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AFRPL-TR-66-173

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**FINAL REPORT
INVESTIGATION OF TECHNIQUES FOR DECONTAMINATION
AND CONTROL OF ADVANCED PROPELLANT SPILLS**

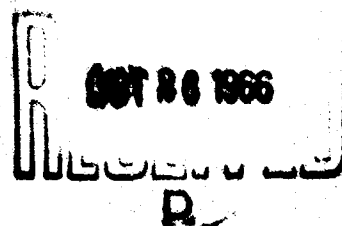
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TECHNICAL DOCUMENTARY REPORT NO. AFRPL-TR-66-173

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ALLIED CHEMICAL CORPORATION
September 1966

AFSC, Air Force Flight Test Center
Directorate of Procurement
R & D Contracts Division, FTMKR-2
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FINAL REPORT
INVESTIGATION OF TECHNIQUES FOR DECONTAMINATION
AND CONTROL OF ADVANCED PROPELLANT SPILLS
(Unclassified Title)

R. B. Jackson

J. M. Siegmund

J. J. Belles, Jr.

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FOREWORD

This report was prepared by the General Chemical Division of Allied Chemical Corporation under USAF Contract No. AF 33(615)-2356. The program was initiated and funded by:

Air Force Aero Propulsion Laboratory
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The program was administered under the direction of the Air Force Flight Test Center, Directorate of Procurement, R & D Contracts Division, FTMKR-2, Edwards Air Force Base, California. The project engineer and technical monitor for the contract was Mr. Hugh E. Malone.

This report covers work conducted from March 1, 1965 to February 28, 1966 to determine suitable decontaminants and techniques for the control of propellant spills. Classified information has been extracted from asterisked documents listed under References. This report was prepared by Messrs. R. B. Jackson, J. M. Siegmund and J. J. Belles, Jr. In addition to the authors, Mr. W. M. Farley had made a substantial contribution to this work.

This technical report has been reviewed and is approved.

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ABSTRACT

Decontaminants for several toxic missile propellants were evaluated and recommendations were made for the most suitable materials.

The investigation was conducted in two phases. Phase I, a practical study of the propellants, consisted of a compilation of information pertaining to general properties, decontamination procedures and toxicity data based on a literature review. The materials thus investigated were fluorine, hydrazine, nitrogen tetroxide, hydrogen, light metal hydrides, beryllizine, Compound A, mixed hydrazine fuels, alumizine and UDMH.

Phase II, a laboratory investigation, involved the experimental evaluation of candidate decontaminants. This work, together with a theoretical evaluation of decontaminants based on the practical study, involved four propellants: Compound A, mixed hydrazine fuels (MHF-3 and MHF-5) and alumizine.

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INTRODUCTION

As propellant systems become more energetic, the hazards involved become increasingly severe. With greater emphasis being placed by the military on high energy propellants, it becomes mandatory that means be developed to combat the potential hazards inherent in handling these materials. Large spills undoubtedly will occur during development programs as a result of equipment malfunction, or from other causes. The hazards to personnel and damage to test stand hardware must be minimized. Accordingly, a laboratory scale investigation was initiated.

The objective of this study was to determine suitable decontamination procedures and materials for combatting toxic missile propellant spills. This program was carried out in two phases. Phase I was a study of both the practical and theoretical aspects of the problem of decontamination and included an evaluation of existing information. A survey of pertinent toxicity data was also included in this section.

Phase II consisted of a bench-scale experimental investigation to determine suitable decontaminants, utilizing the information obtained in Phase I. Four propellants were experimentally investigated in this program. Compound A, MHF-3, MHF-5, and alumizine. Based on the results of this experimental investigation, suitable decontaminants were recommended. A decontaminant to be suitable must meet several criteria. It must react smoothly, readily, and relatively completely. It must in itself produce no additional hazards by nature of flammability, toxicity or corrosivity. In addition the reaction products must not present any undue hazards. Lastly, the decontaminant should be readily available and economically feasible.

It must be emphasized that all of the results and recommendations herein reported were obtained using small laboratory quantities of propellants. Logically, the program should be continued on a larger pilot scale in order to verify the conclusions developed from this work.

The investigation of several other propellants was limited to the practical study only. Decontamination recommendations were made for these materials based upon an evaluation of reported information. These propellants were:

Nitrogen Tetroxide	Beryllizine
Fluorine	Light Metal Hydrides
Hydrazine	Hydrogen
Unsymmetrical Dimethylhydrazine	

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SECTION 1

COMPOUND A

1.1 PRACTICAL STUDY

1.1.1 General

Compound A, chlorine pentafluoride (ClF_5), is a highly energetic oxidizer. Its boiling point is -13.6°C and the freezing point is -103°C . Both the gas and liquid are colorless. The liquid has a relatively high density, 2.100 gm/ml. at -80°C and 1.863 gm/ml at 0°C . The critical temperature is 143°C and ClF_5 is therefore normally handled as a liquid under pressure. Compound A is not shock sensitive and is extremely stable. No decomposition has been observed after long term storage. This material is quite similar to chlorine trifluoride and requires the same normal safety precautions. No extraordinary safety devices or techniques are required to handle this oxidizer.

1.1.2 Decontamination

An extensive literature search revealed that there are no recommended or standard procedures for the decontamination of large spills of Compound A. However, the similarity of Compound A to chlorine trifluoride, a material on which decontamination studies have been made (1), indicates that the same decontaminating techniques should be applicable to Compound A. Therefore, a spray deluge of water or dilute aqueous solutions of ammonia should be effective in neutralizing spills of Compound A.

1.1.3 Toxicity

Range find tests were conducted by Rocketdyne to determine the toxicity of ClF_5 to rats at various concentrations at 10 minute exposure periods (2). Concentrations of 120, 1000, and 2500 ppm produced only slight irritations. At 10 minute exposures to 5,180 and 11,770 ppm, respiratory difficulty was observed but the test animals survived and completely recovered in several days. It was believed that due to the rapid reaction between ClF_5 and moisture, the animals were exposed only to hydrolysis products. Therefore, Rocketdyne concludes that the toxicity level of ClF_5 should be taken as identical to ClF_3 (MAC-0.1 ppm) (3).

Toxicity studies of ClF_5 were also sponsored by Allied Chemical Corporation. Four rats exposed at 108 ppm for 10 minutes showed eye irritation and slight pulmonary effects. Of four rats exposed at 212 ppm for 10 minutes, one died 2 1/2 days after exposure. Eye irritation and slight respiratory difficulty was noted in all rats. Two rats exposed to 412 ppm for 10 minutes

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showed eye irritation, salivation and marked respiratory difficulty. Deaths occurred 60 minutes and 36 hours after exposure. Two rats were exposed to 412 ppm for 20 minutes and deaths occurred 30 and 55 minutes after terminating the exposure. Examination of exposed rats indicated edema of the lungs was responsible for death. Tissue damage was limited to the lungs. On the basis of these toxicity tests, the CT product causing 50% mortality appears to be somewhat greater than 2000. Based on this study, Compound A can be considered to be in the same toxicity range as chlorine trifluoride.

1.2 THEORETICAL STUDY

Compound A is a highly energetic oxidizer and under the proper conditions can be made to react with almost all materials. Only completely fluorinated compounds and certain of the inert gases and nitrogen are completely inert.

It reacts vigorously with most inorganic and organic compounds. Because of its reactivity a great many materials were considered for use as decontaminants for Compound A spills. These candidate materials have been categorized in this report by classes such as oxides, carbonates and hydroxides. The reactions written for this study often indicate the ideal or most complete reaction for the chemical systems. This would result in the formation of completely fluorinated and chlorinated byproducts. It is felt that these conditions would be approached since the decontaminant was applied in great excess in a manner which provided rapid and complete reaction. It must be noted that in many of the Compound A reactions reported in the literature, the resultant byproducts are dependent upon precise mole ratios and carefully controlled temperatures. Nevertheless, the possibility of such resultant byproducts forming under our test conditions have been considered in this theoretical study. This study is based on an extensive review of both classified and unclassified literature and reports.

1.2.1 Oxides

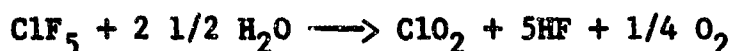
1.2.1.1 Water

The reaction of A with water may yield ClO_2F , ClO_2F , ClO_2 and HF depending upon the reaction conditions (4) (5) (6). These end products are hazardous compounds. The decomposition of ClO_2 at concentrations over about 10% in air can cause low order explosions or puffs; 4% in air can sustain a decomposition wave if set off by a spark (7). A concentration of 45 ppm in air will cause irritation to the eyes and nose. 350 ppm is rapidly fatal to guinea pigs, 150 ppm causing death in 44 minutes (8). ClO_2F and HF are also toxic. The threshold limit value for the latter, for an 8-hour day, 40-hour week being 3 ppm. No T.L.V. has been established for ClO_2F , however, an interim value of 3 ppm has been suggested.

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Generally, the most common products of the hydrolysis of ClF_5 are ClO_2 and HF (9). Fortunately, both ClO_2 (10) and HF are very soluble in water. The products can probably be trapped in an excess of water during decontamination and therefore be made tolerable. The standard heat evolved in this reaction is 105 kilo. cal./mol A reacted.

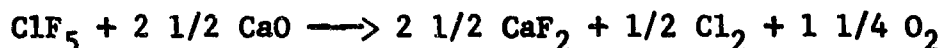


$$\Delta H = -105 \text{ kilo. cal./mol.}$$

Investigators generally agree that most oxides when reacted with ClF_5 are converted to fluorides. Oxygen is always a product and usually the other volatiles produced are ClO_2 , ClO_2F and ClO_3F (3, 11, 12). Metal oxides such as CuO , FeO , and Fe_2O_3 do not react at 105°C (4).

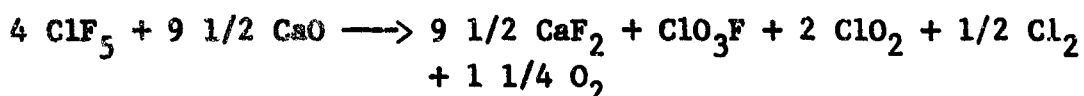
1.2.1.2 Calcium Oxide

The reaction with CaO has reportedly produced chlorine, oxygen and CaF_2 (13). Assuming this to be the case, all of the fluorine would be recovered as insoluble CaF_2 . Chlorine would be the only toxic product. Chlorine represents only about 25% of the total weight of Compound A and it would be diluted approximately $2 \frac{1}{2}$ to 1 by volume with oxygen upon formation. The standard heat of this reaction is high 291 kilo. cal. evolved per mol A reacted. We can write the equation as follows:



$$\Delta H = -291 \text{ kilo. cal./mol.}$$

Should the reaction proceed as is customary with most oxides, we can expect to find toxic oxy-chloro-fluorides as end products. It is probable that some of these will be found. Since there is no experimental data, the chemistry of this type reaction is in doubt. However, we can write the following reaction:



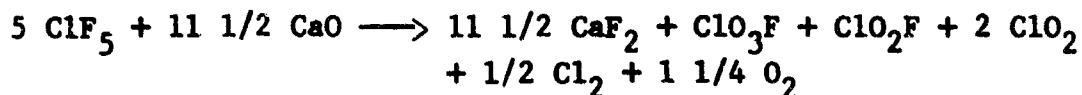
$$\Delta H = -263 \text{ kilo. cal./mol.}$$

This reaction indicates that over 95% of the fluorine would be recovered as insoluble CaF_2 . The remaining 5% would evolve as volatile ClO_3F . The end products would contain approximately 25% toxic volatiles. The heat evolved in this reaction is also high, 263 standard kilo. cal. evolved per mol A reacted.

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In the event chlorine dioxyfluoride is produced, we can write the reaction as follows:

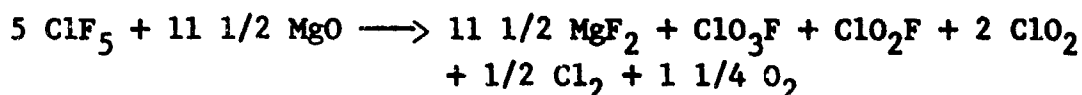


$$\Delta H = -252 \text{ kilo. cal./mol.}$$

According to this reaction, over 90% of the fluorine would be recovered as insoluble CaF_2 . The rest would pass off as ClO_3F and ClO_2F . The yield would consist of approximately 27% toxic gas. The heat evolved in this reaction is 252 kilo. cal. per mol ClF_5 reacted.

1.2.1.3 Magnesium Oxide

The reaction of magnesium oxide with A yields the metal fluoride which is relatively insoluble and the volatiles, ClO_3F , ClO_2F , ClO_2 , Cl_2 and O_2 . The reaction can be written as follows:

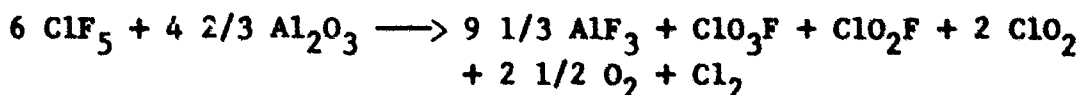


$$\Delta H = -237 \text{ kilo. cal./mol.}$$

Here, as with the CaO , over 90% of the fluorine would be captured as relatively insoluble MgF_2 . The weight yield of toxic gas would be the same. On a percentage basis the yield would consist of approximately 32% toxic gas. The heat evolved is somewhat less than with the calcium oxide, 237 kilo. cal./mol. of A reacted.

1.2.1.4 Aluminum Oxide

The reaction of A with aluminum oxide is a relatively mild one releasing only 118 kilo. cal. per mol of A reacted. The reaction products are similar to those of the other oxides already described. Approximately 94% of the fluorine would be captured as AlF_3 . Unfortunately, the metal fluoride formed is somewhat more soluble than either the calcium or magnesium fluoride. The product yield would consist of approximately 30% volatile toxic products. The reaction can be written as follows:



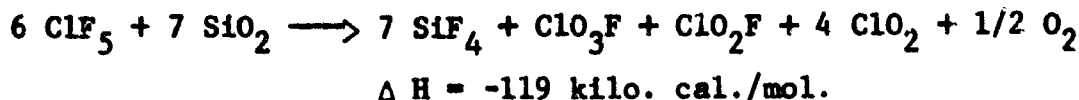
$$\Delta H = -118 \text{ kilo. cal./mol.}$$

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1.2.1.5 Silicon Dioxide

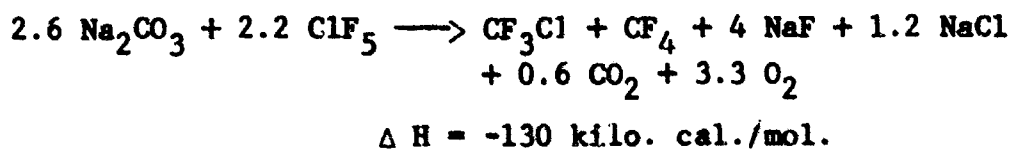
The action of A on silicon dioxide is also relatively mild releasing only 119 kilo. cal./mol. of A reacted. The products are all gases. 94% of the fluorine would be tied up as SiF₄, the remainder in ClO₃F and ClO₂F. 38% of the products formed are toxic of which unstable ClO₂ makes up the major part. The reaction follows:



1.2.2 Carbonates and Bicarbonates

1.2.2.1 Sodium Carbonate

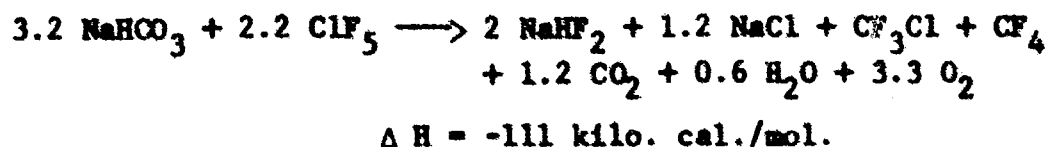
The action of A with sodium carbonate reportedly yields, chlorotrifluoromethane, carbon tetrafluoride, oxygen and an unidentified white solid (13). If we assume the white solid to be a mixture of sodium fluoride and sodium chloride, and further, assume some CO₂ evolves, we can write the equation as follows:



This reaction is ideal from the standpoint of decontaminating A. None of the off gases are toxic, and the solids formed are inert. The heat evolved is reasonable; 130 kilo. cal. per mol A reacted. 36% of the fluorine is captured as inert solid sodium fluoride. The remainder is released in the form of non-toxic gases, Genetron 13 and CF₄.

1.2.2.2 Sodium Bicarbonate

The action of A on sodium bicarbonate reportedly yields sodium bifluoride, chlorotrifluoromethane, carbon tetrafluoride and oxygen (13). If we assume sodium chloride and carbon dioxide are also formed, we can write the reaction as follows:



This reaction is also excellent from the standpoint of decontaminating A. No toxic gases are produced and the solids

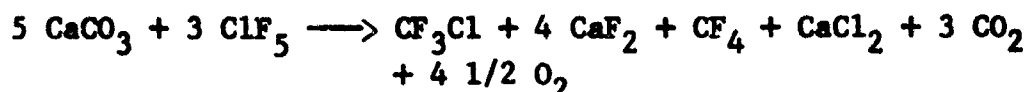
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formed are inert 36.5% of the fluorine would be converted to inert NaHF_2 , the rest would be captured as the inert gases CF_3Cl and CF_4 . The heat evolved is somewhat less than with the sodium carbonate, 111 kilo. cal. per mol A reacted, and somewhat less sodium bicarbonate would be required per mol A decontaminated.

1.2.2.3 Calcium Carbonate

The literature gives no data relative to the products formed by the action of A on calcium carbonate. One reference does state that there is no visible reaction, but upon analysis 33% of the carbonate had reacted (14). If we assume the reaction is similar to that with sodium carbonate, we can write:

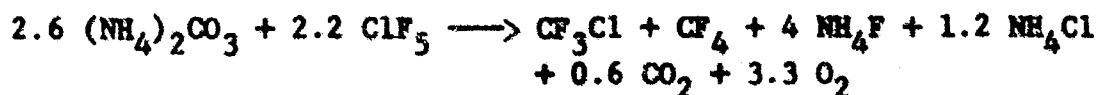


$$\Delta H = -131 \text{ kilo. cal./mol.}$$

This reaction shows excellent potential for decontaminating A. 53.8% of the fluorine would be captured as inert, insoluble calcium fluoride. The rest would be tied up in the inert gases CF_3Cl and CF_4 . No toxic end products would be produced. The heat of this reaction is 131 kilo. cal./mol. A reacted.

