelled by an incomplete explosion, or dispersed by the turbulence or shock of a reaction front. The terminal velocity of the reaction front may be subsonic for a given dust density, but, if a density gradient exists, the communication properties may be affected, opening the possibility of runup to supersonic velocities. Thus, the existence of a dust cloud or the potential for dust dispersal should be regarded as a potentially dangerous situation and worthy of study.

Dust suspensions of the final pyrotechnic mixtures are not the only materials of interest, for the component materials or incomplete mixtures encountered during manufacture may have similar or even more severe runup characteristics. Organic liquids with large vapor pressures, including heptane and acetone, are used in various manufacturing operations. The existence of their vapors in the air-dust mixture may affect reaction rates for a particular dust density, particularly since the presence of vapor increases the fuel-oxidizer ratio.

From a functional point of view, the primary requirement of a dust suspension investigation is to establish the acceleration of the reaction front as a function of its velocity and the dust density, material, and particle size. The availability of this information and the properties of a given dust cloud are sufficient to fully establish the kinematics (location as a function of time) of the reaction front and, hence, the distance and time to detonation. Unfortunately, such an ambitious task is well beyond the scope of this program.

Instead, three programs are proposed which will determine:

- The ability of a dust suspension of certain densities to support combustion.
- The propagation characteristics across a step change in dust density.
- The propagation characteristics in a large scale experiment with a variety of dust densities and density gradients.

3.3.2.3.1 Combustibility (Phase II, Segment 4)

The objective of this test is to establish the limits of dust density of pyrotechnics which will support combustion. The tests could be performed in a Hartmann Apparatus, but, rather than use a minimal energy spark, ignition should be by a positive means so that ignition sensitivity is not a factor. These data will establish a lower limit (and possibly an upper limit) to
consider in later dust runup reaction tests and to establish a safe upper limit for dust densities. The standard Bureau of Mines criteria is to use a 50 millijoule spark at a 500 Hz repetition rate throughout dust dispersal. This technique will be used if applicable.

Pressure inside the vessel as a function of time may be determined by pressure transducer probes. This information would contribute to establishment of the rate and completeness of the reaction.

3.3.2.3.2 Communication Across Density Change Interface (Follow-on)

Two distinct dust densities are maintained on either side of a thin, easily penetrated diaphragm. A reaction will be initiated in the chamber on one side of the diaphragm and allowed to propagate across the interface into a second chamber. The equipment will consist of a modified Hartmann apparatus as shown in Figure 3-8. Instrumentation will determine reaction front characteristics on both sides of the interface, and results will be interpreted in terms of the difference between the two readings as a function of the two dust densities. This data will be normalized to data obtained with equal dust densities.

3.3.2.3.3 Large Scale Gallery (Follow-on)

Simulation of large scale dust cloud reactions must be performed with large scale equipment. Bureau of Mines research has established that boundary influences of confining walls are significant. Because the walls affect reaction front velocities, wall separations should be as close to full scale as practical to properly assess the runup potential.

The results of the "combustibility" tests will establish lower limits on dust densities and the most reactive concentrations. The most positive ignition technique used in the "combustibility" tests will also be used in the gallery.

Three classes of experiments can be performed with a large scale gallery:

- A constant dust density may be maintained to establish the runup to detonation potential versus dust concentration. It is quite possible that the terminal velocity of the reaction front will be subsonic under these conditions.

- By varying the density as a function of distance from ignition point, the reaction front may be induced to run up to supersonic velocities. Therefore, while the former class of experiments is designed to establish the reaction properties of pyrotechnic dust suspension, the latter is designed to establish optimal conditions which lead to runup reactions in dust.

- Another class of experiment is an investigation of the communication characteristics of a dust cloud reaction with undispersed pyrotechnics. This class is discussed in paragraph 3.3.2.4.5.
Figure 3-8. Schematic of Modified Two-Stage Hartmann Apparatus
There are two classes of dust dispersal: prior to passage of the reaction front by external means, or coincident with the reaction front. The latter conditions may be encountered at processing stations in which there are open vessels or piles of pyrotechnic powders or where dust has settled on surfaces (particularly horizontal surfaces) (see paragraph 3.3.2.4.4).

The extensive studies performed by the Bureau of Mines on dust suspensions included dust materials which require an oxidizer to react. The air surrounding the particulate material provided the required oxygen (a maximum runup resulted when a stoichiometric ratio of material/oxygen was maintained). In the case of pyrotechnics, sufficient oxidizer to react with the fuel is already included in the material, but excess oxidizer as supplied by the air may increase the reaction rate by including the other components of the mix in the reaction and changing the energy output of the net reaction.

