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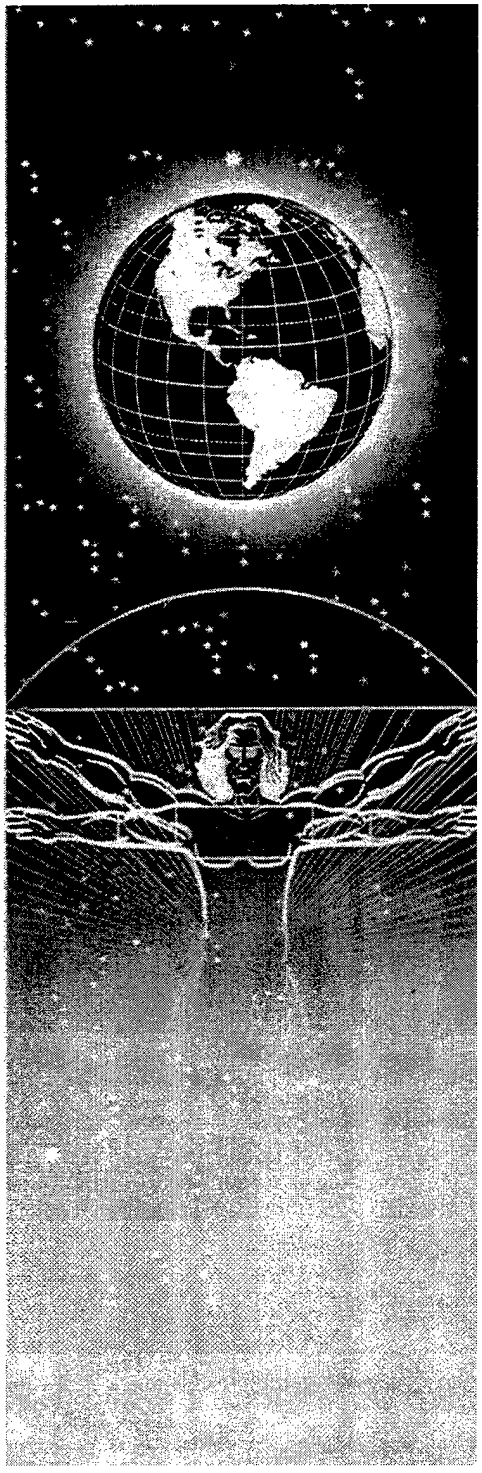

UNITED STATES AIR FORCE
ARMSTRONG LABORATORY

DERMAL ABSORPTION OF MODULAR ARTILLERY CHARGE (XM231)

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TECHNICAL REVIEW AND APPROVAL

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The animal use described in this study was conducted in accordance with the principles stated in the "Guide for the Care and Use of Laboratory Animals", National Research Council, 1996, and the Animal Welfare Act of 1966, as amended.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE DIRECTOR

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13. ABSTRACT *(Maximum 200 words)*

Soldiers handling modular artillery propellant increments may have the potential to absorb chemical components through the skin of the hands. The purpose of this research was to determine if systemic absorption of chemical components of the new Modular Artillery Charge System (MACS) might be a hazard in operational military environments. The MACS includes a low zone XM231 increment and a high zone XM232 increment. For this study we sampled the surfaces of randomly selected XM232 MACS increments, which were stored under extreme environmental conditions, to determine the concentrations of various propellant components (nitrocellulose, dinitrotoluene, dibutylphthalate, and diphenylamine). After eleven months of storage, the only chemical components found on the surface of the cartridges were very small quantities of nitroglycerin and diphenylamine. The precise origin of the nitroglycerin could not be determined. Nitroglycerin is a subcomponent of the ball powder used in the center core igniter but also could have been a residual artifact from previous storage of XM232 increments within the ammunition cans used with XM231 increments in this study. We used excised rat skin in static diffusion cells to investigate dermal absorption of M1 propellant in powdered form. No chemical components of M1 propellant penetrated the skin. Our results suggest that chemical components of the XM231 are not absorbed sufficiently to be a systemic hazard under operational handling and loading conditions.