1.2.2.4 Ammonium Carbonate

The literature gives no data relative to the products formed by the action of A on ammonium carbonate. One reference states that ammonia (NH_3) forms NH_4Cl , NH_4F and nitrogen (15). If we assume the reaction is similar to that with sodium carbonate, we can write:



$$\Delta H = -126 \text{ kilo. cal./mol.}$$

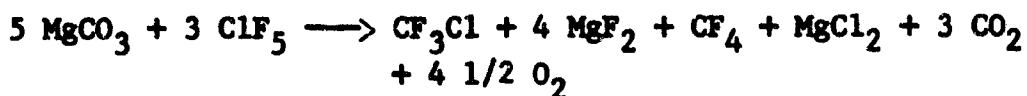
This reaction also shows good potential for decontaminating A. 36 1/2% of the fluorine would be captured as inert ammonium fluoride, the rest would be found as the inert gases CF_3Cl and CF_4 . Again no toxic end products would be produced. The heat evolved here would be 126 kilo. cal./mol. A reacted.

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1.2.2.5 Magnesium Carbonate

Assuming the action of A on magnesium carbonate is similar to that with sodium carbonate, we can write:



$$\Delta H = -129 \text{ kilo. cal./mol.}$$

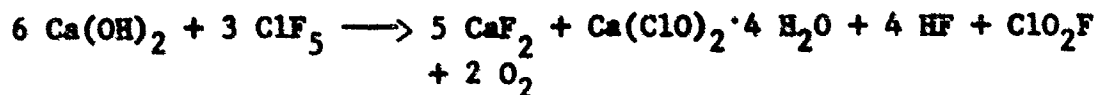
No toxic end products would be formed. 53 1/2% of the fluorine would be captured as relatively insoluble MgF_2 , the rest would be found in the inert gases CF_3Cl and CF_4 . The heat evolved would be 129 kilo. cal./mol A reacted.

1.2.3 Hydroxides

The action of A on hydroxy compounds is usually rapid and complete at ambient temperature. The reaction usually yields HF and O_2 in addition to a fluorinated form of the reactant substrate, Cl_2 , ClO_2 , or ClO_2F (3, 12).

1.2.3.1 Calcium Hydroxide

The action of A on calcium hydroxide reportedly yields CaF_2 , $\text{Ca}(\text{ClO})_2$, HF, O_2 and ClO_2F (4). We can write the reaction:

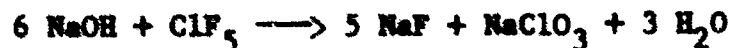


$$\Delta H = -106 \text{ kilo. cal /mol.}$$

Approximately 67% of the fluorine would be tied up as insoluble CaF_2 , the remainder would evolve as toxic gases HF and ClO_2F . The standard heat evolved from this reaction is 106 kilo. cal. per mol A reacted.

1.2.3.2 Sodium Hydroxide

No work is reported on the action of A on sodium hydroxide, however, an excess of NaOH would preclude the presence of HF as a product. ClO_2F reacts with NaOH to yield NaClO_3 , NaF, H_2O and O_2 (16). By analogy one might expect ClO_2F to react in a similar manner. We can write:



$$\Delta H = -302 \text{ kilo. cal./mol.}$$

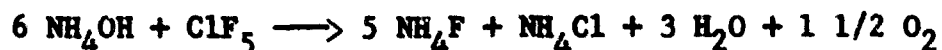
All of the fluorine would be tied up as solid sodium fluoride, no toxic products would be formed.

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1.2.3.3 Ammonium Hydroxide

No work is reported on the action of A on ammonium hydroxide. However, by reasoning similar to that used in the sodium hydroxide case, we can assume no HF will be present with an excess of NH_4OH . We would not expect to find chlorates as a product, if any is formed it would probably decompose to the chloride. We can write:



$$\Delta H = -259 \text{ kilo. cal./mol.}$$

All of the fluorine would be captured as solid ammonium fluoride. No toxic products would be formed.

1.2.4 Hydrates

Hydrous oxides react vigorously, the products being similar to the reaction of A and water. Hydrates of metal fluorides yield ClO_2 , O_2 , ClO_2F and ClO_3F (13). The action of A on sodium tetraborate hydrate reportedly yields only a solid and oxygen (12). BF_3 , HF and HCl are assumed to be tied up by NaF or excess hydrate. The action of A on hydrated sodium metasilicate is reportedly similar to that with A on hydrated sodium tetraborate (13), yielding oxygen, a small amount of chlorine and solid. No data is given on the chemistry of these reactions. It is so involved that no attempt will be made to write them and therefore reaction heats will not be calculated.

1.2.5 Conclusions

Because of its similarity to CTF one would expect that water, or a dilute aqueous solution of ammonia, would be a satisfactory decontaminant. The theoretical study shows that all of the products formed in the water reaction are gaseous and two of them are toxic, HF and ClO_2 . ClO_2 under certain conditions can also be explosive. However, both ClO_2 and HF are very soluble in water. If an excess of water is used as would be the case in decontamination, a high percentage of both the ClO_2 and HF formed can be harmlessly trapped. The heat evolved with water is low, 105 kilo. cal./mol A reacted. The other oxides investigated generally capture a high percentage of fluorine as inert solids ranging from 90-100%. The exception is SiO_2 all of the products of which are gases. The oxides generally produce a variety of toxic and explosive gaseous products. The heats evolved range from about 115 to 300 kilo. cal./mol A reacted.

All of the carbonates have excellent potential as decontaminants for A. No toxic, explosive or incendiary products are

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produced. Approximately 35 to 55% of the fluorine can be captured as inert solids, the rest evolves as non-toxic gas. The heat evolved from the reaction with carbonates is reasonable ranging from about 110 to 130 kilo. cal./mol A reacted.

Of the hydroxides, sodium and ammonium show good potential, neither of these yield toxic products. In each case all of the fluorine is captured as solid inert material.

The action of sodium tetraborate hydrate and sodium metasilicate on A reportedly yields desirable products from the standpoint of decontamination.

1.3 EXPERIMENTAL STUDY

A laboratory investigation to find suitable decontaminants for Compound A was conducted. This problem involved seventy actual decontamination runs with water and aqueous solutions of candidate decontaminants. Ninety-six samples of residual spray liquors were analyzed. This experimental investigation considered the techniques and materials used successfully in ClF_3 decontamination studies (1) as well as candidate materials suggested by the literature search and theoretical study on Compound A.

1.3.1 Apparatus

The decontamination setup (Figure 1.1) consisted of a spray chamber and a test decontaminant delivery system. The chamber was a stainless steel column, 24" high and 6" in diameter. The chamber contained a copper cold finger to condense the propellant. The liquid propellant was then collected in a calibrated centrifuge tube. This glass receiver was held in place by a pair of clamps. An "anvil" was adjusted against the wall of the tube to assure breakage and spillage of the propellant when the trigger mechanism was released. The plexiglass window was sealed to the chamber opening with a Viton A "O" ring which showed satisfactory performance. However, the plastic window became etched and was replaced twice. The chamber had several openings and connections. The dished bottom was provided with an outlet drain with a stopcock. The drain was provided with a stainless steel screen which prevented glass particles from damaging the stopcock valve. A nitrogen purge line extended through the wall into the lower part of the chamber. A vent line was provided near the top of the column. Three 1/8" copper lines extended through the chamber wall and carried the coolant and the propellant.

The spray nozzle was mounted on the bottom of the spray chamber cover. Two types of nozzles were purchased from Spraying

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Systems Company in order to achieve a wide range of spray rates. The lower rated nozzle was an adjustable cone jet No. 5500-X1. This particular model was available only in brass, a material which was not fully resistant to several of the candidate decontaminants. This therefore necessitated frequent calibration and nozzle replacement. The second type nozzle was a No. 1/8 G.G.S.S.-1 stainless steel full jet nozzle. It should be noted these two types were selected because they produced a similar spray pattern. A Hoke solenoid valve, No. 90A140, mounted at the top of the cover, was used to start and stop the spray.

The chamber was connected to the decontaminant reservoir with 1/4" stainless steel tubing. The reservoir was a 500 ml. stainless steel cylinder which was pressurized with nitrogen after it had been filled with the test solution. Not shown in Figure 1.1 are the electric relays and solenoid valves which were used to maintain constant spray pressures during the runs. The relays which operated off the pressure gauge kept the reservoir pressure within ± 1 psig of the preset pressure.

The coolant system likewise is not shown. It consisted of a centrifugal pump which circulated acetone through a dry ice-acetone cooled coil into the cold finger. This system was capable of maintaining a cold finger temperature below -60°C .

1.3.2 Materials

The materials used to make up the decontamination solutions were all B&A, Reagent Grade Chemicals. Reagent chemicals were chosen to eliminate any possible side reactions from impurities that might have interfered with our analysis. This might have occurred if technical or commercial grade materials with their normal impurities had been used. It is not to be construed, however, that reagent materials must be used in actual practice. On the contrary, commercial grades are to be preferred since they are both more economical and more readily available.

1.3.3 Procedure

The first step in the test procedure involved the positioning of the propellant receiver. The receivers were volumetrically calibrated conical centrifuge tubes (Corning Catalogue type No. 8080). Volumetric accuracy was necessary since each run used 2.0 ml. of condensed ClF_3 . At the cold finger temperature the specific gravity of Compound A was 1.9. Thus 2.0 ml. of propellant was equivalent to 3.8 grams.

After the centrifuge tube was positioned and the chamber window sealed, the chamber and propellant line were purged with dry nitrogen. This precaution prevented frost formation on the

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cold finger or condensation on the glass tube. The coolant was then circulated and the propellant condensed. When the desired amount of liquid had been collected, the propellant feed and nitrogen purge were closed off and the trigger pulled to break the glass tube. Two seconds after the spill, the spray was started. The spray was continued for the required time to provide the desired ratio of decontaminant to propellant. The spray rate, which was a function of the reservoir pressure, was always preselected. A timing mechanism was used to control spray duration when short spray periods were required. When low spray rates were selected together with high spray ratios, the duration of the spray exceeded the limit of our timer. For these runs the spray was timed with a stopwatch.

When the spray had been shut off the chamber walls were allowed to drain for 5 minutes before the spent liquor was collected. The volume of this liquor was measured. This provided a quick check of the spray nozzle calibration as well as a check on the spray system and the calculated spray ratio.

The spent liquor was analyzed for fluoride, chloride and oxidizing power. This data was then used to determine the percentage of the propellant that was neutralized or decontaminated. In some runs the walls of the chamber are rinsed and this rinse was also analyzed to provide an indication of chamber hold up. The spray chamber was always cleaned and dried between runs.

1.3.4 Experimental Data

1.3.4.1 Water

The effectiveness of neat water spray as a decontaminant was explored quite thoroughly since it was used to establish optimum ClF_5 to decontaminant spray ratios as well as spray rates. The results of the water tests are shown in Table 1.1. No explosions or other evidence of extremely vigorous reaction were noted in any run. However, on two occasions, a flash was seen when the spill was deluged and on three occasions, a whistling noise was heard. No positive explanation for the whistle-like sound can be given, but it is believed to have been caused by the spilled A entering the drain line and reacting in this relatively confined space.

All test runs were done in duplicate. The results of the duplicate runs did not always check as closely as would have been desired. A possible reason for this discrepancy is that the measured volume of A could be off by ± 0.1 ml. (the limit of reading the tube calibration). This could result in a weight

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error of $\pm 5\%$. Consequently, the difference in recovered equivalents of Compound A in duplicate runs could be as great as 10%.

After certain selected runs, the spray chamber was rinsed with the same quantity of spray and at the same spray rate as was used for the actual run. The purpose of this was to determine the amount of chlorides and fluorides that were deposited on the chamber wall or remained suspended in the chamber vapors. The rinse recovery of fluoride and chloride was appreciable for runs with low spray: ClF_5 ratios and became less significant when the 60:1 ratio was used. You will note that two water runs Nos. 6A and 6B showed very high fluoride and chloride recovery. Four additional runs (28A and B, 31A and B) were made under the identical spray conditions. These additional runs did not achieve the same degree of decontamination. Neat water alone, however, does appear to be a satisfactory decontaminant. The combined recovery of inert chloride and fluoride from the initial spray and the rinse indicated a neutralization in excess of 80% of the ClF_5 under the best spray conditions.

1.3.4.2 Other Decontaminants

The effectiveness of aqueous solutions of candidate decontaminants was also investigated. In anticipation of possible vigorous reaction, a very dilute decontaminant solution (1%) was tried initially to determine its compatibility with Compound A. Stronger solutions were used to establish effectiveness as a decontaminant. The results obtained from these test solutions are shown in Table 1.2. In some duplicate runs the results did not check closely. The technique used for evaluating these materials was identical to that used for the neat water runs and the same comments on accuracy are therefore applicable. Since water alone did a good job of decontamination, solutions of candidate materials were expected to show improvement. Some decontaminant solutions, however, yielded a lower recovery of fluorides and chlorides than was obtained from neat water. The other decontaminants fell in the same general range of effectiveness. However, it should be noted all test materials proved to be safe as used. No explosions occurred although some flashes and whistling were noted.

1.3.5 Analytical Procedure

The analytical procedure used for evaluating the effectiveness of the several decontaminants was based on standard procedure. Since Compound A has the formula ClF_5 , the decontaminant effectiveness was based on the recovered chloride and fluoride

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values in the spent liquor. Water or aqueous solutions of test materials were sprayed in predetermined ratios on spilled Compound A at several spray rates. The residual liquor from the spray which contained the reaction byproducts was collected and analyzed. Gaseous effluents from the spray chamber could not be collected. Therefore, a material balance could not be obtained. In addition to fluoride and total chloride, the spent liquor was also analyzed for oxidizing power which was reported as free chlorine equivalent. The spent liquor was diluted to a constant volume and aliquots were taken for these analyses.

1.3.5.1 Fluoride

An aliquot of the spent liquor was distilled from perchloric acid at a constant temperature of 135°C and 250 cc of distillate collected. Hydroxylamine-hydrochloride was added to an aliquot of the distillate to prevent interference from free chlorine or other oxidizers that might be present. The total fluoride present was then determined by a thorium nitrate titration.

1.3.5.2 Total Chloride

Sulfurous acid was added to a second aliquot of the spent liquor and the solution was evaporated to a small volume. Water was added to this concentrated solution and it was again evaporated to a small volume. The solution was again diluted with water, made slightly basic with dilute NaOH, and one gram of Devarda's Alloy was added. After two additional evaporations and reconstitutions with water as initially performed, the solution was decanted from the alloy. The alloy was rinsed with nitric acid. The decanted solution together with the acid washings from the alloy were then analyzed for total chloride by a Volhard titration.

1.3.5.3 Free Chlorine

Several of the test decontaminants have been reported in the literature to have formed oxidizing compounds when reacted with Compound A. The oxidizing power of the spent liquor was therefore determined and reported as free chlorine equivalents. Some possible oxidizers that could be present were ClO_2 , ClO_4^- , OCl^- and Cl_2 . A third aliquot of the spent liquor solution was made slightly basic with dilute caustic and then filtered. The filtrate was acidified with acetic acid. Potassium iodide was added and the released iodine which was titrated with sodium thiosulfate corresponded to the amount of oxidizer present. Calculations, however, were based on the assumption that the oxidizer was chlorine.

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1.3.6 Economic Evaluation

An economic evaluation of the test decontaminants was made. The estimated cost of decontaminating a one-hundred pound spill of Compound A is shown in Table 1.3. The cost as shown is based on both the lowest price of the decontaminating agent on a ton basis, as well as its relative effectiveness. The cost of water is ignored since it is relatively insignificant and would be roughly equal for each test solution. Of course, the most economical material is therefore neat water. The cheapest decontaminants in ascending order are NH_4OH , NaHCO_3 , Na_2CO_3 , NaOH , and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ all of which were less than \$30.00/100 pounds of Compound A.

1.3.7 Conclusions

In the recommendation of a suitable material as a decontaminant for Compound A, the several criteria previously listed were considered. The nature of the reaction byproducts was carefully considered. On this basis alone neat water, which showed a very high effectiveness, cannot be considered the best decontaminant. The fluoride in the spent liquor is present as HF , a hazardous acid. Likewise, some of the unrecovered fluoride values are assumed to have escaped as toxic HF vapors. On the other hand, NaHCO_3 and Na_2CO_3 captured considerable amounts of A but much of the chlorine was present in the spent liquor as oxidizers (Table 1.4). These three materials would therefore require some secondary treatment to render the reaction products completely inert. Several materials were relatively ineffective as decontaminants (sodium tetraborate, boric acid and sodium silicate) and cannot therefore be recommended. Two materials that were quite effective were NaOH and KOH . However both of these are relatively hazardous. Ammonium carbonate was relatively expensive although otherwise satisfactory. The best materials therefore were ammonium bicarbonate and ammonium hydroxide. Although both materials are effective, the bicarbonate is more expensive. The hydroxide also had the advantage of a very high vapor phase effectiveness as shown by copious fumes of relatively inert NH_4F and NH_4Cl in both the chamber and in the effluent. Considering all these factors, our investigation indicated that dilute aqueous solutions of ammonia best met all the criteria for a suitable decontaminant for Compound A. It should be noted that the decontamination byproducts formed from ammonia are quite soluble and thus may be readily removed by flushing with water. However should the spill occur in an area where the formation of a water soluble fluoride may be undesirable, these residues would be subsequently treated to produce insoluble fluorides. Application of appropriate calcium salts to the residues would produce

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relatively insoluble calcium fluoride thus avoiding possible fluoride infiltration of the terrain.

