United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-215 Oct. 1981

EPA

Project Summary

Modification of Spill Factors Affecting Air Pollution: Volume II. The Control of the Vapor Hazard from Spills of Liquid Rocket Fuels

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The hypergolic rocket fuels, hydrazine and nitrogen tetroxide, are volatile hazardous materials of special interest to the Air Force. Through monitoring of ongoing U.S. Environmental Protection Agency (EPA) programs, the Air Force has maintained cognizance of the developing state of the art in spill control. This Air Force supplement to the basic EPA program was a preliminary evaluation of the potential of cooling and foam covers to mitigate the vapor hazard from hydrazine and nitrogen tetroxide.

Coolants exhibited some control over vapor release from the hypergolic fuels. Liquid nitrogen was the most effective material. Logistics were considered a major disadvantage for the anticipated spill scenarios.

Foams using commercial agents were beneficial with hydrazine, but they were not effective against nitrogen tetroxide. Modified foam systems incorporating acrylic resins were more effective. They were able to maintain hydrazine concentrations at or below 0.5 ppm. Some control was also exhibited with nitrogen tetroxide, but there was intermittent vapor release through the foam.

Based on the results of this study, the acrylic foams are judged to offer a promising approach to the control of the vapor hazard from hydrazine and nitrogen tetroxide.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Liquid rocket propellants present one class of volatile hazardous chemicals, and their toxic hazard is well recognized. The Air Force has monitored the evolving state of the art in spill control for its application to their particular situations. Successes in controlling vapor hazards with aqueous foams and by cryogenic cooling led the Air Force to undertake an investigation of these techniques as mechanisms to control the vapor hazard from spilled rocket fuels.

A program was instituted for the specific purpose of investigating cooling and aqueous foam blankets to mitigate the vapor hazard of hydrazine and nitrogen tetroxide. This study was primarily a survey and was not intended to develop a total system fully. The goal was to use the existing state of the art to the fullest extent.

Discussion of Results

Each technique was pursued independently for each of the propellant materials. The program used a series of laboratory tests to evaluate the various methods and materials for vapor suppression. Vapor concentrations above the two fuel materials were measured using detector tubes. Tests in which the concentrations exceeded the maximum limit of detector tubes (about 35 ppm) were considered failures.

The coolant portion of the study investigated water ice, dry ice, liquid CO_2 and liquid nitrogen. For nitrogen tetroxide, only liquid nitrogen was able to reduce the vapor concentration below the detector tube limit. To maintain the low vapor level, fairly large quantities of nitrogen were required with fairly frequent make up indicated. Water ice had an immediate but small effect that persisted only as long as the ice remained. As liquid forms, it reacts to form nitric acid. The heat of formation more than offsets the cooling effects.

The addition of coolants to hydrazine did reduce vapor levels below the limits of the detector tubes, but they were not able to approach the threshold limit value. Wet ice produced the slowest reduction of vapor concentration with hydrazine, but it also achieved the lowest vapor concentration ultimately. This result was due to the accompanying dilution as the ice melted.

The evaluation of foam systems initially considered commercially available foam agents. Representative materials of protein, fluoroprotein, aqueous film-forming foams (AFFF), and polar solvent and surfactant foams were selected based on the characteristics identified in a previous EPA program.

None of the materials selected were able to exercise any control over the vapor release rate of nitrogen tetroxide. In contrast, nearly all were able to reduce substantially the vapor concentration above hydrazine. These levels varied from 2 to 20 ppm, depending on the foam type. The duration of control also varied as a function of foam type.

A third type of foam system was also tested based on previously developed acrylic modified foams that gel when used on ammonia or amine materials. The gelled foam forms a stable barrier with a low permeation of hydrazine vapor. The drainage mixes with the hydrazine and gels the top liquid layer. The two layers, foam and gel, were able to reduce the vapor concentration to less than 0.5 ppm.

The acrylic foam formulations were also beneficial in reducing vapor release from nitrogen tetroxide. They were not able to give continuous control, however. The vapor build-up beneath the foam layer resulted in intermittent vapor pulses (breathing).

A series of polymeric materials was tested alone and in combination with the acrylic modifier in an effort to improve the control over nitrogen tetroxide. Within the time limit of this program, no major improvements over the original MSA formulations were found.

Conclusions

The study results showed that coolants should be rejected as a method of controlling the vapor hazard from spilled liquid hydrazine or nitrogen tetroxide. Tests showed some reduction in vapor release, but when this was equated with the volume of coolant material required and the logistics involved for projected scenarios, cooling was not considered to be a viable approach.

Aqueous foam systems offered significant benefits for hydrazine. Several commercially available agents were able to reduce vapor levels to the 2- to 5-ppm range. None of the agents were effective against nitrogen tetroxide.

Acrylic modified aqueous foams (developed previously for ammonia and similar materials) were shown to be effective for hydrazine. Foam layers reduced vapor levels to the 0.5-ppm range. These agents also had some positive effects on nitrogen tetroxide. This study concluded that acrylic modified foams offered the best mechanism to control the vapor hazard from the two types of rocket propellant materials.

The full report was submitted in partial fulfillment of Contract No. 68-03-2648, Task 9B, by MSA Research Corporation under subcontract to Rockwell International under sponsorship of the U.S. Environmental Protection Agency.

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The complete report, entitled "Modification of Spill Factors Affecting Air Pollution: Volume II. The Control of the Vapor Hazard from Spills of Liquid Rocket Fuels," (Order No. PB 82-108 390; Cost: $6.50, subject to change) will be available only from:
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☆ U.S GOVERNMENT PRINTING OFFICE, 1981 — 559-017/7397

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