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PREFACE

This is the second of two technical reports addressing the absorption of military propellants through skin. They are designed to provide information that is useful for assessing the potential hazards of soldier's exposures to artillery propelling charges. This report suggests that the Modular Artillery Charge System (MACS), XM231 low zone increment should not be hazardous to the health of soldiers because of dermal absorption. The analytical methods developed for this project were presented at the 1997 American Chemical Society Annual Meeting, San Francisco CA on 13-17 April 1997. Part of the funding for this project was provided by the Program Manager for Crusader Munitions, Picatinny Arsenal, NJ.

The animal use described in this study was conducted in accordance with the principles stated in the "Guide for the Care and Use of Laboratory Animals", National Research Council, 1996, and the Animal Welfare Act of 1966, as amended.

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INTRODUCTION

Potential health hazards of new Army weapon systems are of concern to health and safety professionals, the general public, and weapon system developers. One concern is the potential for dermal absorption materials and chemicals which soldiers may handle. Solid propellants (XM231 & XM232), part of the Modular Artillery Charge System (MACS), are new compounds that need health and safety impact evaluations. These propellants are fairly complex mixtures containing up to a dozen chemical components, including nitroglycerin, diphenylamine, dinitrotoluenes, dibutylphthalate, nitroguanidine, and nitrocellulose. There is no available toxicity information on XM231, but the toxicity of XM232 in female rats was recently investigated and was found to be minimal (Kinkead et al. 1995 & 1996). Dermal absorption of XM232 has been already evaluated in a technical report (McDougal, et al. In press). Dermal absorption measurements for XM231 are required to be able to determine if continued dermal contact with the propellants and propellant casings might be a systemic hazard. The purpose of this effort was to use fluxes from laboratory studies using excised rodent skin and measurements of XM231 component concentrations on the surface of the propellant casing to estimate the potential dermal absorption hazard to soldiers.

Propellants

The XM231 increment is the low zone propelling charge that will replace the current 155mm M3A1 propelling charge. The increment consists of a coated nitrocellulose-based combustible case, M1 propellant, and an ignition system containing black powder and ball powder. Range is adjusted by the number of increments which are placed in the Howitzer. Chemical substances of concern are those comprising the rigid combustible case, the propellant, and combustion product residues which remain on the gun surfaces after firing (Initial Health Hazard Assessment Report, 1994).

Primary components of the M1 propellant are nitrocellulose, (85%); dinitrotoluene isomers, (10%); dibutylphthalate, (5%); diphenylamine, (1%); (ARDEC Hazardous Component Safety Data Sheet, 1987). Nitrocellulose has very little toxicity information available and is assumed to be minimally toxic. No information is available about nitrocellulose absorption through the skin. Dinitrotoluenes may cause hematological aberrations, skin rash, hepatitis, visual disturbances and tremors in humans (Dinitrotoluenes - BUA, 1987). Biological monitoring of workers in an explosive factory suggests that the skin may be the major route of absorption for dinitrotoluenes (Woollen et al., 1985). Dibutylphthalate has no acute toxicity and subacute toxicity is very low, and no irritant or sensitizing effects on the skin or mucosa have been observed (Dibutylphthalate - BUA, 1987). According to Scott and coworkers (1987) phthalate esters are slowly absorbed through human and animal skin. There is very little toxicology information available on diphenylamine and no quantitative information about dermal absorption. One report of poisoning of industrial workers cited the signs as bladder disorders, tachycardia, hypertension and eczema (Diphenylamine - BUA, 1991).

Primary components of the combustible case are Nitrocellulose, (72%); Kraft fiber, (17%); resin & additives, (10%); diphenylamine, (1%) and others (4%), (personal communication, Mr. Raymond Hom, ARDEC).

The ACGIH has determined TLVs™ for dinitrotoluenes (0.15 mg/m^3), diphenylamine (10 mg/m^3) and dibutylphthalate (5 mg/m^3) (ACGIH, 1996). Dinitrotoluenes also have a skin notation which means that there is a "potential significant contribution to the overall exposure by the dermal route".