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TABLE 1.1
LIQUID COMPOUND A SPILLS
WATER SPRAY DECONTAMINATION

Run No.	gms. Comp'd A	Spray Rate ml/min	gm. Ratio H ₂ O:A	% Recovered			Remarks
				Cl ⁻	F ⁻	A*	
1A	3.8	75	15:1	38.1	54.2	50.0	
1B	3.8	75	15:1	23.3	56.6	47.6	
1B-R	-	75	15:1	35.0	20.2	24.2	
2A	3.8	75	30:1	54.4	70.0	65.8	
2A-R	-	75	30:1	19.4	15.4	16.6	
2B	3.8	75	30:1	48.5	88.4	77.6	
3A	3.8	75	60:1	53.4	72.9	67.6	
3A-R	-	75	60:1	11.7	6.5	7.9	
3B	3.8	75	60:1	56.3	70.8	66.8	
4A	3.8	104	15:1	43.7	53.1	50.5	
4B	3.8	104	15:1	34.6	46.6	43.2	
5A	3.8	104	30:1	59.2	75.1	70.8	
5B	3.8	104	30:1	51.5	75.1	68.6	
6A	3.8	104	60:1	69.5	106.1	96.3	
6B	3.8	104	60:1	63.1	106.1	94.5	
7A	3.8	610	30:1	--	--	--	Sample Lost
7B	3.8	610	30:1	48.5	26.7	32.6	
7C	3.8	610	30:1	11.7	70.8	54.8	Flash and noise noted
7C-R	-	610	30:1	28.2	17.7	25.8	
8A	3.8	610	60:1	15.5	53.1	42.9	Whistle heard
8B	3.8	610	60:1	63.1	66.4	65.5	
28A	3.8	104	60:1	62.1	76.9	72.9	
28A-R	-	104	60:1	13.6	6.5	8.4	
28B	3.8	104	60:1	57.3	62.5	61.1	Flash and whistle noted
31A	3.8	104	60:1	41.7	77.7	67.9	
31A-R	-	104	60:1	18.4	12.6	14.2	
31B	3.8	104	60:1	24.3	58.8	49.5	

NOTE: Runs designated by an "R" are rinses of spray chamber after the actual run sample had been collected. For example 1B-R is the rinse from 1B. The rinse was always made at the same spray rate and ratio (gms of rinse) as the actual run.

* Total Cl⁻ and F⁻ recovered calculated as % of Compound A neutralized.

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TABLE 1.2
LIQUID COMPOUND A SPILLS
DECONTAMINATION SOLUTIONS

Decontaminant	Spray Rate = 75 Ratio=30:1			Spray Rate = 75 Ratio=60:1			Spray Rate =104 Ratio=60:1			Spray Rate =610 Ratio=60:1		
	Cl ⁻	F ⁻	A	Cl ⁻	F ⁻	A	Cl ⁻	F ⁻	A	Cl ⁻	F ⁻	A
1% NaHCO ₃										10.5	70.8	56.1 (1)
5% NaHCO ₃	35.9	53.1	48.4	66.0	66.4	66.3	70.9	53.8	58.4	59.2	70.8	67.6
	46.6	62.1	57.9	73.8	67.4	68.4	62.1	76.9	72.9	68.0	70.8	70.0
1% Na ₂ CO ₃				35.9	48.4	45.0 (2)				101.9	79.8	85.8
				63.1	60.3	61.1 (2)						
5% Na ₂ CO ₃	63.1	51.9	55.0 (3)	72.8	60.3	63.7	79.6	78.0	78.4			
	57.3	59.2	58.7	80.6	56.7	63.1	84.4	78.0	79.7			
1% NaOH				54.4	50.2	51.1 (2)						
				45.6	56.7	53.7 (5)						
5% NaOH				68.0	53.8	57.6 (5)						
				68.9	60.6	62.9						
5% Na ₂ B ₄ O ₇ · 10H ₂ O				69.9	25.3	37.4						
				65.0	33.6	42.1						
5% H ₃ BO ₃				51.5	23.5	31.1						
				54.4	21.7	31.1						
5% KOH				72.8	72.9	72.9 (3)	49.5	53.8	52.6 (6)			
				74.8	66.8	68.9 (3)	86.4	90.9	89.7			
5% Na ₂ SiO ₃ · 9H ₂ O				59.2	27.4	36.1						
				62.1	25.3	35.0						
5% NH ₄ HCO ₃				51.2	60.6	58.2 (1)	59.2	78.7	73.4 (4)			
				76.7	89.2	85.8	60.2	72.9	69.5 (4)			
5% (NH ₄) ₂ CO ₃				77.7	63.9	67.6	69.9	72.9	72.1 (4)			
				71.8	54.5	59.2	67.0	74.0	72.1			
1% NH ₄ OH				77.7	65.0	68.4 (2)						
				67.0	65.0	65.8						

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* The rinse pickup showed an excellent duplication for each set of spray conditions regardless of the decontaminant; therefore, the average for the group is given.

- (1) Flash and whistle on initial spray contact.
- (2) Whistling noise approximately 15 seconds after spray started.
- (3) Flash when A spilled.
- (4) Whistling noise on spray contact.
- (5) Flash when A spilled. Whistle 20 seconds after spray started.
- (6) Large flash on spray contact.

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TABLE 1.3
COMPOUND A DECONTAMINATION
ECONOMIC EVALUATION

<u>Decontaminant</u>	<u>* Est. Cost/Ton</u>	<u>Approx. Effect</u>	<u>Lbs. Required</u>	<u>Est. Cost to Neutralize 100 lbs. A</u>
1. H_2O	\$	74%	6000	\$
2. $NaHCO_3$	59	71%	423	12.48
3. Na_2CO_3	62	71%	423	13.11
4. KOH	192	71%	423	40.61
5. NH_4HCO_3	150	72%	417	31.28
6. $(NH_4)_2CO_3$	720	68%	441	158.76
7. NH_4OH	45	60%	500	11.25
8. $NaOH$	60	60%	500	15.00
9. $Na_2B_4O_7 \cdot 10H_2O$	44	40%	750	16.50
10. H_3BO_3	112	31%	968	54.21
11. $Na_2SiO_3 \cdot 9H_2O$	68	36%	833	28.32

* Prices of decontaminant as of November 1965 on 100% basis.

NOTE: All costs are based on decontaminant effectiveness using a 5% aqueous solution at a spray to spill ratio of 60:1.

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TABLE 1.4
COMPOUND A DECONTAMINATION
SPENT LIQUOR OXIDIZER CONTENT

<u>Decontaminant</u>	<u>Average Effectiveness*</u>	<u>Average Free Cl₂**</u>
Neat H ₂ O	74%	2%
5% NaHCO ₃	71%	23%
5% Na ₂ CO ₃	71%	29%
5% NaOH	60%	1%
5% Na ₂ B ₄ O ₇ ·10H ₂ O	40%	25%
5% H ₃ BO ₃	31%	2%
5% KOH	71%	<1%
5% Na ₂ SiO ₃ ·9H ₂ O	36%	34%
5% NH ₄ HCO ₃	72%	3%
5% (NH ₄) ₂ CO ₃	68%	4%
5% NH ₄ OH	60%	3%

* Average of all runs made at 60:1 ratio at spray rates of 75 and 104 ml/min.

** Oxidizer content of residual spray liquor calculated as free chlorine.

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SECTION 2

MIXED HYDRAZINE FUELS

2.1 PRACTICAL STUDY

2.1.1 General

Mixed hydrazine fuels (MHF) are mixtures of monomethylhydrazine, hydrazine and with one exception, hydrazine nitrate. Four specific compositions have been investigated and are identified as follows:

	<u>Monomethyl Hydrazine</u>	<u>Hydrazine</u>	<u>Hydrazine Nitrate</u>
MHF-3	86%	14%	0
MHF-4	50.5	32.5	17%
MHF-5	55	26	19
MHF-1	45.3	23.3	31.4

These fuels are clear, water white liquids. They are strong reducing agents, alkaline, and very hygroscopic. They are also extremely flammable and quite toxic. They are not shock sensitive and are quite stable in storage. In general, these materials present no greater hazard than do the several components taken individually.

2.1.2 Decontamination

The standard practice for combating spills and resultant fires of mixed hydrazine fuels, is to flush with copious quantities of water, use dry chemical extinguishers or use low expansion foam. MHF-1 fires are easily extinguished with either water fog or foam. Salt or fresh water may be used (1). Dry chemical extinguishants reportedly worked as well on MHF as on gasoline. Low expansion foam was nearly as effective on MHF fuels as it was on gasoline. High expansion foam showed excessive breakdown in contact with MHF with resultant erratic action (2).

MHF-3 does not ignite spontaneously upon pouring. Neither electric sparking of the vapors above the surface of MHF-3, nor dropping weights into this fuel during burning, results in detonation. MHF-3 is wholly miscible with water and when diluted in excess of 40% by volume with water it is rendered non-combustible. MHF-3 fires are readily extinguished by all extinguishing agents, mechanical foam, water fog, solid water stream, CO₂, Purple K and NaHCO₃ dry powder (3).

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Under special conditions MMH-1 and MMH-4 can be made to detonate after burning for short periods of time (4).

2.1.3 Toxicity

The literature review did not disclose any toxicity investigations on the mixed hydrazine fuels as such. The toxicity of the mixed fuels is considered to be similar to that of monomethylhydrazine (MMH). This component has the lowest boiling point. MMH is more toxic than hydrazine. The LD₅₀ (rats exposed for four hours) of MMH is 74 ppm as compared to 570 ppm for hydrazine (5). Detection of the odor of MMH should offer warning since it can be detected at 1-3 ppm. The local effects due to acute exposure to MMH are similar to those effects observed for hydrazine (See Section 5 of this report).

MMH was found to produce hemolysis and elevated temperature in exposed dogs. Destruction of red blood cells and central nervous system stimulation occurs with MMH to a greater extent than the other hydrazines.

Contact with the liquid may cause burns, severe skin and eye damage, and systemic poisoning. If the fuel does contact the skin, contaminated clothing should be removed and the exposed area flushed with copious quantities of water. Eyes should be flushed for at least 15 minutes. Where exposure to the vapors has occurred, the victim should be removed to an uncontaminated area and kept as quiet as possible. Medical attention by a physician is advised in all cases of contact or inhalation exposure.

2.2 THEORETICAL STUDY

There is considerably less information on the chemistry of monomethyl hydrazine (MMH) and hydrazine nitrate than on hydrazine. However, one may assume that many of the reactions of MMH are similar to the reactions for hydrazine.

Hydrazine nitrate undergoes decomposition in a vacuum in the neighborhood of 200°C according to the equation:



$$\Delta H = -106 \text{ Kilo.cal./mol.}$$

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It burns rapidly in open air, and if heated under confinement, it will explode violently. Contact with oxidizing agents such as chromate, peroxide and permanganate cause inflammation. Finely divided metals such as copper and zinc cause flaming decomposition (6).

The preferred products of decontamination would be salts, complexes or inert gases. Since one of the components of MHF is hydrazine and the other two components are generally similar to hydrazine, decontaminant materials similar to those used for decontaminating hydrazine are indicated.

2.2.1 Conclusions

Materials suitable for hydrazine decontamination (7) should be suitable for MHF decontamination. Water alone is an excellent decontaminant for spills. It renders the spill non-flammable and reduces the amount of toxic vapors.

However, the only reaction with the hydrazine is the formation of the hydrate. Therefore, complete neutralization can best be accomplished by deluging spills with dilute aqueous solutions of decontaminants such as hydrogen peroxide.

2.3 Experimental Study

A laboratory investigation was conducted to find suitable decontaminants for mixed hydrazine fuels. The experimental program was limited to two fuels, MHF-3 and MHF-5. The criteria used in evaluating candidate decontaminants have been previously stated in the introduction to this report. This investigation considered the techniques and materials used successfully in hydrazine decontamination (7) as well as the information obtained from the literature search.

The most immediate problem associated with a spill of these two fuels is the potential fire hazard. However, both fuels are completely miscible with water and when diluted with water to less than 40% fuel by volume they are rendered non-combustible. An aqueous spray deluged upon the spill is also an efficient means of scrubbing the toxic volatile vapors from the air. We therefore decided to test all candidate decontaminating agents as dilute aqueous solutions. Unfortunately, water alone does not react with the fuels and is therefore ineffective as a decontaminant per se.

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2.3.1 Apparatus

The high boiling points of these fuels (MHF-3, 194°F and MHF-5, 207°F) and their low vapor pressures at ambient temperatures permitted us to use simple equipment for this decontamination investigation. A weighed amount of the fuel was placed in an Erlenmeyer flask. The test solution was then permitted to flow onto the fuel by gravity feed through a glass delivery tube from a reservoir. Since the vaporization losses were negligible, spray rate had no bearing on decontamination efficiency. Therefore spray nozzles were not used in the deluge system. A teflon covered magnetic stir bar was placed in the Erlenmeyer flask and the flask set upon a magnetic stirrer. The stirring assured a uniform contact between the fuel and the test solution.

2.3.2 Materials

In addition to neat water, dilute aqueous solutions of the following materials were tested with both fuels: NaCl, NaHCO₃, H₃BO₃, H₂O₂, NaOCl, NaClO₃, KMnO₄, K₂Cr₂O₇. In addition, NaHCO₃ was applied to the MHF-3 as a dry powder. All these materials were B & A Reagent Grade. An attempt was made to evaluate "Purple K" a KHCO₃ powder used in fire extinguishers but this material proved to be impossible to evaluate.

2.3.3 Procedure

The mixed hydrazine fuels were obtained from Reaction Motors Division of Thiokol Chemical Corporation. A sample of the fuel was transferred to a polyethylene weighing bottle which was weighed on an analytical balance. This fuel sampling was performed in a plastic glove bag in an atmosphere of high purity dry nitrogen to prevent air oxidation. The weighed sample was poured into the reaction flask and the weighing bottle reweighed. In this manner a sample of approximately two grams was used for each run.

The flask was next positioned under the decontaminant delivery tube and the required amount of test solution to provide a 50:1 ratio by weight was added to the reservoir. With the magnetic stirrer operating, the test solution was drained into the flask at a rate of approximately 75 ml/min. The reaction was carefully observed and the reaction temperature noted. The decontaminated solution was quantitatively transferred to a volumetric flask and diluted to 250 ml with distilled water. Aliquots were then taken for analysis.

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2.3.4 Experimental Data

The addition of the decontaminant to the fuel was carefully observed and the nature of the reaction noted. Visual evidence that a reaction occurred was the evolution of gas from the solution, formation of precipitate and color change in the test solution. The vigor of the reaction was rated on the basis of the gas evolution. Copious and rapid gas release caused foaming. However, no decontaminant tested was considered to be unsuitable on this basis alone. As a further check the reaction temperature was noted. The temperature rise generally showed a good correlation with the observed vigor of the reaction as indicated in Tables 2.1 and 2.2. As a safety measure, very dilute solutions of the decontaminants were tested first. Subsequent runs used the more concentrated solutions.

2.3.4.1 MHF-3

A total of 45 runs involving 22 different decontaminants was made. The results of these tests have been summarized in Table 2.1. As may be seen from this table, the spent liquors from many runs were analyzed four times. The first analysis (Series A) was always performed within 15 minutes of the completion of the run and a second analysis 30 minutes after the first. This was done to determine whether the neutralization reaction took place rapidly or whether it proceeded slowly over an extended period. Other analyses were run in which the pH was adjusted to pH 7.5 (Series B). Again samples were initially analyzed within 15 minutes after the run was made and a second analysis was performed 30 minutes later.

In only one run was the reaction considered excessively vigorous. When a 5% solution of NaOCl was added to the fuel, there was a flash and the fuel vapors ignited. On the opposite extreme, dry powder deluges showed no reaction and were, relative to the various solutions tested, difficult to handle and evaluate. One powder "Purple K", a finely divided KHCO_3 used as a fire extinguishant, proved impossible to evaluate. It was added to a fuel spill but the residual powder proved to be nonwetttable and would not go into solution. Therefore analysis could not be made and this run was not included in Table 2.1. The powder deluge was added via a powder funnel into which was dumped a measured amount of the test powder.

2.3.4.2 MHF-5

A total of 42 runs involving 20 decontaminant solutions were made with MHF-5. Many runs were analyzed four times in the manner described for the MHF-3 study. The powder deluges were

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omitted from this section of the investigation since the effectiveness of these materials as decontaminants for MHF-3 was negligible. The results of the several runs involving MHF-5 are shown in Table 2.2.

2.3.5 Analytical Procedure

The effectiveness of the test decontaminant was calculated on the basis of the residual unreacted fuel present in the spent liquor. One gram of NaHCO_3 was added to an aliquot of the spent liquor to buffer the solution at approximately pH 8. In the Series B analyses, however, the aliquot was first neutralized with HCl to pH 7.5 and then the one gram of NaHCO_3 was added. According to Lundell and Hoffman (8), in iodine titration, the alkalinity should be reduced to avoid possible consumption of iodine in the formation of hypoiodic acid. Our results, however, indicate that this was not a significant factor. For all samples, a measured excess of standard iodine solution was then added which reacted with the residual fuel. The excess iodine was then determined by a standard sodium thiosulfate titration and the amount of fuel neutralized was then calculated.

2.3.6 Economic Evaluation

An economic comparison was made of the four decontaminants that showed the highest effectiveness. This evaluation was based on the estimated cost of decontaminating a 100 pound spill of mixed hydrazine fuels. The cost reflects the lowest price of the decontaminant on a ton basis as well as its effectiveness. The cost of water has not been considered in this evaluation since it is not only roughly equivalent for each decontaminant but is also relatively insignificant. The relative costs are shown in Table 2.3.

2.3.7 Conclusions

The results of this investigation show that each of the decontaminants tested behaved in a similar manner with both MHF-3 and MHF-5 and had approximately the same effectiveness with both fuels. These conclusions therefore are similarly applicable to both fuels. The only decontaminants that showed significant effectiveness were 5% aqueous solutions of either H_2O_2 , NaOCl , KMnO_4 , or $\text{K}_2\text{Cr}_2\text{O}_7$. More dilute solutions of these materials, when applied at the same deluge ratio of 50:1, neutralized less of the fuel primarily because stoichiometric amounts of decontaminant were not present at these concentrations. The 5% solutions on the other hand provided up to 50% excess of decontaminant at the applied ratio of 50:1.

