Industrial Hygiene Survey Report
of
Martin Marietta Missile and Electronics Group
Orlando, Florida

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Dates of Survey:
April 25-27, 1988

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Date of Report:
September 9, 1988

Report Number:
134.20.10

Industrial Hygiene Section
Industrywide Studies Branch
Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
Centers for Disease Control
Cincinnati, Ohio

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2. PB89	3. Recipient's Accession No. 9 140180/AS

4. Title and Subtitle Industrial Hygiene Survey Report of Martin Marietta Missile and Electronics Group, Orlando, Florida, Report No. IWS-134-20-10	5. Report Date 88/09/09 6.
7. Author(s) Piacitelli, G., D. M. Votaw, and E. R. Krishnan	8. Performing Organization Rept. No. IWS-134-20-10
9. Performing Organization Name and Address Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH, Cincinnati, Ohio	10. Project/Task/Work Unit No. 11. Contract (C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address	13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstract (Limit: 200 words) A walk through survey was made of the Martin Marietta Missile and Electronics Group, Orlando, Florida to evaluate worker exposures, protective equipment, and engineering controls used to reduce employee exposures to 2-methoxyethanol (109864) (2-ME), 2-methoxyethyl-acetate (110496) (2-MEA), 2-ethoxyethanol (110805) (2-EE), and 2-ethoxyethyl-acetate (111159) (2-EEA). The facility was involved in the design, development, and production of missile and electro optical systems used for aircraft and naval combat weapons programs. Of 38 field samples collected for each of the four target ethylene glycol ethers, only nine samples indicated the presence of any of the compounds and one sample indicated more than one to be present. In 32 long term samples taken, only 2-MEA was detected and only in one area of the facility. The exposures in the Patriot area resulted from the repetitive application of a primer material by hand to a piece of propulsion harness assembly. The potential for exposures resulted from accidental spills of the liquid primer in this area. Some skin protection was afforded by gloves, but the workers wore only ordinary street clothes and no respirators. Peak exposures to 2-EEA in the Hellfire area occurred during the spray painting of missiles. The authors recommend that local exhaust ventilation be installed at work stations in the Patriot area and that impermeable coveralls be given to workers in the Hellfire and Patriot areas.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-Study, IWS-134-20-10, Region-4, Spraying-booths, Organic-solvents, Solvent-vapors, Respiratory-protection, Glycols

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
	22. Security Class (This Page)	

DISCLAIMER

Mention of company or product name in this report does not constitute endorsement by the National Institute for Occupational Safety and Health (NIOSH).

ACKNOWLEDGEMENTS

This report was prepared in cooperation with PEI Associates, Inc. whose responsibilities were completed within the scope of work under Contract No. J-9-F-7-0055 for the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA), Washington, D.C. The OSHA participants during the site visit included Edward Stern, Senior Economist; David Hershfield, Project Monitor (Office of Regulatory Analysis); and Amanda Edens, Environmental Scientist (Office of Health Standards).

PURPOSE OF SURVEY:	To evaluate worker exposures, personal protection equipment and engineering controls in work areas using four ethylene glycol ethers (2-ME, 2-MEA, 2-EE, 2-EEA) proposed for revised regulation by OSHA.
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ABSTRACT

The National Institute for Occupational Safety and Health (NIOSH) is conducting an "Exposure Assessment of Industries Using Ethylene Glycol Ethers" in collaboration with PEI Associates, Inc. (PEI), Cincinnati, Ohio. This work is being conducted at the request of the Occupational Safety and Health Administration (OSHA) which is proposing to revise its current regulations for 2-methoxyethanol, 2-ethoxyethanol, and their respective acetates.

The NIOSH study involves surveying several workplaces where these glycol ethers are manufactured or used as ingredients in process materials. Each survey involves collecting industrial hygiene samples and obtaining information concerning glycol ether usage, process operations and engineering controls, past exposure levels, the potentially exposed workforce, and the corporate industrial hygiene and safety programs. This information is being compiled by PEI and reported to OSHA's Office of Regulatory Analysis for its assessment of the technical feasibility and economic impact of revising the exposure standards for the glycol ethers.