The suggested gallery configuration will have side walls and ceiling-floor separations of 4 feet each to minimize boundary conditions and a length of 32 feet to be consistent with typical maximum room dimensions. The dust will be dispersed by a turbulent air flow technique with predetermined concentrations defined by the mass of material and the gallery volume into which it is dispersed.

Instrumentation requirements include the ability to determine the reaction front velocity as a function of distance (or time), communication of the dust reaction with undispersed powder, and determination of the order of reaction in the pyrotechnic powder.

3.3.2.4 Large Scale Communication/Runup

The potential for occurrence of large scale accidents is limited by the ability of a reacting system to communicate with adjacent systems. If there is insufficient communication to initiate an acceptor system, the donor system is consumed and the accident is contained.

Because of the nature of this study, conditions which occur during manufacture are simulated in a maximum credible condition. The conditions deemed most likely to result in large scale communication are discussed in this paragraph.

3.3.2.4.1 Reamer Simulation (Phase II, Segment 6)

This test will simulate the conditions/environment occurring during normal operation of a reamer (for example, see Figure 1-3). Ignition will be induced by a blasting cap in a canister partially confined by a simulated reamer blade surrounded by settled dust equivalent to that distributed during normal reaming operation.
3.3.2.4.2 Communication Between Separated Concentrations (Phase II, Segment 6 and Follow-on)

This is a study of the parameters involved in the communication of large masses (≥ 1 pound) of pyrotechnic materials and items. Thus, the communication characteristics of existing configurations will be determined and criteria can be established for future design.

3.3.2.4.3 Conveyor Belt Distribution (Follow-on)

The communication of a reaction along a continuous linear distribution of material simulates the conditions which would occur if a fire is started or communicated to a conveyor belt transporting pyrotechnic material.

3.3.2.4.4 Settled Dust (Follow-on)

After dust has been dispersed in the air, gravity will cause it to settle on exposed surfaces (particularly horizontal surfaces). If allowed to accumulate for long periods of time, large concentrations may result, presenting a significant runup potential (see paragraphs 3.3.2.3 and 3.3.2.3.3).

Deflagration of pyrotechnic dust may remain relatively inactive or it may run up. Conditions at the surface are similar to those in a dust suspension, i.e., large ratio of air volume to gain surface exposure, so that runup will be possible, particularly when large areas are exposed. Reaction turbulence may redisperse some or all of the dust so that the reaction can propagate in the dust suspension. If these conditions culminate in reaction runup to detonation, the shock wave may precondition the dust, permitting the detonation to be self-sustaining.

The gallery and instrumentation discussed in paragraph 3.3.2.3.3 can also be used for this test.

3.3.2.4.5 Communication from Dust Cloud to Powder (Phase II, Segment 6 and Follow-on)

Reaction runup in dust suspensions and communication to nondispersed pyrotechnics were discussed in paragraph 3.3.2.3. When the detonation or near detonation reaction front propagates to an interface with pyrotechnic powder, slurry, or end items, it encounters a significantly different environment. Whether it will continue to propagate, run up, run down, or fail to penetrate will depend on the nature of the incident reaction front and on the condition of the target material.

The high velocity reaction front can be generated in the gallery (paragraph 3.3.2.3.3) with the target situated at the downstream end of the gallery. Instrumentation will be sufficient to observe the communication characteristics at the interface and to determine the order of reaction in the target.

Segment 6 testing will simulate the maximum credible runup situation in processing. The dust suspension densities will be determined by considering the situation in which the contents of a
mixing bowl containing 125 pounds of pyrotechnic are spilled in a typical processing room. Worst case dispersal of this dust will be in an increasing density so as to have a minimum density sufficient to support combustion at the ignition end, increasing geometrically towards the other end, and terminating at a second full (unspilled) vessel.

3.3.3 SCALE TESTS

Two types of experiments which have been performed and will be included in the Phase II, Segment 4 final report are introduced, but not discussed in detail, in this section.

In the first test, the most hazardous end item under consideration is allowed to function normally with the objective of determining the hazard potential of the item, establishing requirements for protection from the incident severity and designing a shielding structure capable of suppressing the effects.

The second test is designed to determine the effect on reaction rate of large quantities of end items normally packaged and confined in a simulated tractor trailer van.