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No doubt higher ratios of the more dilute solutions would show increased effectiveness. In actual practice, the tremendous quantities of water required to provide an excess of decontaminant when applied as a very dilute solution makes such concentrations less desirable.

Of the four oxidizers noted as effective decontaminants, the 5% solution of H_2O_2 was the most acceptable. The permanganate and dichromate solutions left a very large, messy solid residue which would introduce severe cleanup problems. In addition, the effectiveness of the dichromate was less than that of the peroxide for both fuels. The 5% sodium hypochlorite solution was not as safe as the peroxide. In one run the reaction was vigorous enough to ignite the fuel vapors. The peroxide on the other hand had a less vigorous observed reaction as well as a lower reaction temperature.

Despite the fact that the hydrogen peroxide is not as economical as the other effective decontaminants, we feel that it best meets the other criteria for a decontaminant. We therefore recommend a 5% aqueous solution of H_2O_2 as the decontaminant for spills of mixed hydrazine fuels.

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2.4 REFERENCES

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TABLE 2.1
MHF-3 DECONTAMINATION

Run No.	Decontaminant	(1) gm Ratio	(3) Decontamination			
			Series A		Series B	
			Immed.	30 min.	Immed.	30 min.
A-4	H ₂ O	125:1	0.0%			
A-5	H ₂ O	125:1	0.4%			
B-1	5% NaCl	50:1	0.4%			
B-2	5% NaCl	50:1	5.4%			
C-1	5% NaHCO ₃	50:1	4.0%			
C-2	5% NaHCO ₃	50:1	1.9%			
D-1	5% Na ₂ CO ₃	50:1	1.0%			
D-2	5% Na ₂ CO ₃	50:1	2.5%			
E-1	5% H ₃ BO ₃	50:1	4.0%			
E-2	5% H ₃ BO ₃	50:1	0.8%			
F-1	NaHCO ₃ Powder	50:1	6.2%			
F-2	NaHCO ₃ Powder	50:1	4.6%			
G-1	Na ₂ CO ₃ Powder	50:1	4.8%			
G-2	Na ₂ CO ₃ Powder	50:1	3.5%			
G-3	Na ₂ CO ₃ Powder	15:1	8.0%			
I-3	1% H ₂ O ₂	50:1	30.2%	31.7%	32.6%	32.6%
I-4	1% H ₂ O ₂	50:1	31.3%	X	X	X
J-5	3% H ₂ O ₂	50:1	72.6%	76.2%	49.4%	81.1%
J-6	3% H ₂ O ₂	50:1	71.3%	X	X	86.5%
K-7	5% H ₂ O ₂	50:1	92.9%	84.7%	71.5%	84.3%
K-8	5% H ₂ O ₂	50:1	82.2%	83.6%	81.5%	86.5%
L-3	1% NaOCl	50:1	28.0%	27.3%	27.0%	27.4%
L-4	1% NaOCl	50:1	28.4%	28.6%	29.5%	30.0%
M-3	3% NaOCl	50:1	60.8%	58.7%	60.5%	57.6%
M-4	3% NaOCl	50:1	63.7%	64.0%	66.9%	67.7%
N-3	5% NaOCl	50:1	81.8%	82.1%	88.9%	88.6%
N-4	5% NaOCl	50:1	85.1%	85.0%	89.6%	87.8%
O-3	1% NaClO ₃	50:1	11.0%	10.4%	5.3%	5.9%
O-4	1% NaClO ₃	50:1	4.6%	4.2%	6.5%	7.1%
P-3	3% NaClO ₃	50:1	3.2%	2.9%	2.1%	2.3%
P-4	3% NaClO ₃	50:1	1.7%	6.5%	2.6%	7.1%
Q-3	5% NaClO ₃	50:1	6.0%	6.5%	4.5%	5.4%
Q-4	5% NaClO ₃	50:1	2.1%	6.0%	2.9%	6.1%
R-3	1% KMnO ₄	50:1	25.7%	25.9%	26.4%	25.6%
R-4	1% KMnO ₄	50:1	33.8%	X	X	X
S-3	3% KMnO ₄	50:1	57.0%	57.4%	57.0%	58.4%
S-4	3% KMnO ₄	50:1	57.0%	X	X	X
T-3	5% KMnO ₄	50:1	81.6%	81.8%	84.4%	83.9%
T-4	5% KMnO ₄	50:1	82.8%	X	X	X
U-3	1% K ₂ Cr ₂ O ₇	50:1	25.9%	23.7%	26.8%	25.7%
U-4	1% K ₂ Cr ₂ O ₇	50:1	25.6%	X	X	X

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(3) Contamination (3) Series B

Immed. 30 min. Immed. 30 min.

(2) Remarks

0.0%				No noticeable heat or reaction
0.4%				No noticeable heat or reaction
0.4%				No noticeable heat or reaction
5.4%				No noticeable heat or reaction
4.0%				No noticeable heat or reaction
1.9%				No noticeable heat or reaction
1.0%				No noticeable heat or reaction
2.5%				No noticeable heat or reaction
4.0%				No noticeable heat or reaction
0.8%				No noticeable heat or reaction
6.2%				No noticeable heat or reaction
4.6%				No noticeable heat or reaction
4.8%				No noticeable heat or reaction
3.5%				No noticeable heat or reaction
8.0%				No noticeable heat or reaction
30.2%	31.7%	32.6%	32.6%	Reaction noticeable, T = 27°C
31.3%	X	X	X	Reaction noticeable, T = 28°C
72.6%	76.2%	49.4%	81.1%	Reaction noticeable, T = 28°C
71.3%	X	X	86.5%	Reaction noticeable, T = 28°C
92.9%	84.7%	71.5%	84.3%	Vigorous reaction, T = 37°C
82.2%	83.6%	81.5%	86.5%	Vigorous reaction, T = 38°C
28.0%	27.3%	27.0%	27.4%	Vigorous reaction, T = 36°C
28.4%	28.6%	29.5%	30.0%	Vigorous reaction, T = 34°C
60.8%	58.7%	60.5%	57.6%	Vigorous reaction, T = 54°C
63.7%	64.0%	66.9%	67.7%	Vigorous reaction, T = 51°C
81.8%	82.1%	88.9%	88.6%	Extremely vigorous, T = 62°C, Flashed!
85.1%	85.0%	89.6%	87.8%	Extremely vigorous, T = 66°C
11.0%	10.4%	5.3%	5.9%	No noticeable heat or reaction
4.6%	4.2%	6.5%	7.1%	No noticeable heat or reaction
3.2%	2.9%	2.1%	2.3%	No noticeable heat or reaction
1.7%	6.5%	2.6%	7.1%	No noticeable heat or reaction
6.0%	6.5%	4.5%	5.4%	No noticeable heat or reaction
2.1%	6.0%	2.9%	6.1%	No noticeable heat or reaction
25.7%	25.9%	26.4%	25.6%	Vigorous reaction, T = 34°C
33.8%	X	X	X	Vigorous reaction, T = 36°C
57.0%	57.4%	57.0%	58.4%	Vigorous reaction, T = 53°C
57.0%	X	X	X	Vigorous reaction, T = 52°C
81.6%	81.8%	84.4%	83.9%	Extremely vigorous, T = 64°C
82.6%	X	X	X	Extremely vigorous, T = 64°C
25.9%	23.7%	26.8%	25.7%	Reaction noticeable, T = 30°C
25.6%	X	X	X	Reaction noticeable, T = 31°C

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TABLE 2.1
CONTINUED

Run No.	Decontamination	(1) gm Ratio	Decontamination			
			(3) Series A		(3) Series B	
			Immed.	30 min.	Immed.	30
V-3	3% $K_2Cr_2O_7$	50:1	47.4%	47.7%	52.2%	5
V-4	3% $K_2Cr_2O_7$	50:1	50.8%	X	X	
W-3	5% $K_2Cr_2O_7$	50:1	69.1%	70.0%	79.8%	7
W-4	5% $K_2Cr_2O_7$	50:1	70.4%	X	X	

- (1) gm Ratio of decontaminant to MHF-3.
- (2) Reaction temperature was reported when it exceeded a 5°C temperature rise.
- (3) Series A is based on analysis of the spent liquor as initially made up. In Series B, the sample was neutralized to pH 7.5 before analysis. Analyses were made immediately after decontamination and again 30 minutes later.

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<u>(3) Decontamination</u>				<u>(2) Remarks</u>
<u>Series A</u>		<u>Series B</u>		
<u>Immed.</u>	<u>30 min.</u>	<u>Immed.</u>	<u>30 min.</u>	
47.4%	47.7%	52.2%	51.6%	Vigorous reaction, T = 36°C
50.8%	X	X	X	Vigorous reaction, T = 36°C
69.1%	70.0%	79.8%	79.7%	Vigorous reaction, T = 46°C
70.4%	X	X	X	Vigorous reaction, T = 48°C

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TABLE 2.2
MHF-5 DECONTAMINATION

Run No.	Decontaminant	(1) gm Ratio	Decontamination			
			(3) Series A		(3) Series B	
			Immed.	30 min.	Immed.	30 min.
AA-5	H ₂ O	50:1	4.0%	3.6%		
AA-6	H ₂ O	50:1	3.0%	X		
BB-1	5% NaCl	50:1	4.3%	4.2%		
BB-2	5% NaCl	50:1	3.9%	X		
CC-1	5% NaHCO ₃	50:1	3.9%	3.3%		
CC-2	5% NaHCO ₃	50:1	4.0%	X		
DD-1	5% Na ₂ CO ₃	50:1	5.3%	6.3%		
DD-2	5% Na ₂ CO ₃	50:1	4.8%	X		
EE-1	5% H ₃ BO ₃	50:1	5.3%	5.3%		
EE-2	5% H ₃ BO ₃	50:1	4.6%	X		
II-1	1% H ₂ O ₂	50:1	24.8%	25.2%	27.8%	27.1%
II-2	1% H ₂ O ₂	50:1	30.0%	X	X	X
JJ-1	3% H ₂ O ₂	50:1	79.1%	78.8%	76.2%	75.9%
JJ-2	3% H ₂ O ₂	50:1	75.9%	X	X	X
KK-1	5% H ₂ O ₂	50:1	83.1%	86.2%	77.4%	84.4%
KK-2	5% H ₂ O ₂	50:1	70.1%	78.1%	70.5%	88.7%
KK-3	5% H ₂ O ₂	50:1	71.2%	62.2%	68.9%	62.7%
KK-4	5% H ₂ O ₂	50:1	80.5%	72.9%	72.6%	73.7%
LL-1	1% NaOCl	50:1	21.0%	20.7%	20.2%	18.0%
LL-2	1% NaOCl	50:1	18.4%	X	X	X
MM-1	3% NaOCl	50:1	46.2%	44.1%	48.4%	46.5%
MM-2	3% NaOCl	50:1	46.1%	X	X	X
NN-1	5% NaOCl	50:1	75.4%	79.4%	79.0%	80.8%
NN-2	5% NaOCl	50:1	78.7%	X	X	X
OO-1	1% NaClO ₃	50:1	2.6%	4.3%	4.3%	6.0%
OO-2	1% NaClO ₃	50:1	3.3%	X	X	X
PP-1	3% NaClO ₃	50:1	7.3%	7.5%	6.9%	7.6%
PP-2	3% NaClO ₃	50:1	4.0%	X	X	X
QQ-1	5% NaClO ₃	50:1	4.0%	4.0%	4.0%	4.5%
QQ-2	5% NaClO ₃	50:1	4.3%	X	X	X
RR-1	1% KMnO ₄	50:1	22.6%	23.6%	21.5%	22.0%
RR-2	1% KMnO ₄	50:1	24.2%	X	X	X
SS-1	3% KMnO ₄	50:1	53.5%	53.6%	55.0%	55.8%
SS-2	3% KMnO ₄	50:1	56.9%	X	X	X
TT-1	5% KMnO ₄	50:1	81.0%	82.7%	85.0%	86.6%
TT-2	5% KMnO ₄	50:1	83.9%	84.5%	87.0%	87.7%
UU-1	1% K ₂ Cr ₂ O ₇	50:1	21.2%	21.6%	X	X
UU-2	1% K ₂ Cr ₂ O ₇	50:1	19.8%	X	17.1%	19.0%
VV-1	3% K ₂ Cr ₂ O ₇	50:1	44.7%	45.4%	50.3%	50.9%
VV-2	3% K ₂ Cr ₂ O ₇	50:1	45.4%	X	X	X

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(3) Decontamination (3) Series B

Immed. 30 min.

Immed. 30 min.

(2) Remarks

4.0%	3.6%			No noticeable heat or reaction
3.0%	X			No noticeable heat or reaction
4.3%	4.2%			No noticeable heat or reaction
3.9%	X			No noticeable heat or reaction
3.9%	3.3%			No noticeable heat or reaction
4.0%	X			No noticeable heat or reaction
5.3%	6.3%			No noticeable heat or reaction
4.8%	X			No noticeable heat or reaction
5.3%	5.3%			No noticeable heat or reaction
4.6%	X			No noticeable heat or reaction
24.8%	25.2%	27.8%	27.1%	Reaction noticeable, T = 28°C
30.0%	X	X	X	Reaction noticeable, T = 27°C
79.1%	78.8%	76.2%	75.9%	Reaction noticeable, T = 31°C
75.9%	X	X	X	Reaction noticeable, T = 32°C
83.1%	86.2%	77.4%	84.4%	Vigorous reaction, T = 54°C
70.1%	78.1%	70.5%	68.7%	Vigorous reaction, T = 50°C
71.2%	62.2%	68.9%	62.7%	Vigorous reaction, T = 44°C
80.5%	72.9%	72.6%	73.7%	Vigorous reaction, T = 43°C
21.0%	20.7%	20.2%	18.0%	Vigorous reaction, T = 34°C
18.4%	X	X	X	Vigorous reaction, T = 34°C
46.2%	44.1%	48.4%	46.5%	Vigorous reaction, T = 51°C
46.1%	X	X	X	Vigorous reaction, T = 51°C
75.4%	79.4%	79.0%	80.8%	Extremely vigorous, T = 67°C
78.7%	X	X	X	Extremely vigorous, T = 69°C
2.6%	4.3%	4.3%	6.0%	No noticeable heat or reaction
3.3%	X	X	X	No noticeable heat or reaction
7.3%	7.5%	6.9%	7.6%	No noticeable heat or reaction
4.0%	X	X	X	No noticeable heat or reaction
4.0%	4.0%	4.0%	4.5%	No noticeable heat or reaction
4.3%	X	X	X	No noticeable heat or reaction
22.6%	23.6%	21.5%	22.0%	Vigorous reaction, T = 34°C
24.2%	X	X	X	Vigorous reaction, T = 33°C
53.5%	53.6%	55.0%	55.8%	Vigorous reaction, T = 53°C
56.9%	X	X	X	Vigorous reaction, T = 54°C
81.0%	82.7%	85.0%	86.6%	Extremely vigorous, T = 64°C
83.9%	84.5%	87.0%	87.7%	Extremely vigorous, T = 65°C
21.2%	21.6%	X	X	Reaction noticeable, T = 30°C
19.8%	X	17.1%	19.0%	Reaction noticeable, T = 30°C
44.7%	45.4%	50.3%	50.9%	Vigorous reaction, T = 36°C
45.4%	X	X	X	Vigorous reaction, T = 36°C

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TABLE 2.2
CONTINUED

Run No.	Decontaminant	(1) gm Ratio	Decontamination (3) Series A		
			Immed.	30 min.	Immed
WW-1	5% $K_2Cr_2O_7$	50:1	63.3%	63.4%	69.6%
WW-2	5% $K_2Cr_2O_7$	50:1	63.6%	63.3%	68.0%

- (1) gm Ratio of decontaminant to MHF-5.
- (2) Reaction temperature was reported when it exceeded a 5°C temperature rise.
- (3) Series A is based on analysis of the spent liquor initially made up. In Series B the sample was neutralized to pH 7.5 before analysis. Analyses were made immediately after decontamination, and again 30 minutes later.

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<u>Decontamination</u>				<u>(2) Remarks</u>
<u>(3) Series A</u>		<u>(3) Series B</u>		
<u>Immed.</u>	<u>30 min.</u>	<u>Immed.</u>	<u>30 min.</u>	
63.3%	63.4%	69.6%	69.7%	Vigorous reaction, T = 42°C
63.6%	63.3%	68.0%	67.6%	Vigorous reaction, T = 43°C

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Series B the sample was
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TABLE 2.3
MIXED HYDRAZINE FUELS DECONTAMINATION
ECONOMIC EVALUATION

<u>Decontaminant</u>	<u>Est. Cost Per Ton</u>	<u>Approximate Effectiveness</u>	<u>Est. Cost to Decontami- nate 100 lbs. of Fuel</u>
1) 5% KMnO_4	\$490(a)	84%	\$73
2) 5% $\text{K}_2\text{Cr}_2\text{O}_7$	380(a)	69%	69
3) 5% H_2O_2	640(b)	77%	148
4) 5% NaOCl	33(c)	83%	33

(a) Cost of one ton 100% basis, December 1965

(b) Cost of one ton 70% H_2O_2 , December 1965

(c) Cost of one ton 15% NaOCl , December 1965

Note: All costs take into consideration the relative effectiveness of the decontaminants as applied at a 50:1 deluge to spill ratio.