Surface Sampling

The surfaces of twelve XM231 Modular Artillery Charge System increments were sampled at Yuma Proving Ground in May 1997 after being stored outside in metal ammunition cans for eleven months. These cans were

exposed to the extreme temperature fluctuations which are normal in the desert during a year (30 to 119 degrees F and 10 to 100% relative humidity). The exterior surface of the increment was sampled by carefully wiping one quarter of the cylindrical surface (280 cm^2) with a dry gauze pad. Samples were transferred to capped centrifuge tubes and carried back to Wright-Patterson AFB for analysis by High Performance Liquid Chromatography (HPLC) with ultraviolet detection. These wipe samples were analyzed for nitroglycerin, diphenylamine, dibutylphthalate, nitroguanidine, nitrocellulose and 4-aminobiphenyl (a potential contaminant of diphenylamine).

Static Diffusion Cell Studies

In *in vitro* experiments, we used static diffusion cells to attempt to measure the flux of chemical across excised WF/PmWp-fz rat skin. Male WF/PmWp-fz rats were euthanized with CO_2, and a circle the size of the diffusion cell flange was marked on the back with indelible ink. The skin on the back was excised and cleaned of hypodermis by scraping with a razor blade. The outer surface of the excised skin was placed between a donor and receptor cell and clamped in place. Figure 1 shows a schematic depiction of the diffusion cell. The receptor cell was maintained at 37°C with a circulating water bath. Powder was placed on the outer surface of the skin and the appearance of chemicals in the receptor solution (0.9% saline) was determined over time, by taking 60 μL samples of the receptor solution. The receptor solution was well-stirred and air was kept out of the system so that the skin was in complete contact with the receptor solution. Concentrations of nitrocellulose, dinitrotoluene, dibutylphthalate, and diphenylamine were analyzed using HPLC.

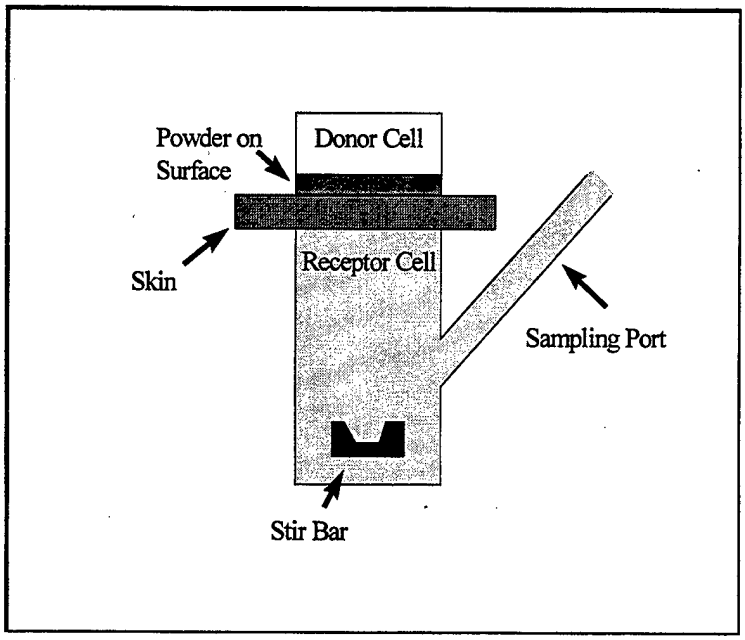

Figure 1. Schematic of a Static Diffusion Cell used for Flux Measurements

Analytical Methods

A variable wavelength/flow gradient HPLC method with nanogram detection limits for each chemical was used to analyze the diffusion cell receptor solution and the surface wipes for all chemicals except nitrocellulose. A Hewlett Packard HPLC with a 220 x 4.6 mm RP-18 column was used. Carrier fluid consisted of 68% methanol and 32% water. Flow rate was 0.4 mL/min. Injection volume was 10 µL. These compounds were stable in both matrices for 72 hours. The presence of trace components was confirmed independently by gas chromatography/mass spectrometry and supercritical fluid chromatography (Tsui et al., 1997).

Nitrocellulose was analyzed by ion chromatography after hydrolysis with sodium hydroxide. The nitrocellulose containing solution was vacuum filtered through an inorganic, 0.02 µm, membrane filter (Whatman, Anodisk 47). The filter was washed with methanol to remove interfering nitrate esters and then soaked in acetone for 15 minutes to dissolve the nitrocellulose. The acetone solution was evaporated under a stream of nitrogen and then hydrolyzed with NaOH at 100 °C for 30 minutes. Nitrocellulose concentration was calculated as the mass of nitrogen found as nitrate and nitrite after ion chromatography.