3.3.3.1 WP Operational Shielding (Phase II, Segment 4)

A 4.2-inch white phosphorous round (M-328A1), deemed the most violently reacting of all pyrotechnic rounds, is used in this test to establish a worst case condition. Open air testing of the round establishes the fragment, fireball/afterburning, pyrotechnic material dispersion, and blast overpressure characteristics. High speed motion picture coverage and fragment penetration in Celotex establishes fragment characteristics (velocity, angular distribution, weight, and distortion). Blast overpressure is measured by side-on pressure transducers. Fireball/afterburning and WP dispersion patterns are recorded by high speed motion picture coverage.

Several concepts in suppressive structure design are tested by exposure to effects of a WP round. Instrumentation requirements are identical to that used for open air testing. Results are interpreted both in absolute terms (survivability adjacent to structure) and in relative terms (percent reduction of incident severity relative to open air results).

3.3.3.2 C/S Trailer Van Simulation (Phase II, Segment 4)

This test is a simulation of the conditions occurring as a result of accidental ignition of one C/S canister located in a filled shipping container aboard a closed trailer van. Two tests are performed, one including nine 48-canister cartons and the other using one 500-canister carton. Both tests are observed with high speed motion picture coverage, internal pressure measurements, and internal and external temperature measurements, and results are compared for the two configurations.
BIBLIOGRAPHY


Doc. 159  Armour, Carl. The Invention of a New Type of Friction Sensitivity Apparatus. AD618 382. Research and Development Department, U. S. Naval Ammunition Depot, Crane, Indiana. 11 June 1965.


A.1 RESULTS OF SEGMENT 2, PHASE II OPERATIONAL SURVEY

It has been concluded from Segment 2, Phase II, 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 A-I, 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>
<thead>
<tr>
<th>Process</th>
<th>Station</th>
<th>Blending/Mixing</th>
<th>Filling</th>
<th>Pressing</th>
<th>Reaming</th>
<th>Miscellaneous</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>M18 Grenades</td>
<td></td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>155mm Canisters</td>
<td></td>
<td>1</td>
<td>-</td>
<td>9</td>
<td>11</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Other Canisters</td>
<td></td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>2</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>XM675 Cartridges</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>XM176 Launchers</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>M126 Bomblets</td>
<td></td>
<td>2</td>
<td>6</td>
<td>4</td>
<td>-</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Starter Mix</td>
<td></td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>5</td>
<td>6</td>
<td>20</td>
<td>13</td>
<td>4</td>
<td>48</td>
</tr>
</tbody>
</table>

(10%) (13%) (40%) (27%) (10%) (100%)

A.2 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 of 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 the Phase II research testing program have been developed for the Phase II program 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 towards a nine-step method that can be adopted to a variety of situations. The results can thus be written in a nine-column matrix with accompanying diagrams. As shown in Figure A-1, the nine-step approach utilized during the Phase II program included:

- Under Segment 2, Phase II, Operational Survey, 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.

Tables A-2 through A-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
Figure A-1. Hazard Analysis and Matrix Sequence Chart
Table A-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)

<table>
<thead>
<tr>
<th>COMPONENT LOCATION</th>
<th>FUNCTIONAL DESCRIPTION</th>
<th>FAILURE MODE</th>
<th>SECONDARY FAILURES</th>
<th>FAILURE EFFECT</th>
<th>NUMBER OF ACCIDENTS</th>
<th>CRITICAL EFFECT</th>
<th>CORRECTIVE ACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die, Ram and Mix</td>
<td>Molding of pyrotechnic mix under controlled pressure conditions in metal containers</td>
<td>1. Misalignment</td>
<td>Jamming of ram in die</td>
<td>Friction: generation of excessive heat concentration by excessive pressure</td>
<td>4</td>
<td>Fire</td>
<td>Check ram and die tolerances and replace steel ram tip with brass ram tip</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Impact</td>
<td>Jamming of ram in die</td>
<td>Friction: generation of excessive heat concentration by excessive pressure</td>
<td>6</td>
<td>Explosion</td>
<td>Check hydraulic pressures in system</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Contamination</td>
<td>Misalignment - in addition, mix not of uniform density</td>
<td>Possibly sensitize mixture and result in lowering of the threshold ignition energy</td>
<td>Unknown</td>
<td>Possible explosion due to heat buildup as a result of excessive heat and pressure</td>
<td>Check compliance with procedures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Improper procedure, excessive mix</td>
<td>Misalignment</td>
<td>Friction: generation of excessive heat concentration by excessive pressure</td>
<td>6</td>
<td>Fire</td>
<td>Have personnel ensure that dies have been thoroughly cleaned and inspect for excessive mix</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>Explosion</td>
<td></td>
</tr>
</tbody>
</table>