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SECTION 3

ALUMIZINE

3.1 PRACTICAL STUDY

3.1.1 General

Alumizine is a gelled fuel consisting of aluminum, hydrazine and an appropriate gelling agent. Alumazines can be made up containing various percentages of aluminum. The aluminum concentration causes negligible changes in many of the physical properties of the gelled material (1) which are almost identical to those of neat hydrazine. Examples are shown below:

	<u>Hydrazine</u>	<u>Alumizine 43G</u>
Boiling Point °F	236.9	237 (estimated)
Freezing Point °F	34.8	32
Flash Point °F	100 - 126	123
Vapor Pressure (psia)	0.2 at 68°F	0.27 at 77°F

The example given, alumizine 43G, contains 43% aluminum. Since these properties remain virtually constant for all alumazines, they all may be considered as similar to hydrazine in these respects. Therefore, the same problems are presented for the decontamination of alumizine and hydrazine and the same techniques are suggested.

3.1.2 Decontamination

No specific instances of the decontamination of actual spills of alumizine were found in the literature. However, references were made to techniques and materials used to flush and clean equipment in which alumizine had been handled. A 6 1/2% solution of hydroxyacetic acid had been used for the Titan II as a cleaner and neutralizer. Other materials used with varying degree of success include 1% and 5% solutions of $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 and H_3PO_4 (1). Reference has been made wherein the fuel system was cleaned with caustic (2).

Hydrazine is the toxic and highly flammable component of alumizine. Therefore, techniques for combatting hydrazine spills are considered to be applicable for alumizine. Hydrazine is flammable in concentrations between 4.7 and 100% in air. Current practice for handling spills is almost universally, dilution with water and subsequent chemical treatment with hypochlorites and H_2O_2 (3). Water sprays have been effective in knocking down vapors from spilled hydrazine. It forms a hydrate which holds the water, has a lower vapor pressure and is less toxic than hydrazine itself. Foams and dry chemicals have also been used successfully in extinguishing hydrazine fires (3).

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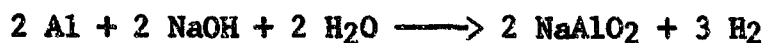
3.1.3 Toxicity

The toxic component of alumizine is hydrazine. The aluminum as such does not present any toxic hazard. Since the vapors evolved from alumizine are entirely hydrazine, and the vapor pressures are virtually identical for both alumizine and hydrazine, the toxicities of the two materials must be considered as identical. The toxicity of hydrazine has been considered elsewhere in this report (Refer to Section 5). The threshold value for hydrazine which has been adopted by the American Conference of Governmental Industrial Hygienists is 1 ppm. Therefore, alumizine must be considered to be a very toxic material and exposure to its vapors and physical contact must be avoided.

3.2 Theoretical Study

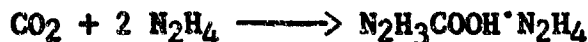
Alumizine is a gel of hydrazine and aluminum. In order to effectively neutralize a gelled propellant, the gel must first be destroyed so that intimate contact between the propellant and decontaminant can be achieved. In the case at hand, after destroying the gel, the problem reduces essentially to neutralizing N_2H_4 .

Investigators examined a number of materials in their search for a de-gelling agent. Neither salt water nor fresh water readily dissolve the gel. A trichloroethylene flush causes the gel to harden. A caustic (NaOH) flush gives good results on stainless steel tanks, evolving large amounts of gas (3). The mechanism of this process is not described. However, the gas evolved is undoubtedly flammable hydrogen. This unfortunately could rule out the use of NaOH.



$$\Delta H = -101 \text{ kilo. cal./mol.}$$

A CO_2 gas purge reportedly breaks the gel and allows the aluminum to settle (3). CO_2 also reacts with hydrazine to form the hydrazine salt of carbazic acid (4).



A carbonated water flush was suggested as a possible means of destroying the gel (3). This latter method appears to have particular merit since the hydrate would be formed along with the hydrazine salt of carbazic acid.



$$\Delta H = -3.9 \text{ kilo. cal./mol.}$$

Hydrazine reacts with various inorganic reagents to yield salts, complexes, nitrogen, hydrogen, hydrogen azide, or ammonia (5, 6, 7). In decontamination of toxic materials, the preferred reaction products are salts, complexes or inert gas. H_2O , $NaHCO_3$,

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($\text{CO}_2\text{-H}_2\text{O}$), H_3BO_3 , H_2O_2 and KMnO_4 were found to be quite effective on spills of neat hydrazine. Many other compounds and chemical groups were considered but ruled out because of the nature of the end products, availability, heat of reaction, cost, etc. (8). Aqueous solutions of hydroxyacetic acid, $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 have been used as flushes for alumizine.

3.2.1 Conclusions

Since the decontamination of a gel presents a two-fold problem, breaking the gel and neutralizing the hydrazine, decontaminants that have demonstrated either capability should be investigated. Therefore, materials such as $\text{H}_2\text{O-CO}_2$, NaOH , $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , NaHCO_3 , H_3BO_3 , CH_2OHCOOH , and dilute solutions of oxidizers warranted bench scale investigation as alumizine decontaminants.

3.3 Experimental Study

A bench scale investigation was conducted to develop adequate means of decontaminating spills of alumizine 33G. The nominal composition of alumizine 33G is: 33% aluminum, 66% hydrazine and 1% carbopol 940, the gelling agent.

Since alumizine 33G is a gel, it was necessary to first destroy the gel to more completely expose the spilled fuel to the decontaminant thereby permitting rapid and complete decontamination. Therefore, a decontaminant for alumizine, as well as for other gelled propellants, must accomplish two purposes -- destroy the gel, and neutralize the propellant. The finely divided aluminum in the alumizine presents no particular problems, since it is nontoxic and relatively non-flammable. The hydrazine, however, is both toxic and highly flammable. Therefore, the decontamination investigation was centered around the hydrazine and the residual aluminum was largely ignored.

Hydrazine is completely miscible with water. It is non-combustible when diluted with water to less than 40% by volume. Application of decontaminating agents in aqueous solutions would not only reduce the fire hazard but would scrub toxic hydrazine vapors from the air. Therefore, all candidate agents were applied as dilute aqueous solutions.

Unfortunately, water alone does not break down the gel, nor does it neutralize the fuel, so it is ineffective as a decontaminant per se. The materials considered as decontaminants were selected on the basis of a prior literature search and theoretical study.

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3.3.1 Apparatus

The low vapor pressure of the alumizine at ambient temperature precluded the necessity of a closed decontamination set up. Therefore, a set up similar to that for the MHF investigation (refer to Section 2) was used. A weighed amount of fuel was placed in an Erlenmeyer flask. The test solution was then added to the fuel by gravity flow through a glass delivery tube from a reservoir. No stirring was provided since the physical dispersion of the fuel would prevent observation of the decontaminant's effectiveness in breaking down the gel.

3.3.2 Materials

The alumizine 33G was obtained from Aerojet-General, Sacramento, California, Department 9630. The following materials used as decontaminants were B & A, Reagent Grade or the highest purity available: NaHCO_3 , NaCl , H_3BO_3 , H_3PO_4 , H_2O_2 , KMnO_4 , NaOCl , NaOH , $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , NaNO_3 , $\text{K}_2\text{S}_2\text{O}_8$, and HNO_3 . The glycolic acid obtained from B & A was manufactured by Eastman Organic Chemicals Cat. No. T998, 70% Technical Grade. The carbonated water was made by saturating distilled water with CO_2 gas.

3.3.3 Procedure

The procedure used in the sampling and deluging of alumizine was identical to that used on the mixed hydrazine fuels (Section 2) with one exception. Alumizine, being a gel, could not be poured from the weighing bottle to the Erlenmeyer flask. Therefore, the transfer was made with a stainless steel spatula. Sampling was done in a plastic glove bag to prevent oxidation. In order to assure a quantitative transfer, the spatula, containing the sample on its tip, was placed in the flask and remained there while the decontaminant flowed onto the sample. Thus, no portion of the sample was lost, and it was not necessary to rinse the sample off the spatula. This avoided dilution of the sample before decontamination was begun. The flask was swirled to provide uniform contact with the fuel after the decontaminant had been added and the rate of gel breakdown had been observed. When the reaction was completed, the spatula was rinsed and removed.

Alumizine samples weighing approximately two grams were used for all runs. Exact sample weights were taken to permit accurate assessment of the decontaminant's effectiveness.

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3.3.4 Experimental Data

The addition of the decontaminant to the fuel was carefully observed and the nature of the reaction noted. A close observation was made to see if the gel broke down, and the aluminum released as a powder which settled on the bottom of the solution. Evolution of gas, formation of a precipitate, and color change in the solution were visual evidence that a reaction took place. In addition, the reaction temperature of the solution was checked. The reactions that appeared to be the most vigorous also showed the greatest temperature rise.

A total of 21 runs was made involving 18 different decontaminants. These results are shown in Table 3.1. Preliminary runs were made on each of the candidate decontaminants to primarily determine its approximate effectiveness in breaking down the gel. However, the residue was also analyzed to determine effectiveness as a decontaminant. Those materials which showed merit were rerun.

The majority of these test solutions were the same as those tested on the mixed hydrazine fuels. These materials displayed approximately the same effectiveness in neutralizing the alumizine as they had shown in neutralizing the mixed hydrazine fuels. However, several of these showed little effectiveness in breaking down the gel.

3.3.5 Analytical Procedure

The effectiveness of the test decontaminant in neutralizing the fuel was calculated on the basis of the residual unreacted fuel present in the spent liquor. The procedure was identical to that described in connection with the mixed hydrazine fuels (Section 2).

As shown in Table 3.1, the spent liquors from these runs were analyzed four times. The first analysis (Series A) was always performed within 15 minutes of the completion of the run, and a second analysis 30 minutes after the first. This was to determine whether the neutralization reaction took place rapidly or whether it proceeded slowly over an extended period. Other analyses were run in which the pH was adjusted to pH 7.5 (Series B). Again samples were analyzed within 15 minutes of run completion and 30 minutes later.

3.3.6 Economic Evaluation

Only three materials, KMnO_4 , NaOCl and H_2O_2 , showed sufficient effectiveness as decontaminants to warrant an economic evaluation. The KMnO_4 however, had an extremely vigorous reaction and left a messy residue. In addition, the indicated effectiveness

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rating for this material is somewhat questionable. The reaction of the 3% NaOCl was also considered too vigorous to consider this material as a satisfactory decontaminant. On the other hand, the peroxide appeared to be satisfactory in all respects.

A comparison of the costs for these three materials to decontaminate a 100 pound alumazine spill is shown in Table 3.2. Despite the apparent economic advantage of the 5% KMnO_4 and the 3% NaOCl as compared to 5% H_2O_2 , we feel that the peroxide is still to be preferred. It should be noted that the economics for the peroxide improve with more dilute solutions. In this evaluation, all water costs have been omitted.

3.3.7 Conclusions

The results of this investigation show that of the 18 candidates, only six broke down the gel on contact. These were 5% NaHCO_3 , 5% NaCl, 3% NaOCl, 5% NaOH, 5% NaNO_3 , and 5% H_2O_2 . A breakdown of the gel was also accomplished with 3% and 1% H_2O_2 , but the reaction of these dilute solutions was less rapid. The 3% peroxide took five minutes while the 1% solution took 10 minutes. Of these compounds, the 5% H_2O_2 and 3% H_2O_2 showed high effectiveness as decontaminants for the hydrazine. Although 3% NaOCl did destroy 46.1% of the fuel, the reaction was considered too vigorous. It was therefore decided not to attempt a run with 5% NaOCl.

The KMnO_4 did not completely break down the gel. On the contrary the by-product material, MnO_2 , adhered to the gel forming a hard coating. It is felt that this coating entrapped unneutralized fuel and prevented further reaction. Since the amount of neutralization was based on the analytic determination of unreacted N_2H_4 , the entrapped material would not be detected. This would give an erroneously high efficiency for this material. In addition, the KMnO_4 produced a very vigorous reaction, the temperature rising to 77°C . Therefore, from both standpoints, KMnO_4 is considered to be unsatisfactory.

The only material which showed a high effectiveness together with no undesirable reaction was hydrogen peroxide. We, therefore, recommend dilute aqueous solutions of H_2O_2 as a decontaminant for spills of alumazine.

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- (5) Jacobson, C. A., "Encyclopedia of Chemical Reactions," Vol. 6, Reinhold Pub. Co., New York, 1956, pp 207, 234, 236.
- (6) Clark, C. C., "Hydrazine," Olin Mathieson Chemical Corp., 1953, p. 4.
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- (8) Siegmund, J. M., Jackson, R. B., Ogden, R. E. and Poon, B. T., "Research on Materials and Methods for Decontamination of Toxic Missile Propellant Spillage," Allied Chemical Corp., Technical Documentary Report No. ASD-TDR-62-64, Contract No. AF 33(616)-7672, June 1962.

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TABLE 3.1
ALUMIZINE DECONTAMINATION

Run No.	Decontaminant	pH(1)	Decontamination				R
			Series A (2)		Series B (3)		
			Immed.	30 Min.	Immed.	30 Min.	
1A	Neat H ₂ O	9.6%	21.5%	13.9%	13.9%	13.3%	G.B. incomplet
2A	5% NaHCO ₃	9.7	6.1	7.3	7.3	6.2	G.B. on contac
3A	5% NaCl	9.4	12.4	4.7	5.6	4.8	G.B. on contac
4A	5% H ₃ BO ₃	8.6	5.8	5.3	6.2	5.8	G.B. incomplet
5A	5% H ₃ PO ₄	3.4	4.4	4.5	5.0	4.5	G.B. incomplet
6A	5% Glycolic Acid	3.8	13.0	8.7	8.9	8.9	G.B. incomplet
7A	5% H ₂ O ₂	8.8	79.1	77.6	71.5	75.9	G.B. on contac
7A-1	5% H ₂ O ₂	8.7	77.7	79.2	76.5	78.3	G.B. on contac
7B	3% H ₂ O ₂	8.6	69.7	71.2	68.2	71.5	G.B. after 5 m
7B-1	3% H ₂ O ₂	8.6	75.3	73.9	73.7	74.7	G.B. after 5 m
7C	1% H ₂ O ₂	8.6	29.5	28.2	27.4	28.5	G.B. after 10
7D-1	1% H ₂ O ₂	8.6	32.4	32.6	21.7	33.2	G.B. after 10
8A	5% KMnO ₄	11.6	84.9	85.3	85.8	86.1	G.B. incomplet adhered to s
9A	3% NaOCl	9.5	46.7	43.9	46.1	46.4	G.B. on contac
10A	5% NaOH	12.1	2.3	6.6	5.0	5.8	G.B. on contac
11A	5% (NH ₄) ₂ SO ₄	8.5	11.7	11.4	11.2	12.0	G.B. incomplet
12A	5% Na ₂ SO ₄	9.4	11.7	12.4	14.2	11.1	G.B. incomplet
13A	CO ₂ -Water	8.4	12.4	14.7	9.4	15.5	G.B. incomplet
14A	5% NaNO ₃	7.8	10.5	12.4	11.4	11.4	G.B. on contac
15A	5% K ₂ S ₂ O ₈	7.5	22.7	23.8	22.6	23.0	G.B. incomplet
16A	5% HNO ₃	2.5	5.3	4.8	6.2	6.5	G.B. incomplet

Notes: Gr - ratio of decontaminant to alumizine was 50:1 for all runs.

- (1) pH of the resultant solution after the decontaminant was added to the fuel.
- (2) Series A is based on analysis of the spent liquor as initially made up. Analysis made immediately after decontamination and again 30 minutes later.
- (3) In Series B, the sample was neutralized to pH 7.5 before analysis. Analyses were made immediately after decontamination and again 30 minutes later.
- (4) Reaction temperature was reported when it exceeded a 5°C temperature rise. G.B. represents gel breakdown.

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Decontamination			
A (2)	Series B (3)		Remarks (4)
30 Min.	Immed.	30 Min.	
13.9%	13.9%	13.3%	G.B. incomplete. No noticeable heat or reaction.
7.3	7.3	6.2	G.B. on contact. No noticeable heat or reaction.
4.7	5.6	4.8	G.B. on contact. No noticeable heat or reaction.
5.3	6.2	5.8	G.B. incomplete. No noticeable heat or reaction.
4.5	5.0	4.5	G.B. incomplete. No noticeable heat or reaction.
8.7	8.9	8.9	G.B. incomplete. No noticeable heat or reaction.
77.6	71.5	75.9	G.B. on contact. Vigorous reaction, T = 35°C
79.2	76.5	78.3	G.B. on contact. Vigorous reaction, T = 33°C
71.2	68.2	71.5	G.B. after 5 minutes. Vigorous reaction, T = 28°C
73.9	73.7	74.7	G.B. after 5 minutes. Vigorous reaction, T = 29°C
28.2	27.4	28.5	G.B. after 10 minutes. Reaction noticeable.
32.6	21.7	33.2	G.B. after 10 minutes. Reaction noticeable.
85.3	85.8	86.1	G.B. incomplete. MnO ₂ caked in gel. Hardened and adhered to surface. T = 77°C. Extremely vigorous.
43.9	46.1	46.4	G.B. on contact. Very vigorous reaction, T = 65°C
6.6	5.0	5.8	G.B. on contact. Vigorous reaction, T = 48°C
11.4	11.2	12.0	G.B. incomplete. No noticeable heat or reaction.
12.4	14.2	11.1	G.B. incomplete. No noticeable heat or reaction.
14.7	9.4	15.5	G.B. incomplete. No noticeable heat or reaction.
12.4	11.4	11.4	G.B. on contact. No noticeable heat or reaction.
23.8	22.6	23.0	G.B. incomplete. No noticeable heat or reaction.
4.8	6.2	6.5	G.B. incomplete. No noticeable heat or reaction.

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TABLE 3.2
ALUMIZINE DECONTAMINATION
ECONOMIC EVALUATION

<u>Decontaminant</u>	<u>Est. Cost Per Ton</u>	<u>Approx. Effect.</u>	<u>Est. Cost Decontaminate 100 lbs. Fuel</u>
5% H_2O_2	\$640 (a)	78%	\$149
3% H_2O_2	640 (a)	72%	97
1% H_2O_2	640 (a)	30%	67
5% $KMnO_4$	490 (b)	85%	72
3% $NaOCl$	33 (c)	47%	35

(a) Cost of one ton 70% H_2O_2 , December 1965

(b) Cost of one ton 100% $KMnO_4$, December 1965

(c) Cost of one ton 15% $NaOCl$, December 1965

NOTE: All costs take into consideration the relative effectiveness of the decontaminants as applied at a 50:1 deluge to fuel ratio.

