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MASS SPECTROSCOPIC ANALYSIS OF POLYETHER AND POLYURETHANE FOAM PLASTICS DEGENERATION IN THE SPH-4 HELMET

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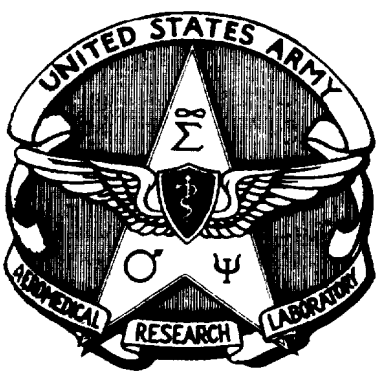

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Two components of plastic manufacture, n-butyl-phthalate and ethyl-methyl ketone have been found in high concentrations contained in the low gaseous transfer coefficient polyethylene protective bag for the SPH-4 aviator helmet. These agents are the cause of the deterioration of the SPH-4 helmet polyether and polyurethane foam lining material.

The use of mass spectrographic and gas chromatographic techniques provided the sampling of chemical compounds contained within the polyethylene bag. The

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solution to prevent foam liner deterioration is to remove the SPH-4 helmet from the protective bag.

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SUMMARY

The United States Army Aeromedical Research Laboratory, through its Life Support Equipment Retrieval Program as directed by Army Regulation 95-5, constantly evaluates all aspects of life support equipment. The deterioration of foam lining material of new SPH-4 aviator helmets was an operational problem identified through the life support equipment program. The application of advanced biomedical mass spectrographic and gas chromatographic technology provided the identification of two chemical compounds causing deterioration of stored SPH-4 helmets. The removal or opening of the polyethylene protective bag will allow off-gasing of the chemical compounds developed by the curing process occurring during storage. This study and the simple corrective action will save the United States Army approximately $122,000 in the salvage of only 10% of SPH-4 helmet stocks and additional inestimable dollars in helmet procurement.

ROBERT W. BAILEY
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MASS SPECTROSCOPIC ANALYSIS OF POLYETHER AND POLYURETHANE FOAM PLASTICS DEGENERATION IN THE SPH-4 HELMET

INTRODUCTION

The Biochemistry Branch of the Aviation Medicine Research Division, US Army Aeromedical Research Laboratory (USAARL), through coordination with the Bioengineering and Life Support Equipment Division, USAARL, evaluated the problem of deterioration of the SPH-4 aviator helmet (Federal Stock Numbers 8415-00-144-4985 and 8415-00-144-4981) foam lining material. The Life Support Equipment Branch, through the Life Support Equipment Retrieval Program (AR 95-5) and continuing evaluation of life support equipment, had found the foam lining material of new SPH-4 aviator helmets in the original storage condition to be unserviceable. The SPH-4 was sealed in a polyethylene protective bag at the time of manufacture. To evaluate the possibility of liquid or gas solvent contamination at the time of production, a mass spectroscopic analysis of the plastic foam, associated polymers, and contents of plastic protective bag was undertaken.

MATERIALS AND METHODS

The SPH-4 contains polyether and polyurethane foam in the helmet liner and ear cups. The ear cup liners are contained in a polyvinyl ear seal. An unopened SPH-4 helmet was obtained in its original plastic protective container, Lot Number 97427, sealed in June 1970.

Analysis and identification of major components were accomplished by use of JEOL DMS 100-231/241 Mass Spectrometer and Hewlett Packard 5714 Gas Chromatograph (MS-GC). Gas samples from the protective liner were withdrawn and injected onto two meter, two millimeter (mm), OV-1 column isothermal at 60°C. Helium (He) was utilized as the carrier gas at 12 milliliters per minute (ml/min). The MS utilized the following conditions:

> Separator 100°C, two stage; ion chamber 120°C; ionizing voltage 75eV, regulated; ionizing current 300 μA; and mass range 0-300, 10 seconds/decade.