Table A-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)

<table>
<thead>
<tr>
<th>COMPONENT LOCATION</th>
<th>FUNCTIONAL DESCRIPTION</th>
<th>PRESSURE ROOM</th>
<th>PUNCH AND PRESSURE CYLINDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die and Ram</td>
<td>Shorting between ground leads</td>
<td>5.</td>
<td>2.</td>
</tr>
<tr>
<td></td>
<td>Unpowered die and ram.</td>
<td>6.</td>
<td>Unknown</td>
</tr>
<tr>
<td></td>
<td>Press Room</td>
<td>Self-explanatory</td>
<td>Pressure which raises and lower ram and stand which supports assembly</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SECONDARY FAILURES</th>
<th>FAILURE EFFECT</th>
<th>NUMBER OF CRITICAL EFFECTS</th>
<th>CORRECTIVE ACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charge buildup between die and ram and eventually charge transfer</td>
<td>1.</td>
<td>Fire</td>
</tr>
<tr>
<td></td>
<td>Toxic atmosphere and poor visibility</td>
<td>1.</td>
<td>Fire</td>
</tr>
<tr>
<td></td>
<td>Improper heat dissipation from lighting fixtures and surrounding machinery</td>
<td>2.</td>
<td>Fire</td>
</tr>
<tr>
<td></td>
<td>Misalignment</td>
<td>1.</td>
<td>Pressure</td>
</tr>
<tr>
<td></td>
<td>Vibration</td>
<td>2.</td>
<td>Excessive pressure</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PRIMARY FAILURES</th>
<th>NUMBER OF ACCIDENTS</th>
<th>EFFECT ACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fire</td>
<td>Explosion</td>
</tr>
<tr>
<td></td>
<td>Fire</td>
<td>Explosion</td>
</tr>
<tr>
<td></td>
<td>Fire</td>
<td>Explosion</td>
</tr>
<tr>
<td></td>
<td>Fire</td>
<td>Explosion</td>
</tr>
<tr>
<td></td>
<td>Fire</td>
<td>Explosion</td>
</tr>
</tbody>
</table>

A-5
<table>
<thead>
<tr>
<th>COMPONENT LOCATION</th>
<th>FUNCTIONAL DESCRIPTION</th>
<th>FAILURE MODE</th>
<th>SECONDARY FAILURES</th>
<th>FAILURE EFFECT</th>
<th>NUMBER OF ACCIDENTS</th>
<th>CRITICAL EFFECT</th>
<th>CORRECTIVE ACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press and Press Stand (cont'd)</td>
<td>3. Ungrounded press</td>
<td>Shorting between ground leads</td>
<td>Charge buildup and transfer</td>
<td>Possible fire/explosion</td>
<td>Check grounds</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-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)

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

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

<table>
<thead>
<tr>
<th>COMPONENT LOCATION</th>
<th>FUNCTIONAL DESCRIPTION</th>
<th>SECONDARY FAILURE</th>
<th>FAILURE MODE</th>
<th>NUMBER OF ACCIDENTS</th>
<th>EFFECT</th>
<th>CORRECTIVE ACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reamer Mix, Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Damaged bevel, placed canister in canister or backwards</td>
<td>Improper procedure</td>
<td>2</td>
<td>Fire</td>
<td>Safety instruction on procedures</td>
</tr>
<tr>
<td>Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Jamming of bevel in canister, damaged by bevel abrading canister and mix</td>
<td>Damaged bevel, placed canister in canister or backwards</td>
<td>9</td>
<td>Fire</td>
<td>Check check for misalignment</td>
</tr>
<tr>
<td>Reamer Mix, Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Misalignment of bevel in canister, damaged by bevel abrading canister and mix</td>
<td>Misalignment</td>
<td>2</td>
<td>Fire</td>
<td>Require 100 percent inspection for conformity</td>
</tr>
<tr>
<td>Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Misalignment of bevel in canister, damaged by bevel abrading canister and mix</td>
<td>Misalignment</td>
<td>100</td>
<td>None</td>
<td>Safety instruction on procedures</td>
</tr>
<tr>
<td>Reamer Mix, Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Damage to canister which could result in explosion</td>
<td>Impact by high pressure</td>
<td>5</td>
<td>Possible fire/ explosion</td>
<td>Check grounding leads</td>
</tr>
<tr>
<td>Canister</td>
<td>Mix in canister, flat faced or flattened by bevel</td>
<td>Damage to canister which could result in explosion</td>
<td>Impact by high pressure</td>
<td>5</td>
<td>Possible fire/ explosion</td>
<td>Check grounding leads</td>
</tr>
</tbody>
</table>
Table A-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)