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SECTION 4

NITROGEN TETROXIDE

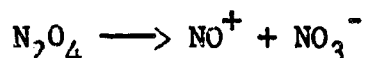
4.1 PRACTICAL STUDY

4.1.1 General

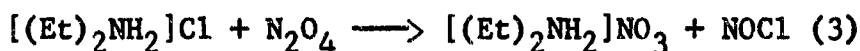
Nitrogen tetroxide is a heavy, brown liquid melting at -11.2°C and boiling at 21.15°C (1)(2). There is a temperature dependent equilibrium in the liquid between N_2O_4 and NO_2 . At 27°C the ratio of N_2O_4 to NO_2 is 4 to 1 while at 100°C the ratio is 1 to 9. The color of nitrogen tetroxide fumes varies from yellow to reddish-brown depending on the equilibrium point. Since NO_2 has unpaired electrons, it is paramagnetic, and therefore, colored (red-brown) while N_2O_4 , having only paired electrons, is diamagnetic and, therefore, colorless (1)(2)(3).

Nitrogen tetroxide is a powerful oxidant. While it is not flammable, it does support combustion and is, in fact, a hypergolic compound. It is insensitive to shock, heat, or detonation (4).

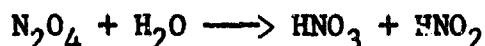
The low conductivity of nitrogen tetroxide is due to its autoionization:



Thus, it is a nonprotonic solvent with the cation NO^+ considered the acid radical and the anion NO_3^- considered the base (3)(5). Some reactions are explained on the basis of this ionizing characteristic:

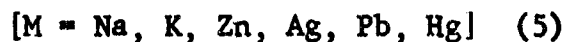
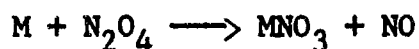


N_2O_4 reacts with water:

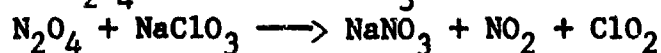
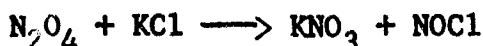


followed by $3\text{HNO}_2 \longrightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ (3)

With metals the following reaction occurs:



With salts, nitrates are formed: (5)



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4.1.2 Decontamination

4.1.2.1 Literature Review

The procedures employed for handling nitrogen tetroxide spills are dependent on whether or not there is a resultant fire.

For simple spills the procedures are directed towards minimizing the vaporization of nitrogen tetroxide. Sprays of water or aqueous solutions for scrubbing vapors from the air and for preventing further liquid vaporization have been tested. While several of the solutions have proven satisfactory, none has offered any significant advantage over the use of the water spray alone (6).

A recommended procedure for application of water by spraying is to provide two sets of fog nozzles, the first set at ground level with the spray pointed upward at a 45° angle and the second set overhead with the spray pointed down (7). It is also recommended that water application not be too forceful to prevent splashing and resulting boiloff of nitrogen tetroxide (8).

Of the solutions evaluated, NaOH, NaHCO₃, and H₂O₂ were satisfactory for vapor scrubbing while NaOH and H₂O₂ were effective for liquid retention (6).

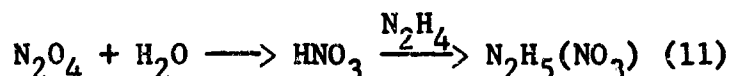
Absorbants, powders, gellants, and thickeners proved ineffective in controlling and decontaminating spills. Foams, however, were highly effective with less than 1% of nitrogen tetroxide vapor escaping through a 6 inch layer of foam in one hour (6).

The controlled neutralization of N₂O₄ may be accomplished by using 2 immiscible liquids in contact with each other. The bottom liquid, a completely halogenated hydrocarbon, is inert and completely miscible with N₂O₄. The top liquid is an aqueous solution of sodium, potassium, or ammonium hydroxide. The N₂O₄ is added to the bottom liquid which acts as a diluent. As the N₂O₄ diffuses through the interface, it is neutralized with the upper basic solution. Both liquids act as heat sinks for the heat of reaction (13).

Since nitrogen tetroxide is an oxidizer, spills with fuel will result in fires or explosions. Other effects of this strong oxidizing power of nitrogen tetroxide are explosions with organic solvents and spontaneous ignition with paper, cloth, wood, and other organic debris (8)(9).

Water is again the best extinguishing agent for nitrogen tetroxide fires, and, in fact, appears to be the only recommended agent. For N_2O_4 -fuel fires about twice as much water is needed as for an air-fuel fire. A 1:1 dilution of N_2O_4 with water will prevent fire or explosion with a fuel of 50/50 N_2H_4 -UDMH (10).

In some cases there is a delayed detonation of N_2O_4 - N_2H_4 mixtures after the application of water. This is believed to be the result of the formation of hydrazine nitrate and its subsequent violent decomposition. The reaction would be:



The table below gives figures on hydrazine concentrations which are hypergolic or burn with nitrogen tetroxide (10).

Temperature, °F	% By Weight of N_2H_4	
	Hypergolic with N_2O_4	Burns with N_2O_4
80	60	60
140	55	45
205	--	35

4.1.2.2 Recommendations

Water is the recommended decontaminating agent for use with N_2O_4 , for removing toxic vapors from the atmosphere, or neutralizing liquid spills. It is also the best extinguishing agent for use against fires caused by N_2O_4 spills.

4.1.3 Toxicity

Nitrogen tetroxide is considered a very toxic compound. Its MAC in air is 5 ppm as NO_2 (or 2.5 ppm as N_2O_4) (4). The LD₅₀ is 67 ppm for four hours exposure and 138 ppm for 30 minutes exposure. The initial symptoms are irritation of the eyes, nose and throat which lead in more severe exposure to cyanosis and dyspnea. Pulmonary edema is the result of severe exposure (4) (12) (14).

Emergency Exposure Limits (EEL's) for toxic gases are more meaningful and of greater importance than MAC's to rocket personnel. At rocket test areas, missile ranges, etc., exposures will generally be predictable, infrequent, and of short duration. The current recognized short-term EEL's established by the American Industrial Hygiene Association for N_2O_4 are as follows:

<u>Time (Minutes)</u>	<u>Limits - ppm</u>	
	<u>As NO₂--</u>	<u>As N₂O₄--</u>
5	35	17
15	25	12
30	20	10
60	10	5

Emergency tolerance values recently set by the National Academy of Sciences, National Research Council Committee on Toxicology at the request of the USAF are similar (15).

Liquid N₂O₄ in contact with the skin causes severe burns while vapor exposure leads to erythema, burns and blisters (12). In case the skin is exposed to liquid or vapor N₂O₄, decontamination by immediate flushing of the exposed areas with copious quantities of water for a minimum of 15 minutes is recommended (14).

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SECTION 5

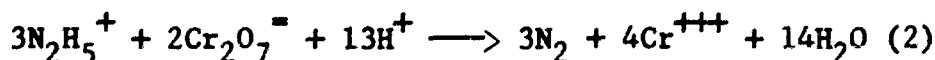
HYDRAZINE

5.1 PRACTICAL STUDY

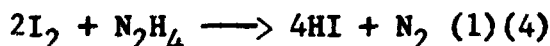
5.1.1 General

Hydrazine is a colorless, hygroscopic liquid, freezing at 1.8°C and boiling at 113.5°C. Its density is 1.0144 gm/ml at 15°C (1). Hydrazine is a combustible compound, its limits of combustibility in air are 4.67 to 100% by volume. Nitrogen, helium, water vapor and heptane have a quenching effect on its combustibility (2). The liquid is neither shock nor impact sensitive (3).

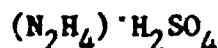
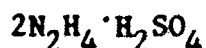
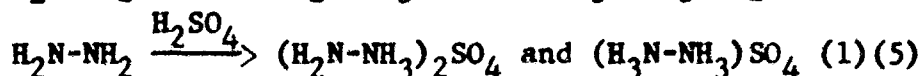
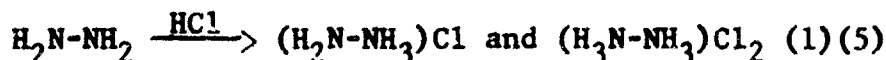
Hydrazine is a highly polar compound, completely miscible in water and soluble in the lower alcohols, ammonia, and amines (2). With water hydrazine hydrate is formed (1). This is a colorless compound, fuming in moist air. Hydrazine has strong reducing properties as shown in the reaction with dichromate:



It is autoxidized in dilute and concentrated solutions with the immediate formation of hydrogen peroxide and then nitrogen and water. Hydrazine is violently oxidized by the halogens:



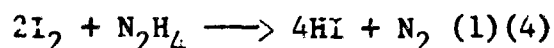
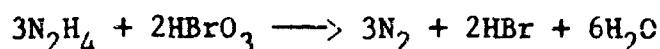
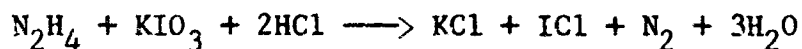
Two series of salts are produced with acids-- $(\text{N}_2\text{H}_5)^+$ and $(\text{N}_2\text{H}_6)^{++}$.



dihydrazine sulfate monohydrazine sulfate

Hydrazine nitrate is formed by the reaction of hydrazine with ammonium nitrate (6). It burns rapidly in air and explodes if heated in a confined area. It is decomposed under vacuum at 200°C to oxides of nitrogen and by concentrated sulfuric acid to nitric oxide and nitrogen. In the fused state it reacts vigorously with metals and burns with finely divided metals such as zinc and copper (2).

Hydrazine's reactions with I_2 , KIO_3 (2) and $HBrO_3$ (7) are utilized in analytical determinations.



5.1.2 Decontamination

5.1.2.1 Literature Review

The procedures used in handling hydrazine spills are dependent upon whether or not the material burns following the spillage.

For nonburning spills the procedure is to minimize vaporization and subsequent formation of flammable air-hydrazine mixtures. The most recommended procedure is to flush hydrazine with water followed by neutralization with aqueous solutions of materials such as chlorine, hypochlorite, or peroxide (8). Another possible disposal technique is controlled burning. It is also believed that a reaction occurs between hydrazine and chemicals in the soil (8). This suggests that seepage into the ground is not only permissible but may be beneficial.

Other reported decontamination procedures include the use of aqueous solutions to effect reaction, the use of solids as suppressants, and the use of foams (8).

Examples of the aqueous solutions tested are $NaHCO_3$, H_2O_2 , and $KMnO_4$. While they are suitable decontaminants, their effectiveness is no greater than water alone for the removal of N_2H_4 vapors from the air.

Examples of satisfactory powders tested are CMC (type 7HS) cellulose gum and Natrosol 250 hydroxyethyl cellulose (both from Hercules Powder Company).

Foams also proved effective in containing hydrazine spills. The results, however, show them to be merely an additional way of applying water or aqueous solutions to the spill.

Those spills which result in fire are subdivided into air-hydrazine and oxidizer-hydrazine types. There are three procedures for fire extinguishment--water, foam, and dry powder (11).

Water extinguishment is the best procedure for air-hydrazine fires. The hydrazine must be diluted to 50-60% by weight. For oxidizer-supported fires about twice as much water is needed. The table below gives figures on hydrazine concentrations which are hypergolic with nitrogen tetroxide (11).

<u>Temperature, °F</u>	<u>% By Weight of N_2H_4</u>	
	<u>Hypergolic with N_2O_4</u>	<u>Burns with N_2O_4</u>
80	60	60
140	55	45
205	--	35

Water applied as a fog is not too effective for fighting fires due to evaporation of the water.

Foams are, in effect, just gentle applications of water since the foams break under heat, forming a water layer on the hydrazine. The maximum foam required is one that yields 0.1 gallon of water in the foam/sq. ft. of hydrazine spill.

The best dry powder extinguishers are $NaHCO_3$ and $KHCO_3$. Recommended application rate is 0.02 lbs/sec./sq. ft. One disadvantage of their use is that reignition could occur if the entire fuel surface is not covered. The above also appears to be applicable to oxidizer fires (11).

Water, fog, and $NaHCO_3$ base extinguishers on large scale fires should be used with caution because of the possibility of back flashes and explosive ignition (12).

The use of halogenated compounds is not recommended for fire extinguishment since there is evidence that hydrazine reacts with such materials. CH_2BrCl , for example, increases the fire intensity and forms dense fumes (11). Hydrazine also reacts with rust to form compounds susceptible to explosive decomposition (13).

5.1.2.2 Recommendations

Water is the decontaminant recommended for hydrazine spills. The contaminated areas and equipment should be flushed with large quantities of water. The area should be ventilated completely and thoroughly. If seepage and diffusion of the dilute aqueous hydrazine into the soil cannot be tolerated, for instance because of water table problems, neutralization can be effected using materials such as hypochlorite or peroxide. Water extinguishment is also recommended for air- or oxidizer-supported hydrazine fires.

5.1.3 Toxicity

The Maximum Allowable Concentration (MAC) for hydrazine vapors has been reported as 1 ppm. In the presence of vapors at 0.25 ppm of a hydrazine-UDMH mixture, this is decreased to 0.5 ppm (9, 14). This value may be exceeded by a factor of 10 for short term exposures (9). Pulmonary edema results from inhalation (14).

The LD₅₀ (internal dosage which will cause death in 50% of those so treated) is variously reported as 64-75 mg/kg. (milligrams of hydrazine per kilogram of body weight) (15, 16, 17). The pharmacological action is chiefly central nervous system involvement (toxic and chronic convulsions) and vomiting (14, 15). There is also liver and kidney involvement. Protective agents are arginine and ornithine (16).

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SECTION 6
UNSYMMETRICAL DIMETHYLHYDRAZINE

6.1 PRACTICAL STUDY

6.1.1 General

UDMH is a clear, hygroscopic liquid, miscible in all proportions with water and soluble in water, ethanol, and most petroleum fuels. It freezes at -61.6°F and boils at 145.4°F. The liquid density is 49.6 lbs./cu. ft. and the vapor density is 2.07 (air = 1) (1). UDMH's spontaneous ignition temperature is 482°F and its explosive limits in air are 2.5 to 95% by volume (1)(2). Its temperature limits of flammability in air at 1 atmosphere are 5°F to 140°F. UDMH is thermally stable well above its boiling temperature and there is no explosive decomposition up to 112°F at 0 psig or up to 939°F at 200 psig (1)(2).

UDMH is very insensitive to shock even at elevated temperatures. Admixture with metals or metal oxides commonly found in storage systems resulted in no indication of an increase in shock sensitivity. There may be some effect with CuO or Hg and further investigation is suggested (2).

6.1.2 Decontamination

6.1.2.1 Literature Review

Any leakage of UDMH will result in a flammable air-UDMH mixture when the temperature is in the range 5-140°F (3). As with hydrazine spills the procedure is to minimize vaporization and subsequent formation of the flammable air-UDMH mixtures. For non-burning spills, the most widely recommended procedure is a water deluge (3, 4, 5).

In addition to the water application, the possible use of aqueous solutions, foams, and solids as vapor suppressants and fire preventatives have been evaluated. Aqueous solutions of NaHCO₃, H₃BO₃, carbonated water, H₂O₂, NaOCl, and KMnO₄ were effective in controlling vaporization by dilution and reaction with UDMH. Foams also proved effective while adsorbent solids proved ineffective (4). None of the above were significantly more effective than water alone.

UDMH gels present less of a hazard than does the liquid fuel when spilled since the gelled material will not splash or spread over a wide area. However, the gel requires the same safety precautions since gelling does not reduce toxicity, vapor pressure or reactivity (6).

It is recommended that UDMH be stored under an inert nitrogen blanket to minimize the possibility of fires from the for-

mation of flammable air-UDMH mixes. Since UDMH reacts with carbon dioxide to form a white solid, carbon dioxide is not recommended as a blanket (7).

When a UDMH spill results in a fire, the extinguishing procedure may vary depending on whether the fire is of the air-UDMH or oxidizer-UDMH type.

Water is the best extinguisher for the air-fuel fire. UDMH must be diluted to about 30-40% to extinguish the fire. A larger volume of water is needed for UDMH than for hydrazine fires since there is no stratification with an upper water layer as with hydrazine (3, 8, 9). A recommended water application rate is 0.8 g.p.m./sq. ft. of fire with a total application of 2.5 gal. H₂O/gal. fuel (9).

Alcohol-type foams, consisting of 60% alcohol foam with a 10:1 expansion ratio have also proved effective in fighting air-UDMH fires. The recommended application is 0.25 gal. of liquid/sq. ft. applied at a rate of 0.4 g.p.m./sq. ft. The quantity of foam depends on the fuel depth and the mixing conditions of foam and fuels (9).

Dry chemical powders, chiefly NaHCO₃ and KHCO₃, have proved effective when applied to fires at the rate of 0.02 lbs./sq. ft. x sec. The total application is 0.1 lbs./sq. ft. More of the powder is needed than for hydrazine-air type fuels (9).

Trichlorotrifluoroethane (Genetron 113) has also been found to be effective in fighting UDMH fires. Although reignition may occur, the resulting fire will not be as intense. The compound is believed to work through a combination of dilution and blanketing plus the combustion retarding action of the halogens. It is more effective than the water sprays but less effective than NaHCO₃ (9).

There are two recommendations against the use of water fog, CO₂ or NaHCO₃ extinguishers for large fires because of the possible back-flash and explosive reignition (5, 8).

With oxidizer-UDMH fires, water is again the most recommended extinguishing agent providing it does not react with the specific oxidizer. Twice as much water is needed for the oxidizer type fires as for the air type fires (8, 9).

At 80°F, 60% by weight of UDMH in water is hypergolic with nitrogen tetroxide while 30% by weight of UDMH will

still undergo combustion with nitrogen tetroxide (9).

While foams and dry powders may also be effective in extinguishing oxidizer-fuel fires, there are no specific references to their use.

