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CHARACTERIZATION OF PHOSPHINE PRODUCTION DURING EXTENDED STORAGE OF THE KM03 RED PHOSPHORUS FLOATING SMOKE POT

Robert L. Kristovich
Kathy L. Crouse
David A. McCaskey

RESEARCH AND TECHNOLOGY DIRECTORATE

Charles L. Crouse

SCIENCE APPLICATIONS
INTERNATIONAL CORPORATION
Gunpowder, MD 21010-0068

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Kristovich, Robert L.; Crouse, Kathy L.; McCaskey, David A (ECBC); and Crouse, Charles L. (SAIC)

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The U.S. Marine Corps (USMC) Floating Smoke Pot (FSP) MK 7 MOD 0 Program was established to redesign the previously fielded M4A2 Hexachloroethane (HC) FSP. Although the HC pots were extremely effective as an obscurant, there were safety concerns from manufacturing and operational perspectives. Red phosphorous (RP) has been widely used in screening applications and was chosen as a replacement for the smoke payload. The smoke payload (approximately 8 kg) contained within the FSP MK 7 (KM03 pot) is a specific formulation developed by Diehl BGT Defence (Überlingen, Germany). One compound of particular concern with RP is the potential generation of phosphine gas during long-term storage. The phosphine concentration inside the storage hobbock was evaluated following 3 years of storage under ambient conditions. The smoke pots were then functioned to determine reliability following long-term storage .

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PREFACE

The work described in this report was funded and supported by the Program Manager, Ammunition (PM-AMMO), Marine Corps Systems Command (MARCORSYSCOM), Quantico, VA. This work was started and completed in December 2008.

Records were maintained in official U.S. Army Edgewood Chemical Biological Center Laboratory Notebooks in the Life Sciences Official Archives or in the Technical Library. Studies were conducted under, and in compliance with, current GLP standards and reviewed periodically by either the QA Coordinator or his designee. The performance of this study was consistent with the objectives and standards in "Good Laboratory Practices for Non-clinical Laboratory Studies" (21 CFR 58, Food and Drug Administration, U.S. Department of Health and Human Services, April 1988).

This report was published through the Technical Releases Office; however, it was edited and prepared by the Technical Information Specialist, Toxicology, Aerosol Science and Obscurants Division, Research and Technology Directorate, U. S. Army Edgewood Chemical Biological Center.

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QUALITY ASSURANCE

(U) This study, conducted as described in the final report titled, "Characterization of Phosphine Production During Extended Storage of the KM03 Red Phosphorus Floating Smoke Pot", was examined for compliance with Good Laboratory Practices as published by the U. S. Environmental Protection Agency in 40 CFR Part 792. The dates of all inspections and the dates the results of those inspections were reported to the Study Director and management were as follows:

Phase Inspected	Date	Reported
Data and Final Report	16 Oct 09	19 Oct 09

(U) To the best of my knowledge, the methods described were the methods followed during the study. The report was determined to be an accurate reflection of the raw data obtained.

Dennis W. Johnson
DENNIS W. JOHNSON
Quality Assurance Coordinator
Toxicology, Aerosol Sciences and
Obscurants Senior Team

CONTENTS

FIGURE

TABLES

CHARACTERIZATION OF PHOSPHINE PRODUCTION DURING EXTENDED STORAGE OF THE KM03 RED PHOSPHORUS FLOATING SMOKE POT

1. INTRODUCTION

The military has long used smokes and obscurants for various applications including: concealment, deception, and training. The U.S. Marine Corps (USMC) has established a program (The USMC Floating Smoke Pot [FSP] MK 7 MOD 0) to develop a replacement for the already fielded M4A2 Hexachloroethane (HC) FSP. Although the HC pots are extremely effective in their role as an obscurant, there are very real occupational, operational, and manufacturing safety concerns (Toxicity of Military Smokes and Obscurants, 1997).[1] Toxicological concerns about the resulting hexachloroethane and zinc chloride obscuration cloud are among these concerns. Because human deaths have been directly attributed to the inhalation of this smoke material,[1] a new smoke formulation, which retained operational efficiency, while providing a wider margin of operational and occupational safety, was required.