Data were analyzed by elemental mapping and computerized mass marking. Spectral information was confirmed using manual interpretation of a Varian Mass Spectrometer at 180°C inlet scanning at 10 Atomic Mass Units (AMU)/minute mass 15 through 350.

RESULTS

Samples were from SPH-4 helmet, Lot Number 97427, sealed in June 1970.

Capillary leak of 200 μ liter (μl) from two liter flask at 20 micron revealed all masses present to be less than 300 on five minute scan from 0-800 at resolutions of greater than 5000.

The total ion current (TIC) study demonstrated four components in addition to normal atmospheric constituents with retention index (RI) from 1:12 to 2:29 (Table I).

TABLE I

SUMMARY OF MASS SPECTROGRAPHIC ANALYSIS

COMPONENT	PEAK NUMBER	RI	PARENT MOLECULAR ION
di-n-butyl phthalate	1	1:12	278
n-butyl phthalate	2	1:37	160
ethyl-methyl ketone	3	1:44	72
n-methyl amino	4	2:29	31

RI = Retention Index

Components 2 and 3 are present in sufficient concentration at the time of sampling to create a decomposition potential. Peak 4 was at the limit of flame ionization detectability (FID) at $4x10^{-11}$.

DISCUSSION

Potential sources of chemical attack against the polyether and polyurethane foam contained in the SPH-4 aviator helmet were considered. The possibility a solvent present in the storage area penetrated the plastic liner is considered improbable. The very low gaseous transfer coefficient of the polyethylene of the helmet ear cups would require extremely high levels of solvents for a prolonged period to attack the polyether foam ear cup pads which had deteriorated. This would require an exterior solvent capable of penetrating two dissimilar, low transfer coefficient polymers.

The most probable cause was that the solvent was present in helmet construction at the time of sealing in the polyethylene protective bag. Retention of solvent or catalyst during completion of curing or thermal cycling during storage could result in extremely high solvent concentrations disrupting the polymer structure of the foam.

Following identification of the major helmet foam components, gas samples from a sealed helmet were analyzed using multiple ion matching Mass Spectrometer (MS) techniques. Four peaks were defined as shown in Table I. Peak 1, di-n-butyl phthalate, and Peak 4, n-methyl amino, are common off-gasing products in plastic polymerization indicating that cure was incomplete at the time the helmets were sealed. Peak 2, n-butyl phthalate, is used in polyvinylchloride (PVC) plastics such as the ear seals. Peak 3, ethyl-methyl ketone, is used as a catalyst with fiberglass resins such as the SPH-4 helmet shell. Components 2 and 3 are present in sufficient concentration to effect decomposition of the polyether and polyurethane foam liners of the SPH-4 helmet by containment within a sealed, extremely low gas transfer coefficient polyethylene protective bag. Additionally, the effects of heat during storage could create further off-gasing of the agents.

Solution to the problem is extremely simple:

a. Provide holes in the present polyethylene protective bag to allow off-gasing of the gaseous products of the curing process.

b. Discontinue the use of protective bags.

The cost benefits of this technique to the US Army are calculated as follows:

7,170 SPH-4 helmets currently in stock (Oct 1976) X $170.00 per helmet = $1,218,900.00 investment.

The loss of only 10% of the helmet stock would cost:

(10% X 7,170 X $170.00) = $121,890.00

Eliminate polyethylene protective bag (FSN 8105-00-104-9850), cost per bag x total helmets: 7,170 X $0.07 per bag = $504.00 savings.

Thus, the total savings realized by this evaluation considering only 10% of helmet stock and elimination of bag would equal $122,394.00.

RECOMMENDATIONS

1. All SPH-4 aviator helmets currently in stock should be removed from, or the seal broken with numerous holes placed in a loosely wrapped polyethylene protective bag.

2. In future manufacture, the helmet should be placed in highly porous, unsealed protective material.