6.1.2.2 Recommendations

Water is the decontaminant recommended for UDMH spills. The contaminated areas and equipment should be flushed with large quantities of water. The UDMH water solution can be neutralized by treating with hypochlorites or hydrogen peroxide. Copious water flushing is also recommended for personnel decontamination. Water sprays and fogs are recommended for removing UDMH vapor from the air.

Air or oxidizer supported UDMH fires may best be extinguished by application of large amounts of water in the form of a coarse spray.

6.1.3 Toxicity

The MAC for UDMH vapors has been tentatively set at 0.5 ppm (10, 11, 12). There is one reference which states that a human could be exposed to 10 mg/day without harmful effects (13). UDMH is a central nervous system irritant, the toxic effect being tremors, convulsions, hemolytic anemia, and cardiovascular collapse (10, 14).

The LD₅₀ for UDMH has been reported as 101 to 122 mg/kg (15, 16, 17). Pyridoxine hydrochloride and aminooxyacetic acid are reported to be protective agents (14, 15). For example, the administration of 25 mg/kg. of pyridoxine raised the LD₅₀ to 250 mg/kg (17). Recommended dosages range from 25 mg/kg (14, 17) to 50-200 mg/kg (15). The first sign of significant toxicity is emesis. Therefore, the protective agents should be administered whenever nausea and/or vomiting occur (14).

There is one report of a human exposure to liquid UDMH on the skin and eyes with the subsequent inhalation of the vapors for about one minute (18). The immediate effect was a burning sensation on the eyelids. Symptoms lasted about 24 hours while the first degree burns on the eyelids, face and forearms cleared up in about one week. The first-aid consisted of immediate washing with water followed by flushing of the eyes with normal saline solution.

Exposure to toxic propellants at rocket test sites and launch areas will always be of short duration. Therefore, emergency exposure limits (EEL's) are of greater importance to rocket personnel than MAC's. The American Industrial Hygienic Association has set the following EEL's for UDMH:

<u>Time</u>	<u>PPM</u>
5	600
15	200
30	100
60	50

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SECTION 7

HYDROGEN

7.1 PRACTICAL STUDY

7.1.1 General

Liquid hydrogen is a transparent, colorless, odorless liquid with a boiling point of -423.2°F (-252.9°C). At its boiling point, the liquid density is 4.37 lb./ft.³ and the gas density is 0.083 lbs./ft.³. The gas density at 32°F is 0.0056 lbs./ft.³. Hydrogen's limits of flammability in air are 4 to 74.2% by volume, while its autoignition temperature is 1075°F . The critical temperature and pressure are -400°F and 12.8 atmospheres, respectively (1, 2, 3). When liquid hydrogen is exposed to the atmosphere, it forms a white, voluminous vapor cloud.

The hydrogen molecule is present in two forms--ortho and para. This classification is based on the direction of the spin of the nuclei in the molecule. The equilibrium which exists between the two forms gradually shifts to parahydrogen as the gas approaches liquefaction. (At room temperature the equilibrium composition is 75% orthohydrogen and 25% parahydrogen while at -423.2°F the equilibrium composition is 99.79% parahydrogen and 0.21% orthohydrogen). Since the conversion from ortho to parahydrogen is an exothermic one, the resulting heat causes additional evaporation of the liquid. To minimize this loss, the ortho form is converted to the para form prior to liquefaction by the use of catalysts (1, 3).

Although liquid hydrogen is chemically stable, it reacts violently with strong oxidizers, igniting easily with oxygen and spontaneously with fluorine and chlorine trifluoride (3).

The effects of the low temperature of liquid hydrogen on the properties of materials of construction are important. Most ferrous metals and mild steels, for example, become brittle. Metals suitable for use with liquid hydrogen include stainless steel (300 series or other austenitic series), copper, bronze, brass, Monel and aluminum (1).

7.1.2 Decontamination

7.1.2.1 Literature Review

The procedures to be used following spills of liquid hydrogen are dependent on whether or not fires result. For minor spills with no ensuing fire, the liquid will vaporize rapidly. Even for major spills the likelihood of ignition is not as great as with other fuels. There is a slight possibility that spontaneous deflagration could occur. However, since this would require

a strong shock wave source, this possibility is rather remote (4, 5).

One recommended procedure is to provide, in areas where spillage may occur, pavement with a high specific surface to aid rapid dispersal by vaporization. Recommended surfaces include gravel, asphalt, sand and loose soil (2).

The rapid vaporization of liquid hydrogen spills leads to the formation of flammable hydrogen-air mixtures. However, results, based on a large number of experimental spills, show not only the absence of any detonations but also the absence of any evidence of a tendency to detonate. These results also indicate that both the duration of the fires and the resultant radiation flux density are less than that from fires of ordinary hydrocarbon fuels (4).

Some work has been carried out on ignition and combustion of hydrogen-air mixtures. Ignition of liquid hydrogen in a Dewar resulted in implosion and subsequent explosive vaporization of liquid hydrogen. Ignition of liquid hydrogen in a Dewar followed by spillage resulted in a burst of flame and rapid burning until all the liquid vaporized. Ignition of hydrogen-air mixtures in open spaces above a liquid spill caused rapid burning flames. It was further determined that the flame dimensions were dependent on the volume spilled, the rate of spilling, the nature of the surface on which spilled, the location of the ignition source, and when the ignition occurred (2).

Fires may be fought using the common extinguishing agents: water, carbon dioxide, and steam (3). However, other references do not recommend the use of water fog, steam, or nitrogen (4, 6).

Additional recommended fire fighting techniques are:

a) On fires resulting from spills less than two inches in depth the best procedure is to let the fire burn itself out. Using powder extinguishing agents will only increase the intensity of the fire. Water sprays should be used to prevent the possible spread of the fire.

b) For fires resulting from spills of larger than two inch depth, the fire is extinguished by a combination of a high expansion ratio mechanical foam containing nitrogen or air followed by application of KHCO_3 as the dry chemical. The nitrogen foam is applied at the rate of 0.35 gal. of liquid per sq. ft. of burning hydrogen per second, while the KHCO_3 is applied at the rate of 0.7 lbs./sq. ft. x sec. At these rates, extinguishment is accomplished in five seconds. The foam does not extinguish the fire but reduces the flame volume so that applicable rates of KHCO_3 are effective (6).

When KHCO_3 is used alone, the minimum rate of application is 3 lbs./sq. ft. x sec. to put out fires in Dewars or deep pools. Carbon dioxide will extinguish fires in Dewars and deep pools at the minimum rate of application of 1 lb./sq. ft. x sec. Neither compound is suitable alone for large spills because of the quantities required (6).

NaHCO_3 is not effective against hydrogen fires even at the rate of 44 lbs./sq. ft. x sec. ABC powder, a silicone treated monoammonium phosphate, is also not effective. Vaporizing liquids, such as CF_3Br , proved to be ineffective (6).

It was also noted that the rate of application of the extinguishing agents was more important than the total amount applied. Fires were extinguished rapidly at a given rate or they were not extinguished at all (6).

Additional hazards to be considered with the use of liquid hydrogen are the possibility of condensing oxygen to form shock sensitive mixtures and the possibility of condensing "ice" crystals by exposure to air. These hazards can be overcome by using an inert gas such as helium or nitrogen as a blanket (4).

One conclusion reached in the study of the hazards of liquid hydrogen was that certain additives (such as nitrogen, methane, and methyl chloride) considerably increased the minimum energy necessary for a spherical detonation (6).

The major conclusion reached was that liquid hydrogen is much safer to handle than many other propellants. In unconfined areas, even with air, it does not detonate. Radiation effects from hydrogen fires are less than those from fires of conventional hydrocarbon fuels. However, vapor ignition is quite easy. Therefore, extreme care should be exercised in removing all sources of ignition from areas where liquid hydrogen is handled or stored (4).

7.1.2.2 Recommendations

On fires resulting from spills less than 2 inches in depth, the best procedure is to let the fire burn itself out. Water sprays are recommended to prevent the possible spread of the fire.

For fires resulting from spills of greater than 2 inch depth, the fire is best extinguished by a combination of a high expansion ratio mechanical foam containing nitrogen or air followed by application of KHCO_3 as the dry chemical. The nitrogen foam is applied at the rate of 0.35 gal. of liquid per sq. ft. of burning hydrogen per second. The KHCO_3 is applied at the rate of 0.7 lbs./sq. ft. x sec. At these rates extinguishment is accomplished in five seconds.

7.1.3 Toxicity

Hydrogen is not considered toxic in the usual sense. However, inhalation of concentrated hydrogen will cause anoxemia and asphyxiation due to exclusion of oxygen (7).

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SECTION 8

FLUORINE

8.1 PRACTICAL STUDY

8.1.1 General

Fluorine is a pale yellow gas which condenses to a heavy (1.507 g/ml) amber-colored liquid at -306.5°F . It freezes at -363.3°F . The critical temperature and pressure are -200°F and 55 atmospheres respectively (1) (10). Combined fluorine is widely distributed in nature, and according to recent estimates accounts for about 0.065% by weight of the earth's crust. Among the elements it is about thirteenth in the order of abundance.

Fluorine reacts with practically all organic and inorganic substances except metal fluorides in their highest valence state, a few pure, completely fluorinated organic compounds, and compact metals. It is the most powerful oxidizing agent known releasing high heats upon reacting. Most reactions take place with ignition (10). It combines with all of the elements and even some of the noble gases. Fluorides of xenon, radon, and krypton have been prepared by direct combination with elemental fluorine (3) (4). It reacts with all metals at elevated temperature. Fortunately, the formation of stable fluoride coatings on some metals, retards further attack and makes them satisfactory for handling and storage (1) (10). Fluorine does not react with helium or nitrogen, nor does it react directly with oxygen under ordinary conditions. However, four oxygen fluorides are known (5). Most organic materials, solvents, etc., react spontaneously. Generally, the reaction of fluorine with organic compounds is violent. Saturated hydrocarbons under controlled conditions react to give perfluorocarbons (6).

8.1.2 Decontamination

8.1.2.1 Literature Review

The reaction of fuel with liquid fluorine is so rapid that attempts to extinguish the resulting fire are futile. Fire control here must be directed toward minimizing damage from secondary fires. In any case, if possible, one should cut off the supply of fluorine, and make certain that the decontamination system has been activated. The secondary fire should be treated as simple fire (1) (2) (8).

Small quantity spills of liquid fluorine can be neutralized with sodium carbonate. Dry chemical-type fire extinguishers are recommended for this. This material not only neutralizes the fluorine, but assists in extinguishing secondary fires (1). Large spills may be decontaminated with water spray, water fog, or sodium carbonate (7) (12).

8.1.2.2 Recommendations

Small spillages of liquid fluorine can be decontaminated with powdered sodium carbonate. The dry powder should be sprayed onto the contaminated area from a fluidized system similar to that used with dry chemical fire extinguishers. Large spills can be controlled with water in the form of a fine spray or fog. The fluorine in the latter case is converted to hot light gases which rise vertically and diffuse quickly into the atmosphere. The residual dilute aqueous HF may then in turn be neutralized with sodium carbonate if seepage into the soil is undesirable.

8.1.3 Toxicity

Fluorine gas and liquid fluorine are extremely corrosive and irritant to skin tissue. Inhalation of minor concentrations irritates the respiratory tract. Inhalation of high concentrations results in severe lung congestion. A high concentration can cause death in a few minutes. The victim should be moved to fresh air, and given oxygen immediately (1) (2) (8) (10). The present threshold limit value for fluorine published by the American Conference of Governmental Hygienists is 0.1 ppm in air for an eight hour work day, 40 hour week (2) (8) (9).

Machle reported, based on human case histories, that intermittent exposure to concentrations of ten to 20 mg/cu m caused no ill effects (11). Lyon published data which show that intermittent exposures to concentrations up to 20 mg/cu m, for periods of five to 30 minutes, cause no ill effects (11). Ricca infers that short term exposures to fluorine at 20 mg/cu m for five minutes would cause no irreparable respiratory damage to humans, and that five mg/cu m for short single exposures should be tolerable from a comfort standpoint (11).

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SECTION 9

BERYLLIZINE

9.1 PRACTICAL STUDY

9.1.1 General

Beryllizine is a gelled mixture containing various amounts of beryllium in hydrazine as the carrier. The term is a generic one which does not designate the metal concentration or the stabilizing agents. The nominal composition of beryllizine, for use in combination with nitrogen tetroxide as the oxidizer, is 20% beryllium powder and 80% hydrazine (1).

Gelling agents such as Shawinigan Chemicals Co., Shawinigan Acetyline Black; Dow Chemical Co., DOW ET-435; Hercules Powder Company, CMC-7H; and Reynolds Metals Co., Reynolds 40XD are the most effective in hydrazine formulations. The addition of the gelling agent is made at the expense of the hydrazine concentration (1).

The density of metal powders and gelling agents in a liquid carrier can be calculated if the volumes of the components are assumed to be additive. The densities of properly prepared samples are within 0.005 gm/cc. of the calculated values. Mixing and dispersion must be conducted, in the absence of contaminating gases, at the vapor pressure of the liquid phase. When processed under a protective atmosphere of nitrogen, the measured densities are less than the calculated values because of entrained gas. It is very difficult to remove the gas from a poorly processed gel. The density of beryllizine with a nominal composition of 20% beryllium and 80% hydrazine is 1.12 gm/cc. at 77°F. Its Brookfield viscosity (spindle No. 4) at the same temperature is 7,000, 6,000 and 1,500 cps at 6, 12 and 60 RPM, respectively (1).

Since no true solute-solvent system exists, the vapor pressure of the liquid phase in a gelled metallized propellant is not affected by the gel structure. The vapor pressure is entirely temperature dependent. There is, however, a marked reduction in the rate at which the equilibrium vapor pressure is developed (1).

9.1.2 Decontamination

9.1.2.1 Literature Review

No specific references to decontamination studies or

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to actual spills of beryllizine were found in the literature. Reference is made to the use of water to flush and clean equipment after containing beryllizine (1). Since beryllizine is a gel, it would seem necessary that any decontaminant must be capable first of destroying the gel in order to intimately contact the components, hydrazine and beryllium.

Dilute aqueous H_2O_2 was found effective in destroying alumizine gels and neutralizing the hydrazine. Therefore H_2O_2 might be expected to act similarly with beryllizine. However, in this latter case we still have the very toxic beryllium to contend with. Since beryllium and most of its compounds are extremely toxic, it may be necessary in the case of a spill to collect the waste material in a settling pond and treat the residues as radioactive wastes (8).

The beryllium powder which is the more toxic component of the fuel will be little affected by a deluge of a decontaminant solution which would neutralize the hydrazine. The surface of the metal particles would be oxidized with a superficial coating of oxide which would inhibit further reaction. It is little affected by even long exposure in cold water. In fact it is slowly converted to a hydroxide by boiling water (9). It forms oxides when reacted with steam (10). Beryllium will react with acids and unlike other Group II metals, the reaction is not vigorous (10, 11). The reaction between a caustic and beryllium is also different than the other Group II metals in that a beryllate ion is formed (10).



In both acid and alkali reactions, hydrogen is released.

Beryllium will form halides which are soluble and easily hydrolyzed. The fluoride may be prepared by reacting the powder with hydrofluoric acid. On the contrary the oxide which is a very stable compound is highly insoluble. Beryllium hydroxide, $Be(OH)_2$, is precipitated from beryllium salt solutions by hydroxide ions (12, 13). Although many beryllium compounds can be formed (9, 10, 11, 12, 13) no compound has been noted that can be considered completely non toxic.

9.1.2.2 Recommendations

The size of the beryllium particles is an important factor in its toxicity. It therefore appears that a chemical treatment of the fine powder is warranted. The formation of a soluble salt or a gelatinous precipitate would reduce the in-

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halation hazard produced by air-borne particulate matter. However, it does not appear feasible that a decontaminant could both safely neutralize the hydrazine and react completely with the beryllium. A two step decontamination process is therefore indicated.

A spill of beryllizine should be cleaned up as much as possible by mechanical means. The beryllium powder is firmly attached to the gel and therefore presents the minimal toxicity hazard. Deluging the spill on the contrary would break the gel and spread the fuel over a larger area (14). The effluent gas from the hydrazine neutralization could conceivably carry along the micron sized beryllium particles, increasing the attendant hazard.

Therefore we conclude that a spill of beryllizine should not be deluged but should be collected. The residual fuel should be flushed to a sump or waste pond where hydrazine neutralization can be accomplished and the beryllium converted to less hazardous compounds such as the oxide or hydroxide prior to ultimate disposal. Disposal of these beryllium salts can be accomplished by the methods used for radioactive waste disposal (8) or by controlled release into the ground (14).

9.1.3 Toxicity

Both components of beryllizine, beryllium and hydrazine, are extremely toxic. The toxicity of hydrazine is covered elsewhere in this report and will not be repeated here (for details see Section 5).

Beryllium and most of its compounds are extremely toxic. In fact, beryllium is the most toxic of all the metals. Its threshold value is 2 micrograms/cu meter (2, 3), with a maximum daily peak of 25 micrograms/cu meter (4).

Hazard from contact with the skin is minor except in the case of pre-existing open wounds. The greatest danger is from finely divided beryllium powder. Most illnesses have resulted from the inhalation of dust or fumes of beryllium compounds causing acute inflammatory lesions of the eye, skin, and respiratory tract (4).

All salts of beryllium are toxic. Soluble salts tend to present a similar magnitude of hazard regardless of preparation technique whereas the toxicity of insoluble salts is dependent upon the formation temperature. BeO₂ for example when

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formed at low temperature is highly toxic. However, BeO_2 calcined at high temperatures, above 2800°F , is less toxic. The difference in toxicity is believed to be due to the lower surface area of the calcined material (3, 5, 15).

Acute pneumonitis has been produced by the inhalation of the metal, as well as its oxide, sulphate, fluoride, chloride, and hydroxide (3). This pneumonitis may be rapid or delayed depending on the magnitude and duration of the exposure.

A beryllium ulcer can result from the contamination of a pre-existing abrasion, laceration, or puncture wound. Such an ulcer is slow-healing and painful.