Red phosphorus (RP) has been used widely as an obscurant for various regions of the electromagnetic spectrum (Anthony et al., 2006).[2] The RP allotrope has intermediate chemical reactivity and is the most widely available natural allotrope of phosphorus, giving it advantages over other allotropes of phosphorus. Unfortunately, by reacting with water in the air, RP produces phosphine (PH_3), a highly toxic gas.[2] Under normal circumstances, the production of PH_3 in a well ventilated area would be slow enough for toxicity to be of no concern. The KM03 smoke pot is stored in a hermetically sealed steel bucket (hobbock) for protection during long-term storage. During storage of these smoke pots, PH_3 could possibly concentrate in the hobbock, leading to a potentially dangerous situation during unpacking of the smoke pot before deployment. In an accelerated long-term storage study, investigators observed that PH_3 concentrations well above levels considered safe were produced.[2] Such unsafe concentration levels required elevation of the ambient storage temperature to simulate a longer storage period. This storage parameter is unrealistic and could have influenced the results. Therefore, characterization of the PH_3 concentration in the hobbock before unpacking following long-term storage is important.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 KM03 Red Phosphorus FSP

Three MK 7 KM03 FSPs were transported to the U.S. Army Edgewood Chemical Biological Center (ECBC) from the Naval Surface Warfare Center, Dahlgren Division (NSWCDD), VA, and stored at the ECBC Engineering Directorate's Ammunition Storage Facility. All smoke pots were kept sealed in the hobbock during storage to prevent the possible entry of moisture. Approximately 90% of the smoke mixture is comprised of RP. Since RP, and therefore the smoke mixture, is hygroscopic, moisture entering the hobbock could lead to PH_3

formation. The pots were stored under ambient conditions for 3 years before analysis and testing. On the day of testing, the smoke pots were delivered from the storage facility to M-field at the Edgewood Area, Aberdeen Proving Ground (EA-APG) for PH_3 analysis inside the hobbock and functioning. PH_3 analysis was performed by gas chromatography - mass spectrometry (GC-MS) on an Agilent 6890 GC (Palo Alto, CA) equipped with an Agilent 5973 mass selective detector and also by Kitagawa PH_3 seleetive deteetor tube analysis (part #8014-121U, Matheson Tri-gas, Montgomeryville, PA).

2.1.2 PH_3 Calibration Standard

A 5 ppm PH_3 and 34 L nitrogen gas mixture was obtained from AL Compressed Gases (Spokane, WA). A series of volumes was pulled onto detector and tenax tubes for calibration standards.

2.2 Methods

2.2.1 Collection of PH_3 Samples for Analysis

On the day of testing, the smoke pots were transported from the storage facility to M-field at the EA-APG for sample colleetion and functioning. Once at M-field, a small hole was drilled through a specially designed valved fitting to allow for the removal of air from the hobbock for analysis without dilution of the air inside the hobbock with ambient air. First, the Kitagawa detector tubes were attached to the fitting, the valve was opened, and a 100 mL sample was pulled through the tube and the colorometrie change was read for phosphine content (unit = parts per million (ppm)). The valve was closed, and a second 100 mL sample was pulled on carboxin and earbosil sorbent tubes for analysis by GC-MS.

2.2.2 Function Testing

Following collection of samples for phosphine analysis, the FSP were removed from the storage hobbock and functioned. All smoke pots were disseminated in accordance with locally established standard operating procedures for the safe handling of pyrotechnies. Disseminations were conducted on the large measurement grid at M-field at EA-APG that is routinely used for outdoor obscurant field tests. Ignition was performed by pulling the MDN 89 igniter on the top of the smoke pot per manufaeturers' instructions. The burn time for each pot was recorded for comparison to previously established functional parameters.

3. RESULTS

Samples were taken from the "dead volume" inside the hobbocks, containing the FSPs to determine if PH_3 had been produced and trapped inside the hobbock during natural long-term storage of the smoke pots under ambient conditions. Samples were taken at M-field at EA-APG on December 12, 2008. The ambient temperature was recorded as 45°C with a relative humidity of 33% at time of testing. The samples were taken by drilling a small hole in the hobbock through a valve specially designed to prevent air from passing back into the hobbock, diluting the samples (Figure).