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

A.3 CONCLUSIONS

In paragraph A.2 a fairly comprehensive program for identifying processing conditions under which ignition can occur was developed. In order to cover the results of these findings and indicate their relevancy to specific process ignition mechanisms, a fault tree analysis (Figures A-2 through A-5) 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.
Figure A-2. Fault Tree Analysis of Pressing Operation
Figure A-3. Fault Tree Analysis of Blending/Mixing Operation
Figure A-4. Fault Tree Analysis of Reaming Operation
Figure A-5. 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.

A.3.1 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 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

A.3.2 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.
A.3.3 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.

A.3.4 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 B
RELATED MATERIAL PROPERTIES

B.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, and transition.
- Energy release characteristics to assess the margin of safety of the manufacturing operation.

B.2 TNT EQUIVALENCY
Mathematical techniques are applied to obtain a relationship between blast overpressure of pyrotechnic materials tested and that of TNT. (Refer to the Phase I report for the methodology and concepts of TNT equivalency determination.)

B.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.

B.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.

B.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.

B.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 B.5), assuming an ideal gas and determination of the gas temperature.

B.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.

B.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.

B.9 BULK MODULUS

The modulus, $\beta$, of volume elasticity can be expressed as

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

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.
B.10 ELECTRICAL CONDUCTIVITY

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

B.11 DIELECTRIC CONSTANT

The dielectric constant of a medium is defined by $\varepsilon$ in the equation

$$F = \frac{Q Q'}{\varepsilon r^2}$$

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

B.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.

B.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 B.14).

B.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.
APPENDIX C
HAZARDS EVALUATION FROM DATA ANALYSIS OF DUST EXPLOSIONS

Using a standardized technique developed by the Bureau of Mines for comparing the explosion hazards of dusts, values of the parameters affecting ignition and explosion of a test sample will be compared to those of the Bureau of Mines standard, Pittsburgh coal. The advantage of comparing results to the Bureau of Mines standard is that conclusions and data obtained can relate to Bureau of Mines minimum safety classification concerning dust explosions.

The explosibility index is a product of the ignition sensitivity and explosion severity which are defined as follows:

- Ignition Sensitivity = \( \frac{\text{Ignition temperature} \times \text{minimum energy}}{\text{Coal}} \frac{\text{Ignition temperature} \times \text{minimum energy}}{\text{Sample}} \)
- Explosion Severity = \( \frac{\text{Maximum explosive pressure}}{\text{Coal}} \frac{\text{Maximum explosive pressure}}{\text{Sample}} \)
- Explosibility Index = Ignition sensitivity \times explosion severity

The explosibility index is a numerical rating which facilitates comparison of the potential hazards of any dust suspension and is normalized to unity for samples having ignition and explosion characteristics equal to coal. The relative explosion hazard of mixtures may be further classified by adjective ratings of weak, moderate, strong or severe. The adjective rating may be correlated with the empirical index as shown in Table C-1.

Table C-1. Adjective Rating of Relative Explosion Hazard Correlated with Empirical Index

<table>
<thead>
<tr>
<th>Type of Explosion</th>
<th>Ignition Sensitivity</th>
<th>TNT Equivalency</th>
<th>Explosibility Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>&lt; 0.2</td>
<td>&lt; 0.5</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Moderate</td>
<td>0.2-1.0</td>
<td>0.5-1.0</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Strong</td>
<td>1.0-5.0</td>
<td>1.0-2.0</td>
<td>1.0-10</td>
</tr>
<tr>
<td>Severe</td>
<td>&gt; 5.0</td>
<td>&gt; 2.0</td>
<td>&gt; 10</td>
</tr>
</tbody>
</table>

The aforementioned classification technique and rating are established by Bureau of Mines methodology. Application of these standards to pyrotechnic dust suspensions is a new concept. The advantage of using this technique for pyrotechnics is its relevancy to hazards classification, its applicability to all dust suspensions, and the ability to classify pyrotechnics relative to other dusts.