The specific results from a survey conducted at the Martin Marietta Missile and Electronics Group facilities in Orlando, FL are presented in this report. The potential for inhalation exposures was found to be minimal since airborne concentrations of glycol ethers were generally non-detectable. These results are largely attributable to the infrequent usage by minimal personnel of small quantities of glycol ether-containing materials and to the effectiveness of engineering controls. A higher potential existed for dermal exposures in a few work areas where manual handling of glycol ether-containing formulations was required and adequate control techniques were lacking.

INTRODUCTION

Adverse central nervous system (encephalopathy) and hematotoxic (anemia, leukopenia) effects in workers exposed to 2-methoxyethanol (2-ME) were first noted in the late 1930s [Donley 1936; Parsons and Parsons 1938]. The hematotoxic effects of exposure to 2-ME and other ethylene glycol ethers were later confirmed in animal studies [Miller et al. 1983; Werner et al. 1943ab]. In the late 1970s, studies reported adverse reproductive effects, including testicular atrophy, infertility, fetotoxictiy, and fetal malformations in laboratory animals exposed to different ethylene glycol ethers [Doe et al. 1983; Miller et al. 1982, 1984, Brown et al. 1984].

Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) were established for eight glycol ethers (including 2-ME (25 parts per million or ppm), 2-methoxyethyl acetate or 2-MEA (25 ppm), 2-ethoxyethanol or 2-EE (200 ppm) and 2-ethoxyethyl acetate or 2-EEA (100 ppm) in 1981 based upon the 1968 American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs®). The TLVs® were based on the hematotoxic and neurotoxic effects and on exposure concentrations reported in the early case reports of human health effects. However, more recent information from experimental animal studies indicates that adverse reproductive effects may occur at exposure concentrations below the current OSHA PELs. Therefore, because of the increased concern about their potential to cause reproductive and embryotoxic effects, OSHA is currently developing a proposal to revise its regulation of these four glycol ethers.

Under contract to OSHA's Office of Regulatory Analysis (ORA), PEI Associates, Inc. (PEI) is assessing the technical feasibility and economic impact of revising the exposure standard for ethylene glycol ethers. This work involves compiling information concerning: glycol ether usage patterns, workplace exposures, control technology, and compliance costs. Data are being collected through both mail questionnaires and site visits.

The National Institute for Occupational Safety and Health (NIOSH) is assisting OSHA in the evaluation of workplace exposures by cooperatively conducting industrial hygiene surveys with PEI at approximately 11 different plants representing the major usage groups (e.g., industrial coatings, jet fuel additives, commercial printing, aircraft painting, automobile refinishing, maintenance painting, and electronics manufacture) of the four regulated glycol ethers. Each survey involves industrial hygiene sampling and collecting information concerning process operations and engineering controls, glycol ether usage patterns, the potentially exposed workforce, and exposure control methods.

This report presents the results of a site visit conducted at two of the Martin Marietta Missile and Electronics Group facilities during April 25-27, 1988.

BACKGROUND

Physical and Chemical Properties. The glycol ethers 2-methoxyethanol and 2-ethoxyethanol, and their respective acetates, are part of the family of ethylene glycol ethers; their chemical and physical properties are summarized in Table 1. The ethylene glycol ethers are manufactured by the reaction of ethylene oxide with the appropriate alcohol (e.g., ethanol, methanol); the glycol ethers are used to form acetates by their reaction with acetic acid. In general, glycol ethers and their acetates are colorless liquids with versatile solvent properties (e.g., miscible in water and most hydrocarbon solvents, low vapor pressure, slow evaporation rate) which make them useful in a wide variety of industrial applications.

Production, Use, and Exposure. The total U.S. production of the regulated ethylene glycol ethers and acetates in 1983 is listed in Table 2.

