DEVELOPMENT OF A PRELIMINARY HAZARD ANALYSIS (PHA)

OF

BINARY REACTOR

BY

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LITERATURE CITED

1. Military Standard 882B, System Safety Program Requirements, 30 March 1984.

PREFACE

This report was developed in support of the Chemical Research and Development Center (CRDC) Safety Office. Although it addresses many of the health and safety aspects of a safety program during the evaluation process of a Standing Operating Procedure (SOP), this publication cannot be all encompassing. Supplementary and/or specific guidance is contained in the selected references.

1. INTRODUCTION

The Chemical Research and Development Center (CRDC) mission is to conduct research and to provide life cycle engineering for chemical weapons, and chemical and biological defense. For CRDC to meet its mission requirements, operations must be conducted utilizing chemical agents. One means used by the Safety Office to ensure compliance with safety and operational requirements is to require a Standing Operating Procedure (SOP) for all hazardous operations. During the SOP review process, a preliminary hazard analysis (PHA) is develcped for new operations involving chemical agents.

The purpose of this report is to define the requirements for a PHA, the methodology used to develop a PHA, and to show the applicability of a PHA for use with chemical agent operations.

The operation being evaluated by PHA in this report is the binary reactor. The binary reactor is a pressure vessel specifically designed to simulate a munitions formation of binary lethal agents under various test conditions.

2. METHODOLOGY

A PHA is a working document developed during the planning stages of the operation. It is used as a comprehensive safety evaluation of the operation. The PHA identifies hazardous conditions, causes of these situations, hazard severity, hazard probability, and the recommended corrective actions to be taken to alleviate the hazardous conditions.

A PHA should be developed for new operations involving chemical surety materiels. A PHA is developed in the following sequence. The rough draft of the SOP is received from the operating division for review. During the review process, a PHA is developed for the SOP. The information used in the PHA is derived from the rough draft SOP, interviews with the operators, and pre-operational runs with simulants. During the review process, hazardous conditions are identified and corrective actions are developed to eliminate or control the hazard. The corrective actions from the PHA are provided to the operating division and incorporated into the SOP. The SOP is then submitted for final approval.

Various formats are used when developing a PHA, the more commonly used are columnar, narrative or logical diagram. The format currently being used for the development of PHA's by the author is the columnar format for the procedural analysis with a narrative introduction. The introduction has a section on the hazard severity and hazard probability tables being used from MIL-STD-882B, the statement of work, a description of the decontamination solutions require for the operation, the chemicals being used in the operation and chemical surety materiel formed, miscellaneous hazards, and the personal protective clothing and equipment required for the operation.

The columnar portion of the PHA is divided into seven sections. The sections include System Event(s) Phase, Hazard Description, Effect on System, Risk Assessment, Recommended Action, Effect of Recommended Action on Risk Assessment, and Remarks.

The System Event(s) Phase section is used as a identifier of the hazard described within the SOP. Each paragraph in a SOP is numbered and that number is placed in this column for ease of locating the hazard in the SOP.

The Hazard Description Section identifies the hazardous situation or critical safety concern within that specific step of the operation.

The Effect on System section describes the possible injury to the operators due to the hazard, the damage to the equipment, and the possibility of chemical surety materiel being released from containment.

The Risk Assessment section utilizies the symbols from the tables in MIL-STD-882B for the coding of hazard severity and hazard probability for a given hazardous situation.

The "Recommended Actions" section contains corrective actions formulated to reduce or eliminate the hazardous situation and/or the associated risk with a specific step of an operation. In some instances there are several alternative recommended actions which may be employed to alleviate a hazardous situation.

The "Effect of Recommended Action(s)" on the Risk Assessment section evaluates the recommended action to be employed for a given hazardous situation and reassigns a new risk assessment code to the specific step of the operation.

The Remarks section is used to list references and other significant comments.

Each section of the columnar format is used for every identified hazardous situation and the recommended action is incorporated into the SOP prior to final approval from the Safety Office.

3. PROCEDURAL

The operation being evaluated by this report is the binary reactor. The SOP for this operation is entitled "Binary Lethal Agent Reaction Studies". The SOP contains sections which list the materials and equipment being used, hazards involv with the operation, specific safety requirements, operational procedures, and emergency procedures. The PHA evaluates these procedural sections of the SOP. Appendix A is a portion of the SOP submitted to the CRDC Safety Office for review.