RESULTS AND DISCUSSION

Propellant on Increment Surfaces

Surface amounts of constituent chemical components contained in the XM231 increment are shown in Table 1. Only nitroglycerin and diphenylamine were found (in extremely small amounts) on the surface of the combustible case. The source of the nitroglycerin could not be definitively determined. Nitroglycerin is a constituent of ball powder contained within the ignition subsystem. However, it is also possible that the exterior surfaces of the increments were contaminated with nitroglycerin during manufacture, handling, or packaging. The metal ammunition cans used to package the XM231 increments had been previously used for other artillery propelling charges that may have contained nitroglycerin. Diphenylamine is a minor component of both the propellant and the combustible case. Because of this, diphenylamine might be expected to be available on the surface of the increment.

Table 1. Mass and mass/surface density of chemical components of XM231 increments found with a gauze wipe on the increment surface after prolonged storage.

Chemical	Mass recovered (µg ± S.D.)	Mass/surface density (µg/cm^2)
Nitroglycerin	8.6 ± 2.2	0.03
Diphenylamine	4.7 ± 1.0	0.02

Using our methods we would have been able to detect the following amounts of chemical on the surface of the increments: 2.8 micrograms for nitrocellulose, 0.21 nanograms for nitroguanidine, 0.96 nanograms for nitroglycerin, 0.25 nanograms for diphenylamine, 0.48 nanograms for 4-aminobiphenyl, 1.62 nanograms for dibutylphthalate, and 0.99 to 4.38 nanograms for dinitrotoluenes. Standard curves were made up in receptor solution.

We also used methanol soaked gauze to wipe a different quadrant of the same increments. Because methanol was a good solvent for these chemical constituents, the methanol soaked gauze removed up to seven times more dinitrotoluene from the surfaces of the increments. The amount of nitroglycerin collected with the methanol was approximately the same as with the dry wipes, indicating that the nitroglycerin was probably on the surface. It appeared that the methanol wipes may have been desorbing dinitrotoluene from inside the combustible cases instead of from the surface. Dry gauze is a much better surrogate to estimate transfer to soldier's hands.

Dermal Absorption of Increment Components in Rat Skin

We attempted to measure the absorption of nitrocellulose, dinitrotoluene, dibutylphthalate and diphenylamine through excised rat skin in the static diffusion cell after placing powdered M1 propellant on the surface of the skin, as described above. Only hints of dinitrotoluene could be detected in the saline receptor solution, but the mass was below the reliable detection limit. The other chemicals did not penetrate well enough to be found at all. Unlike M30A1 contained in XM232 increments, where we reliably found small amounts of nitroglycerin absorbing through skin in a diffusion cell (McDougal, et al., in press), we conclude that the components of M1 propellant do not absorb through rat skin.

Dermal Absorption of Combustible Case Components in Rat Skin

Wipes from the combustible case were assayed for nitrocellulose and diphenylamine. Only diphenylamine, in extremely small amounts, was recovered from the surfaces of the combustible cases (Table 1) which were stored for eleven months. We attempted to measure the appearance of diphenylamine in the receptor solution during a six- and twelve- hour exposures of isolated WF/PmWp-fz rat skin to pure diphenylamine powder on the skin surface, as previously described. No diphenylamine was detected in the receptor solution after six hours. A barely detectable unidentified peak was found after six hours which may be a metabolite of diphenylamine which we could not identify.

SUMMARY AND CONCLUSIONS

Developers of the new Modular Artillery Charge Systems need information about the dermal absorption of propellant residue from increments. With the PM Crusader Munitions and US Army Armaments RD&E Center at Picatinny Arsenal, we have developed a program to answer these questions. We measured mass of chemical constituents on the surface of XM231 MACS increments stored for eleven months and attempted to determine the flux of chemical components from powdered propellant across rat skin in the laboratory.