Ethylene glycol ethers and acetates have been used commercially for over 50 years, primarily as solvents in the manufacture of protective coatings such as paints, lacquers, metal coatings, baking enamels, phenolic varnishes, epoxy resin coatings, and stains [NIOSH 1983]. Ethylene glycol ethers and acetates are also used as solvents for printing inks, textile dyes and pigments, and leather finishes; as anti-icing additives in military jet fuels; and in the manufacture of printed circuit boards. Many of these uses require direct handling of the glycol ethers by workers during the formulation and/or evaporation stages, thus leading to the potential for occupational exposure via inhalation and/or skin absorption [Dugard et al. 1984]. Based on data obtained during the National Occupational Hazard Survey (NOHS) conducted by NIOSH during 1972-1974, an estimated 2.5 million men and women may be occupationally exposed to glycol ethers (NIOSH 1977). The numbers of workers potentially exposed to the regulated glycol ethers are presented in Table 3.

TABLE 1

PHYSICIAL AND CHEMICAL PROPERTIES OF FOUR ETHYLENE GLYCOL ETHERS

Property	2-ME	2-MEA	2-EE	2-EEA
IUPAC Chemical Name	2-methoxyethanol	2-methoxyethyl acetate	2-ethoxyethanol	2-ethoxyethyl acetate
CAS No.	109-86-4	110-49-6	110-80-5	111-15-9
RTECS No.	KL5775000	KL5950000	KK8050000	KK8225000
Empirical formula	$C_3H_8O_2$	$C_5H_{10}O_3$	$C_4H_{10}O_2$	$C_6H_{12}O_3$
Molecular weight	76.1	118.1	90.1	132.1
Specific gravity	0.97	1.01	0.93	0.97
Density (lbs/gal)	8.04	8.37	7.75	8.10
Vapor pressure (mmHg) 25°C	9.7	2.0-3.7	5.7	2.8
20°C	6.0	2.0	4.0	2.0
Boiling point (°C)	124.5	145.0	135.0	156.0
Flash point (°F) open cup	115	140	120	138
1 ppm=mg/m3 (25°C,760mmHg)	3.11	4.83	3.69	5.41
1 mg/m3=ppm (25°C,760mmHg)	0.32	0.21	0.27	0.19
Other identifiers:	methyl cellosolve ethylene glycol monomethyl ether Dowanol EM	methyl cellosolve acetate ethylene glycol monomethyl ether acetate	cellosolve ethylene glycol monoethyl ether Dowanol EE	cellosolve acetate ethylene glycol monoethyl ether acetate

Clayton and Clayton, 1982

TABLE 2

U.S. PRODUCTION OF FOUR ETHYLENE GLYCOL ETHERS

Compound	1983 Production (pounds)
2-ME	83,000,000
2-MEA	1,000,000
2-EE	187,000,000
2-EEA	153,000,000

SRI 1984

TABLE 3

ESTIMATE OF U.S. WORKERS POTENTIALLY EXPOSED TO ETHYLENE GLYCOL ETHERS AND ACETATES

Compound	Number of Workers
2-ME	100,000
2-MEA	20,500
2-EE	407,000
2-EEA	321,000

NIOSH 1977

Toxicology. The effects of the short-chain ethylene glycol ethers (2-ME, 2-MEA, 2-EE, and 2-EEA) on reproduction and fetal development have been studied extensively in rats, rabbits, and mice. The results uniformly show developmental toxicity, including increased incidences of fetal malformations and resorptions. In general, the evidence suggests that the glycol ether acetates have the same toxicologic activity as their parent glycol ethers. Some studies have indicated that behavioral teratogenic effects may occur in the offspring of rats treated with 2-ME and 2-EE [Nelson and Brightwell 1984]. Testicular damage has also been caused in rats after acute exposures to 2-ME [Doe et al. 1983].

Changes in the blood and adverse effects on the bone marrow and thymus have been observed in rats, mice, and rabbits exposed to 2-ME. The effects of lowered red and white blood cell counts appear to be the result of bone marrow suppression. Recent studies [Miller et al. 1983a] have confirmed histologically the reported depressant effect of 2-ME on the bone marrow and thymus of rats and rabbits. Grant et al. [1985] have reported at least partial reversal of these effects in rats following short-term exposure to 2-ME. Limited information suggests that 2-EE, 2-EEA, and 2-MEA also produce adverse effects in the peripheral blood of rats [Werner et al. 1943b], mice [Nagano et al. 1979], and dogs [Werner et al. 1943a].