4. Evaluation

The completed PHA is attached as Appendix B and the major findings of that document are as follows:

Hazard: Overpressurization of the binary reactor during operation.

Corrective Action: To equip the binary reactor with both a manual and an automatic relief valve. The automatic relief valve is preset at 90 psi and the operator actuates the manual relief valve when the internal pressure within the binary reactor exceeds 120 psi.

Hazard: Pressure builds up within the binary reactor.

Corrective Action: Have the binary reactor hydrostatically pressure tested prior to use. The binary reactor will be tested for pressures in excess of the safety relief valves and the expected pressures to be produced by the reaction.

Hazard: The ventilation system fails during the operation.

Corrective Action: The operators will stop the operation as soon as possible. The individuals within the laboratory will don protective mask. The operators will containerize any open agent and then all personnel will evacuate the laboratory.

Hazard: Aluminum foil burst disk not installed properly or is leaking during the filling of the second component of the binary reactor.

Corrective Action: During the filling of the second component of the binary reactor, monitor the temperature of the first component on the recorder readout. If the thermal readout indicates leakage (increase in temperature), stop the filling operation, let the reacted material cool and then initiate cleanup procedures.

Hazard: Flammable solutions within the glovebox when electrically functioning the sampling and injection solenoids.

Corrective Action: Remove all flammable solutions from the glovebox prior to electrically functioning of the sampling and injection solenoids.

5. Conclusions

A PHA was very useful during the review process of SOP entitled "Binary Lethal Agent Reaction Studies". Several hazards were identified and the safeguards which were developed were placed into the SOP. These safeguards will enable the operator to conduct the operation of the binary reactor in a safer manner. It is felt by the author that a PHA should be developed for all hazardous operations.

APPENDIX A

Appendix A
will be furnished upon request.

Appendix B

This section of the report presents the results of the PHA which was developed for the SOP entitled "Binary Lethal Agent Reaction Studies" at Edgewood Area, Aberdeen Proving Ground.

a. Introduction:

The PHA identifies the hazards, possible causes, and formulates the risk assessment for each identified operational phase. Recommended actions to eliminate or control the identified hazards and to develop safety criteria for the operation.

2. Risk Assessment Tables:

ATTACHED

3. Statement of Work:

Conduct laboratory binary lethal agent reactions to study their formation in support of various binary agent munition programs. Several combinations of agent intermediates and catalysis will be mixed in a hastelloy reactor to determine the approximate agent reaction times, maximum temperatures, maximum pressures, purity of timed samples under controlled conditions. The data will be recorded for support of engineering and designing binary munitions.

4 Decontamination Solution:

There must be a readily available supply of an appropriate decontamination solution as well as adequate dispensing equipment. Personnel involved with the operation be properly trained in use of the decontamination solution and the dispensing equipment. Decontamination crews must have access to personnel protective clothing and equipment, and be trained in their use.

The following decontamination solutions are required dependent on the chemical agent being generated.

a. STB and HTH. US Army super tropical bleach (STB) is solid calcium hypochlorite stabilized with calcium oxide for storage in the tropics, and HTH is commercially available High Test Hypochlorite. HTH has a higher available chlorine content. The terms STB and HTH are interchangeable for use in this paragraph. Both STB and HTH are bleaches, strong oxidizers, and when the neat (solid) bleach is mixed with oxidizable materials (i.e., HD, alcohols), flames can be produced. STB and HTH are to be used as a 40/60 slurry (40 parts bleach stirred into 60 parts water). Bleach slurry is effective due to its base content and its oxidizing properties.

b. Household Bleach. Commercial chlorine household liquid bleach is a five percent to 5.25 percent sodium hypochlorite solution in water, sold as "Clorox", "Purex", and other trade names, these are also effective due to their basicity and oxidizing properties.

c. Sodium Hydroxide. Also known as caustic soda, lye. Sodium hydroxide is normally used as a five percent and a 10 percent solution in water (aqueous), or in a 50/50 alcohol-water solution (alcoholic). The alcohol could be methanol, ethanol, isopropanol, or methylcellosolve depending on availability, intended use, and flash point (fire safety) concerns. CAUTION: Mixtures of alcoholic caustic and chlorinated solvents slowly degas, therefore, those mixtures must not be put into a closed container.

d. Water. Water reacts with some of the chemical agents rapidly, but with others it reacts very slowly to not at all. Water is not in itself considered a good general decontaminant because of lack of reactivity and solubility. However, soap and water, and/or a safety shower, are suggested for the first step in personnel decontamination. A soap and water wash of hands and arms is required after handling toxic materials. In these cases, the toxic material is physically removed from the skin by a combination of mechanical and solvent action.