Of the five primary components measured on the surface of XM231 MACS increments stored for eleven months, only nitroglycerin and diphenylamine could be detected in trace amounts. Although nitroglycerin is not a component of XM231, it is also possible that nitroglycerin contamination during the manufacturing process or from storage in metal cans previously used for a nitroglycerin containing propellant such as M30A1. Diphenylamine could have come from the combustible case or from the propellant.

When powdered M1 propellant was placed on rat skin in the laboratory, no chemical components were found in the receptor solution even though we had extremely good detection capability. When pure diphenylamine was placed on rat skin in the diffusion cell, to simulate absorption from the surface of the combustible case, no diphenylamine was found in the receptor solution. The components of XM231 can be ruled out as a systemic hazard from dermal absorption.

We found that in nearly a year of storage at very warm temperatures, only nitroglycerin (a component of the propellant ignition system, but possibly resulting from contact with a previously used ammunition can) and diphenylamine (component of the combustible case) could be found on the increment surface. We also learned that when rat skin was exposed to the powdered propellant mixture, no chemicals penetrated well enough to be detected. Based on our measurements and calculations, it is extremely unlikely that XM231 would constitute toxicological hazard to soldiers by dermal absorption.

REFERENCES

ARDEC Hazardous Component Safety Data Sheet, Propellant; M1, 10 July 1987.

Dibutylphthalate. Beratergremium fuer Umweltrelevante Altstoffe (BUA), vol 22., Swedish National Chemicals Inspectorate Library, Solna Sweden, 1987.

Dinitrotoluenes (methyldinitrobenzenes). Beratergremium fuer Umweltrelevante Altstoffe (BUA), vol 12., Swedish National Chemicals Inspectorate Library, Solna Sweden, 1987.

Diphenylamine (n-phenylbenzeneamine). Beratergremium fuer Umweltrelevante Altstoffe (BUA), Gesellschaft Deutscher Chemiker, Weinheim Germany, 1991.

Initial Health Hazard Assessment Report (RCS MED 388) on the XM230 155MM Unicharge. USA Environmental Hygiene Agency Health Hazard Assessment Office, Aberdeen Proving Ground, MD 21010, February 1994.

Kinkead, E.R., Feldman, M.L., Wolfe, R.E., Flemming, C.D., Pollard, D.L., Caldwell, D.J., and Miller, C.R. Range-finding Study for a Reproductive Screen of Modular Artillery Charge System (XM232) Administered in the Diet of Sprague-Dawley Rats (AL/OE-TR-1995-0136). ManTech Environmental Technology, Inc., Wright-Patterson AFB OH., 1995.

Kinkead, E.R., Feldman, M.L., Wolfe, R.E., Flemming, C.D., Pollard, D.L., Caldwell, D.J., and Eggers, J.S. General Toxicity/Reproductive Toxicity Screen of Modular Artillery Charge System Administered in the Diet of Sprague-Dawley Rats (AL/OE-TR-1996-0170) ManTech Environmental Technology, Inc., Wright-Patterson AFB OH., 1996.

McDougal, J.N., Yu, K.O., Tsui, D.T., Zhang, H., Pollard, D.L. and Jepson, G.W. Dermal Absorption of Modular Artillery Charge (XM232). (AFRL-HE-WP-TR-1998-0051).

Scott, R.C., Dugard, P.H., Ramsey, J.D., and Rhodes, C. In vitro Absorption of Some o-phthalate Diesters through Human and Rat Skin. Environ. Health Perspect. 74:223-7, 1987.

ACGIH Threshold Limit Values for Chemical Substances and Physical Agents - Biological Exposure Indices, American Conference of Governmental Industrial Hygienists. 1996.

Tsui, D.L., Pollard, D.L., Tsui, D.T., Zhang, H.M., McDougal, J.N., and Yu, K.O. Development and Validation of High-Performance Liquid Chromatographic Analysis of Trace Components of Modular Artillery Charge Systems (MACS). Abstracts of Papers, American Chemical Society 213th ACS National Meeting, April 13-17, 1997, Anyl. 70.

Woollen, B.H., Hall, M.G., Craig, R., and Steel, G.T. Dinitrotoluene: An Assessment of Occupational Absorption during the Manufacture of Blasting Explosives. Int. Arch. Occup. Environ. Health 55(4):319-330 1985.