The manifestations of beryllium poisoning are usually insidious (4). The poison reaches the circulation slowly, and deposits remain in body tissues for many years after exposure. Beryllium has been detected in urine as long as ten years after exposure (6).

Approximately 15% of the acute cases of beryllium poisoning die within the third or fourth week, and the rest recover within four months. Chronic symptoms may occur within a few months or up to 10 years after exposure and continue indefinitely. In 35% of the cases in which chronic symptoms develop, the results are fatal (7). E. Browning (16) is suggested as an additional reference for information on the toxicity of beryllium.

All beryllium wastes are sealed in a drum and disposed of through a certified contractor who treats them as radioactive wastes (8).

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9.2

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SECTION 10

LIGHT METAL HYDRIDES

10.1 PRACTICAL STUDY

10.1.1 General

Light metal hydrides are being evaluated as fuel additives for rocket propellants. The addition of hydrides generally result in an improvement in both the specific and density impulses for the particular propellant system. Our investigation has been limited to those hydrides which are presently receiving the most consideration in propellant systems. These materials are lithium hydride (LiH), beryllium hydride (BeH₂), and aluminum hydride (AlH₃).

In practice the metal hydrides are generally used in conjunction with a liquid fuel as a gelled propellant or as an ingredient in solid propellants. In view of the very many propellants with which they can be used, this discussion will be limited to the treatment of the hydrides per se rather than the decontamination of the associated liquid or solid fuels.

10.2 LITHIUM HYDRIDE

10.2.1 General

Lithium hydride is an ionic type compound where the hydrogen is present as the negatively charged ion. It is a white or gray crystalline solid with a structure similar to NaCl. The melting point is approximately 680°C with a dissociation pressure equal to 27 mm. Other dissociation pressures are 0.07 mm at 500°C and 760 mm at approximately 850°C. LiH has a density of 0.76 to 0.8 gram/cc. The heat of formation is approximately 22 Kcal/mole (1).

10.2.2 Decontamination

10.2.2.1 Literature Search

In massive form LiH reacts fairly briskly with a large excess of water without ignition. The reaction produces a hydroxide together with the evolution of hydrogen:



However, the addition of a small amount of water to a sizable amount of finely divided material results in the generation of sufficient heat to ignite the mass of hydride (1). Lithium hydride is stable in dry air or oxygen at ambient temperatures but will slowly decompose in moist air. In fact very finely powdered LiH has been observed to ignite spontaneously when exposed to very humid air (1). It has also been reported that LiH will react with water but will not generally ignite (2).

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LiH has a limited solubility in polar organic solvents such as dioxane and diethyl ether. However, the flammability of these solvents alone rule them out as possible materials for decontaminating LiH spills. LiH is reported to be less reactive chemically than other alkali hydrides except in an organic solvent medium (3). Therefore, the possibility of chemical decontamination is not encouraging. In addition, many reactions that do occur take place in an organic solution or with materials which are themselves highly hazardous. For example, the reaction between LiH and an inorganic halide may be represented by the following equation:



Since both the reactant and resultant product would be similarly hazardous, this type of reaction is not a practical decontamination approach.

One of the greatest hazards of powdered LiH is its high flammability. As previously stated it may be ignited quite readily even by moisture in the air. In controlling a spill of this material therefore the possibility of combating a LiH fire must be considered. The usual fire extinguishants such as water, CO₂, and CCl₄ (or other chlorinated hydrocarbons) must be avoided. These materials will be reduced by the LiH in an extremely exothermic reaction (1). In fact, such extinguishants may cause violent and destructive explosions (2). Small fires may be smothered with an inert gas such as N₂ (1), but this is not practical for large spills. Smothering with dry ground dolomite or Ansul Metal-X is suggested (2) for large spills.

10.2.2.2 Recommendations

Spills of LiH should be deluged with an inert powder such as ground dolomite followed by removal of the material to a disposal area. There it can be adequately disposed of by burning (2). In the event that the spill ignites, the fire should be extinguished with ground dolomite or Ansul Metal-X and the residue disposed of as previously described. Although small spills of LiH can be disposed of by dropping small portions in a large volume of water (1), the impracticability of neutralizing a large spill in this manner is obvious. We therefore recommend that aqueous deluges be avoided and LiH spills be deluged with a dry ground powder such as dolomite.

10.2.3 Toxicity

Lithium hydride is not volatile and therefore does not present a serious internal toxicological problem. LiH, as well as other

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hydrides, is toxic only to the extent that the parent metal is toxic (2). Lithium itself or its salts present no hazard but lithium hydride is an intensely corrosive and irritant material, which in high concentrations should be potentially hazardous to workers inhaling it (4). However, LiH is a strong reducing and dehydrating agent. Therefore, it will react with moisture and the reaction products are irritating and corrosive to skin and body tissue. The dust is quite irritating to the membranes of the nose and throat. In the event that LiH contacts the skin, it should be flooded off with large volumes of running water (1). The toxic effects of LiH have been observed from animal experiments. Although concentrations of 10 mg per cu.m. attacked fur and skin, and irritated the eyes and mucous membrane of test animals, the lesions were similar to thermal burns. The injuries were what could be expected from a strong alkali rather than to any specific action of lithium. Animals exposed for one week to concentrations of 5 mg per cu.m. (4 hours daily) showed emphysema in the lungs of some animals. However, mortality was low and examination 5 months after exposure showed no lesions in any organ attributable to lithium hydride. It was concluded that working atmospheres containing 25 micrograms per cu.m. would constitute no toxic hazard (5).

10.3 BERYLLIUM HYDRIDE

10.3.1 General

Beryllium hydride is a white to gray amorphous powder comprised of polymerized molecules held together by hydrogen bridge bonding. The formula may therefore be represented as $(\text{BeH}_2)_x$. The heat of formation (25°C) is -4.53 ± 1.0 Kcal/gram formula weight (13). The reported density is 0.64 ± 0.02 gms/cc (13). However, several investigators are attempting to synthesize BeH_2 at a higher density. Rocketdyne has achieved a density of 0.77 gm/cc (14). The thermal stability of BeH_2 is lower than LiH but greater than AlH_3 . Initial decomposition occurs at 215-225°C and becomes fairly rapid between 235-250°C (13). Reaction Motors reports (6,10) that the decomposition rate at 70°C corresponds to approximately 1% per year. The decomposition rate is dependent upon particle size, the smaller material having a higher rate. Like LiH, BeH_2 is a strong reducing agent.

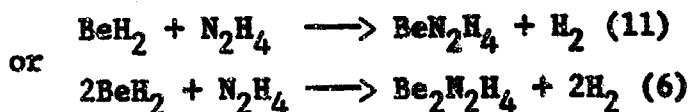
10.3.2 Decontamination

10.3.2.1 Literature Search

Beryllium hydride does not react in air or dry oxygen at ambient temperature (1,3,13). It is insoluble in all common solvents with which it does not react (13). It reacts rapidly with hydrazine and ammonia (10,11,13). The reaction is as follows:

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BeH₂ reacts slowly with MMH, UDMH, and H₂O₂ (13) and shows no reaction with heptane or JP-4 (10).

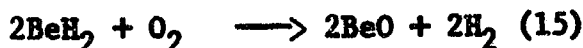
Unlike LiH, BeH₂ is reported to be compatible with water. As received it is reported to be compatible with a water-heptane emulsion (6). Reaction Motors investigated the water compatibility of several samples of BeH₂ obtained from different lots. They found that reaction occurred after an induction period ranging from 500 to 2100 hours. The lowest induction period was reported for a BeH₂ sample which had been ball milled to produce very fine particles (7). The reaction initiation was noted by slight pressure rise. In no case could the reaction be considered vigorous. The stability of BeH₂ in water was further established by Reaction Motors who subjected BeH₂-water slurries to a Trauzl block test and found it didn't detonate (11). It should be noted that several older references were found (1,3) which stated that BeH₂ and H₂O react vigorously. This result was undoubtedly due to impurities present in the BeH₂. Such contaminants are not present in the material presently produced for propellant usage.

Some of the other reported reactions of BeH₂ are as follows:

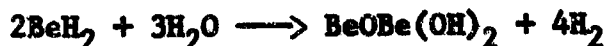
With F₂ as an oxidizer,



With O₂ as an oxidizer,



With water,



heat of reaction is -111 Kcal/mole (15)

10.3.2.2 Recommendations

Since BeH₂ appears to be compatible with water, aqueous solutions of decontaminants appear to be feasible for treating spills. BeH₂ is being considered for propellant use as a component of gels of materials such as MMH or UDMH. Assuming a spill of such a fuel, a dilute aqueous solution of hydrogen peroxide would adequately neutralize the modified hydrazine component and still not cause a violent reaction with the hydride. The residual hydride

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can then be flushed to a sump or waste pond where it would slowly decompose. The residual oxide or hydroxide could then be disposed of in the same manner as radioactive wastes are handled or slowly disposed of in the ground. Spills of the powdered BeH_2 can be disposed of in a similar manner. In this case, decomposition could be hastened by the addition of dilute ammonia which would react with the hydride releasing hydrogen.

10.3.3 Toxicity

Finely divided beryllium and beryllium compounds are extremely toxic. The hydride being a strong reducing agent possibly presents an additional hazard. Dow has conducted toxicity investigations of various beryllium compounds including the hydride. Two studies (12) involved intratracheal injection of rats with BeH_2 . One study showed that the mortality rate for this group of rats was much higher than in any other group of rats similarly treated with other beryllium-containing materials. In general the injections caused acute chemical pneumonitis and resulted in death in many cases.

The A.E.C. has setup standards for airborne beryllium dusts. The allowable limit is 2 micrograms per m^3 as an average over an 8 hour day. This is also the threshold limit value for beryllium adopted at the Annual Meeting of the American Conference of Governmental Industrial Hygienists, 1965. On the basis of the Dow tests, BeH_2 is at least as toxic as beryllium and possibly even more hazardous.

10.4 ALUMINUM HYDRIDE

10.4.1 General

Aluminum hydride is being evaluated as an additive for both solid and liquid propellants. It is less thermally stable than either lithium or beryllium hydride, but considerable research is being expended toward improving this property. As a result of this continuing research, the literature abounds with conflicting statements since the hydrides referred to are often not identical. The AlH_3 has often been treated to improve stability.

Aluminum hydride originally was reported to be a highly polymerized compound having the general formula of $(\text{AlH}_3)_x$. The AlH_3 molecules being held together by hydrogen bridge bonding (1,3). It has since been determined that AlH_3 in many distinct crystal structures can be isolated depending on the preparation techniques. Some of these crystals have been identified by Dow and

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Olin Mathieson and are referred to in the field by number. Comparison of Dow and Olin Mathieson nomenclature for the most prevalent crystal forms is as follows (16):

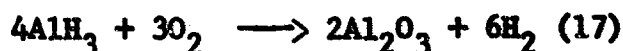
Dow 1444 - Olane 57
Dow 1451 - Olane 58
Dow 1433 - Olane 60
Dow 1443 - Olane 62

Other crystal forms are known as well as etherated and amorphous forms. However, the most stable form and most highly desired is Olane 58 - Dow 1451 (16). This report therefore will be limited to an evaluation of this particular form of AlH_3 . Olane 58 is a crystalline solid with a specific gravity at 25°C of 1.45 to 1.53. It has no melting point as such, since it decomposes on heating. It also decomposes in water and in alcohol. The auto-ignition temperature is >300°C (16).

10.4.2 Decontamination

10.4.2.1 Literature Search

AlH_3 (Olane 58) is a flammable white powder stable in dry air at room temperature. Above 120°C it decomposes releasing hydrogen. It will also decompose in the presence of moisture forming hydrogen which may ignite because of the heat evolved (16). The reactions with air (oxygen) and water are as follows:



The hydrolysis rate is affected by surface area or particle size and pH. The rate increases with pH.

Olin Mathieson (16) reports that equipment contaminated with AlH_3 should be washed with kerosene with provision for hydrogen venting and purging with nitrogen. The kerosene waste is then removed from the area for disposal. The kerosene wash is then followed with a water rinse followed by a 1-2% caustic-water wash and subsequent rinsings.

The practicality of this method for combatting a large spill in the open air is questionable. The flammability of kerosene would in itself present a hazard. On the other hand, it has been reported (18) that the reaction between water and AlH_3 proceeds slowly, at 25°C it was approximately 50% completed after 3 hours.

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There is also a possibility that a spill of AlH_3 may ignite. A fire should be smothered with powdered limestone or Metal-X extinguishers. CO_2 or dry chemical extinguishers are not to be used. The smothered residue can then be mechanically removed to another area for waste disposal. Disposal can be accomplished by burning (16).

10.4.2.2 Recommendations

A spill of AlH_3 can be handled in several ways. A water deluge, although releasing hydrogen, does not appear to present any undue hazard. If the spill is in an area where it can burn without presenting a hazard to adjacent areas, burning is an effective method of disposal. Deluging a spill with an inert powder such as limestone renders the material less susceptible to ignition. The AlH_3 thus diluted can be safely removed to a disposal area.

10.4.3 Toxicity

Aluminum hydride cannot be considered a highly toxic material. The residue after hydrolysis is a caustic solid. Contact with the skin will therefore produce caustic type burns and would require similar treatment. Particles of AlH_3 should be brushed off immediately and the affected area doused with large volumes of water (16). Dow (19) has conducted toxicity studies on AlH_3 and determined that it has a low acute oral toxicity and should present no ingestion problem. Eye contact investigations showed it to be an irritant producing slight conjunctivitis which subsided in 24 hours. AlH_3 was also applied to the skins of animals and the tests indicated that it would not produce appreciable skin irritation. In general AlH_3 can be safely handled using reasonable care and cleanliness.

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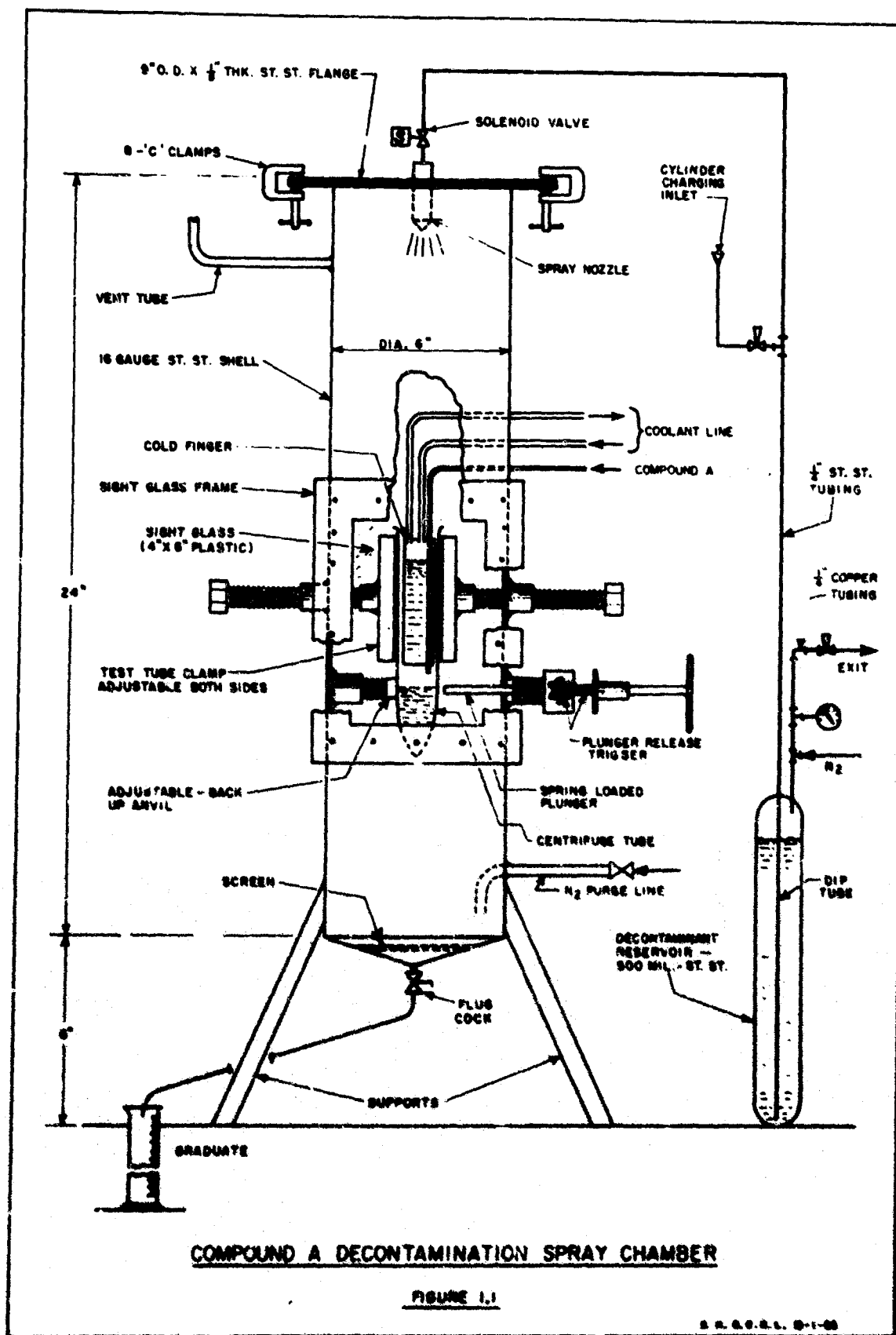
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11. ABSTRACT Decontaminants for several toxic missile propellants were evaluated and recommendations were made for the most suitable materials. The investigation was conducted in two phases. Phase I, a practical study of the propellants, consisted of a compilation of information pertaining to general properties, decontamination procedures and toxicity data based on a literature review. The materials thus investigated were fluorine, hydrazine, nitrogen tetroxide, hydrogen, light metal hydrides, beryllizine, Compound A, mixed hydrazine fuels, aluminizine and UDMH. Phase II, a laboratory investigation, involved the experimental evaluation of candidate decontaminants. This work, together with a theoretical evaluation of decontaminants based on the practical study, involved four propellants: Compound A, mixed hydrazine fuels (MHF-3 and MHF-5) and aluminizine.		

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