5. Chemicals being generated or being used during the operation.

a. Nerve gas

1. The principal hazard from nerve agents is agent vapor inhalation with sonsequent absorption through the respiratory tract, although all the agents may be absorbed on contact through the intact skin, through eyes, and through gastrointestinal tract, if ingested. All are highly toxic and quick acting. At ambient temperatures, GB is a liquid with moderate vapor pressur . When dispersed as large droplets, GB is moderately persistent; it

is nonpersistent when dispersed as a cloud of very fine particles. VX and GD are persistent and are primarily a liquid hazard. Inadvertent skin contact is the principal hazard from these agents. Percautaneous exposure to either liquid or vapor may be fatal, although the dosage by the percautaneous route is much higher than the respiratory route.

2. Some agents, GD in particular, are mixed with a thickener resulting in a solution or gel resembling rubber cement or glue. Swabs, pipettes, or hypodermic needles may trail stringers or filaments of solution. This effect is most pronounced in solutions having viscosities in the range of 1000-3000 centistrokes. These stringers may be distributed by air streams resulting in contamination at the working area. One technique for dealing with this hazard is to hold a towel downstream from swab, pipette, or hypodermic needle and to wipe the tip of the device before proceeding with the operation.

a. Methyl Phosphonic Difluoride(DF) is a strong acid which reacts violently with water; exposure will cause burns/rash. Prolonged exposure to vapors causes damage to the nervous membranes and may cause bronchitis, hazard to the eyes.

b. Alcohol/Amines are a non-hazardous component of the reaction, slight flame hazard, skin and eye irritant.

c. QL can irritate the mucous membranes and cause headaches.

d. Diisopropylcarbodiimide (DICDI) causes severe erythema on contact with the skin and will cause corneal damage upon contact with the eye. DICDI is a suspected mutagen or carcinogen due to its chemical structure.

6. Electrical Equipment. Electrical equipement shall be free from hazards that are likely to cause death or serious physical harm to employees. Compliance with OSHA 1910.303, 304, 305 and the National Electrical Code is mandatory. All flammable liquids will be removed from the glove box prior to the starting of the operation.

7. Personal Protective Clothing and Equipement (PPC&E). Personnal protective clothing and equipment to be worn during the operation are listed in Section 6d of the SOP. The hazards likely to cause death or serious physical harm to employees when wearing PPC&E are not suiting up properly, wearing improper or damaged protective clothing, and tearing protective clothing while conducting the operation.

System Binary Lethal Agent Reaction Studies

Subsystem _____

Component _____

Prepared by: _____

Issue Date: 5 July 83

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(1) (7a 5)	The reuse of non-standard glove-box gloves for an operation.	Possible skin contact with agent through a hole/tear in the glove or by agent which has penetrated through the glove.	I	B	Replace non-standard glove-box gloves prior to every operation. In the event of an actual or suspected liquid agent contamination, the gloves will be decon-taminated and removed as soon as feasible. All gloves will be leak tested prior to use.	III C	IAW DARCOM R 385-102, para 4-2 (g)(2)
(2) (7a 6) (7a 13)	Handling binary intermediate chemicals with-out gloves or approved gloves.	Possible skin irritation from amines and QL. Possible erythema from DICDI and burns/rash from DF.	II	B	Use protective rubber gloves when handling amines and QL. The operator will wear protective rubber gloves, rubber apron, and chemical goggles or face-shield when handling DICDI and DF.	III D	