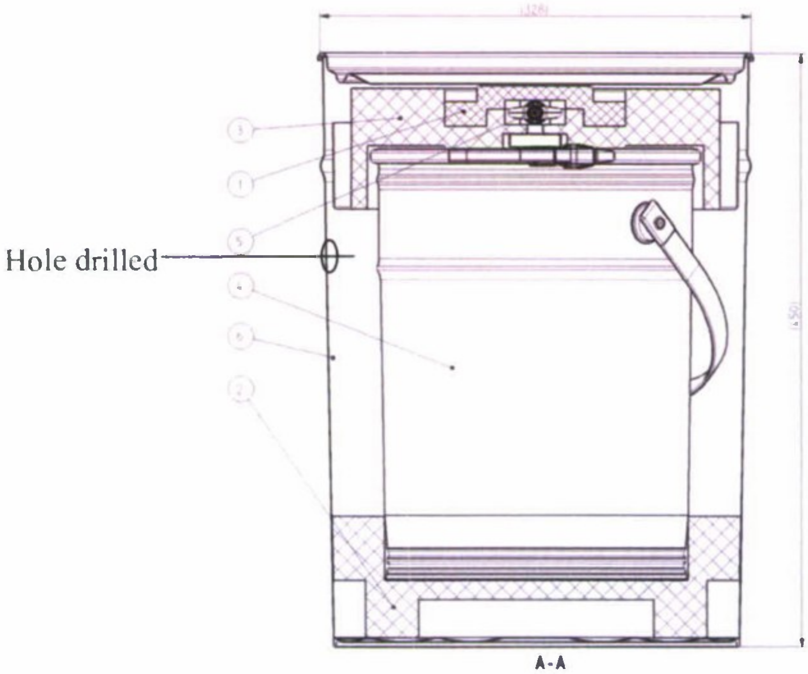

Figure. Schematic of inside smoke pot, indicating the location of hole drilled to sample dead space.

PH_3 was analyzed using two complimentary methods: Kitagawa PH_3 sensitive detector tubes and GC-MS analysis. The results are recorded in Table 1. The average PH_3 concentration by Kitagawa detector tube analysis was determined to be 0.72 ppm. The average PH_3 concentration was determined by GC/MS to be 0.76 ppm.

Table 1. PH_3 Concentration as Determined by Kitagawa Tube Analysis and GC-MS Analysis.

Can No.	PH_3 Concentration Kitagawa Tube Analysis (ppm)	PH_3 Concentration GC-MS Analysis (ppm)
1	0.90	0.76
2	0.50	0.58
3	0.75	0.91

Following collection of samples for PH_3 analysis, the FSPs were ignited to determine if 3 years of long-term storage had any effect on the pots' functionality. Table 2 contains the individual burn times for the pots, but the average burn time was 21 min 48 s.

Table 2. Burn Times for Individual FSPs.

Can No.	Burn Time (min, s)
1	23, 1
2	19, 19
3	22, 56

4. DISCUSSION/CONCLUSIONS

Artificial aging that simulates the long-term storage of munitions was used to study the off-gas products following storage of Floating Smoke Pots. This was accomplished previously by storing the FSPs under elevated temperatures for a given period of time using the Arrehenius relationship. Elevated temperature could lead to changes in the products produced by providing enough energy to cross activation energy barriers. Currently, this artificial aging mechanism is the only way to simulate storage other than natural aging. The artificial aging study indicated that phosphine (PH_3) concentration inside the storage hobbock could be a problem with an average concentration of 4657 ppm.[3] This is well above the short-term exposure limit (STEL) of 1 ppm (CDC, 2009).[3] To determine the effect of the elevated storage temperatures used during artificial long-term storage, a natural aging study was conceived to study PH_3 concentration following 3 years of storage. The average PH_3 concentration following 3 years of natural aging was 0.76 ppm by GC-MS analysis. This is below the STEL for PH_3 exposure.

LITERATURE CITED

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