System Binary Lethal Agent Reaction Studies — Prepared by: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(1) (7a 5)	Wearing non-standard gloves beyond specified time limit.	Possible loss of protection from non-standard gloves and potential exposure to operators by agent penetration of gloves.	II	B	When using non-standard gloves, use a timing device with an audible alarm to prevent usage of gloves past the specified time limit.	IV D	IAW CSL SOP 385-1 para 4-7 (b) (2)
(4) (7a 10)	Flammable solutions within the glovebox when electrically functioning the sampling and injection solenoids.	Possible ignition of flammable solution.	I	B	Remove all flammable solutions from glovebox prior to electrically functioning of the sampling and injection solenoids.	IV D	

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(5) (7a 14)	Aluminum foil burst disk not installed properly or is leaking.	Possible premature formation of agent.	II	B	During filling of the second component, monitor the temperature of the first component on the recorder readout. If thermal readout indicates leakage (increase in temperature), stop filling operation, let reacted material cool and then initiate clean-up procedures.	III C	
(6) (7a 18)	Operator keepirg hands inside of the glovebox during the mixing of the material within the binary reactor.	Possible pressure build-up during mixing process and reactor vents.	II	B	Operator will remove hands from the glovebox during the production of agents.	III C	

System Binary Lethal Agent Reaction Studies — Prepared by: _____

Subsystem _____ — Issue Date: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(7) (7a 20)	The automatic relief valve (spring loaded) does not actuate at the preset pressure.	Possible pressure build-up and possible rupture of reactor and operator injury.	II	B	a) If automatic relief valve (spring valve) does not actuate and pressure builds within the binary reactor, the operator will actuate the manual relief valve to vent the binary reactor, until the internal pressure is 0 psi. b) Change automatic relief valve (spring valve) to a simpler type of a relief valve (i.e, burst disk).	II C	

System Binary Lethal Agent Reaction Studies

Subsystem _____

Component _____

Prepared by: _____

Issue Date: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(8) (7a 23)	Removal of sample bottles from the glovebox	Possible agent release from contaminated bottles.	II	B	Operator cleans contaminated gloves with appropriate decontamination solution. Wipe the bottles with decontamination solution and then test bottles with M8 paper. Repeat test until no agent is indicated. Seal sample bottles with parafilm and pass bottles through the passbox to the hood. Bottles will be placed with a can and sealed and then placed within another can and then sealed. Properly label outside of storage containers.	III D	

System Binary Lethal Agent Reaction Studies

Subsystem _____

Component _____

Prepared by: _____

Issue Date: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(9) (7a 26)	Clean-up Operation of binary reactor and glovebox.	Possible agent exposure to personnel.	II	C	All excess agent will be containerized in a bottle. The reactor and components will be washed down with acetone and the washings will be poured in the same bottle that the excess agent was placed into. The bottle will be cleaned and sealed with parafilm and passed to the passbox. Paper waste refuse and solid waste will be placed into a solid waste container. The lower portion of the glovebox will be washed down with a caustic (bleach) acetone mixture (only the lower surface of the glovebox). Decontaminate and remove gloves and place in solid waste can, pour removing decontamination solution over solid waste.	III D	

System Binary Lethal Agent Reaction Studies — Prepared by: _____

Subsystem _____ — Issue Date: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(10) (7a 29)	Operators leave work area without washing hands.	Possible that operators' hands are contaminated with intermediate chemicals or agent.	III	C	IAW good laboratory practices operators should was hands and arms with soapy water prior to leaving the work area.	IV D	
(11)	Ventilation failure during the operation.	Glovebox losses negative pressure and hood drops below 150 ± 30 lfpm. Possible agent migration from ventilated containment.	II	B	Stop operation as soon as possible, individuals in laboratory don mask, containerize any open agent and evacuate laboratory.	III C	

System Binary Lethal Agent Reaction Solution — Prepared by: _____

Subsystem _____ — Issue Date: _____

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System Event(s) Phase	Hazard Description	Effect on System	Risk Assessment Sev.	Risk Assessment Prob.	Recommended Action	Effect of Recommended Action	Remarks
(12)	Glovebox leaks material after reactor vents contents.	Possible exposure to unprotected personnel.	II	B	Operators mask and help in the evacuation of the building.	III C	
(13)	Pressure builds up within the binary reactor during the operation.	Reactor ruptures. Possible release of agent. Possible damage to glovebox and injury to operating personnel.	I	B	Have binary reactor hydrostatically pressure tested prior to use. Have reactor equipped with an automatic relief valve and a manual relief valve.	III C	