Methoxyacetic acid (MAA) has been isolated and identified in urine as the major metabolite of 2-ME in rats [Miller et al. 1983]. Although all of the glycol ethers are not metabolized via a single pathway, it has been suggested that the major metabolites of 2-ME and 2-EE, MAA and ethyoxyacetic acid (EAA), respectively, act to cause the testicular [Miller, et al., 1982, 1984], developmental [Brown et al. 1984], and hematotoxic [Miller et al. 1982] effects observed in rats treated with 2-ME or 2-EE.

Neurologic and hematologic effects were observed in workers following inhalation and dermal exposure to 2-ME [Donley 1936; Greenburg et al. 1937; Zavon 1963; Ohi and Wegman 1978]. A cross-sectional study assessing fertility among men engaged in the production of 2-ME reported decreases in testicular

size [Cook et al. 1982]. A cross-sectional evaluation of semen quality among men exposed to 2-EE found significantly lower sperm count per ejaculate (NIOSH 1986). Painters exposed to both 2-EE and 2-ME had sperm abnormalities including reduced sperm counts, and abnormalities of both red and white blood cells [Welch and Schrader 1986].

APPLICABLE STANDARDS AND RECOMMENDED LIMITS

Based on toxicological data, NIOSH recommended in Current Intelligence Bulletin (CIB) No. 39 The Glycol Ethers, with Particular Reference to 2-Methoxyethanol and 2-Ethoxyethanol: Evidence of Adverse Reproductive Effects that 2-ME, 2-EE, and structurally related glycol ethers be regarded in the workplace as having the potential to cause adverse reproductive effects in male and female workers. Also noted were and embryotoxic effects, including teratogenesis, in the offspring of the exposed pregnant females [NIOSH 1983]. The NIOSH current recommended exposure limit (REL) is therefore "reduction of workplace levels to the lowest extent possible." Since publication of CIB No. 39, additional data on the glycol ether compounds have been published (as summarized in ECETOC 1985). These data are currently being evaluated during the development of a criteria document for the ethylene glycol ethers.

The current NIOSH RELs, OSHA PELs and ACGIH TLVs® established for the targeted glycol ethers are summarized in Table 4.

TABLE 4

APPLICABLE STANDARDS AND RECOMMENDED LIMITS

Compound	Exposure Limit[a] (ppm) NIOSH REL	OSHA PEL	ACGIH TLV®
2-ME	*	25[S]	5[S]
2-MEA	*	25[S]	5[S]
2-EE	*	200[S]	5[S]
2-EEA	*	100[S]	5[S]

CFR 1984; ACGIH 1987

[a] 8-hour time-weighted-average (TWA_8)
[S] Skin notation
* Reduce exposure to lowest feasible level

HISTORY AND DESCRIPTION OF THE FACILITIES

In 1956, the Glenn L. Martin Company made an initial purchase of acreage in central Florida to begin its missile system operations. By the end of 1957, the Missile Systems Center in Orlando was opened on Sand Lake Road and began operations with 2700 employees.

In 1961, the Martin Company merged with American-Marietta Company, forming the Martin Marietta Corporation. Subsequent expansion resulted in the opening of another Missile Systems facility in nearby Ocala in 1970 and the start-up of an Electronics System Center in Orlando in 1985.

Today, Martin Marietta Corporation is an international aerospace and defense contractor; its Missiles and Electronics Group is headquartered in Orlando. The three Orlando area facilities are primarily involved in the design, development, and production of missile and electro-optical systems used for aircraft and naval combat weapons programs. These operations occupy approximately 16,000 total acres and employed 14,581 workers in 1987.

Descriptions of each of the three Missiles and Electronics Group facilities in the Florida area are presented below:

A. SAND LAKE Missile Systems Facility (Orlando, FL)

The 11 work areas in which formulations containing any of the four subject chemicals are used include:

1. Hellfire Remote Area
2. General Services Building (GSB) Spray Painting Area
3. Patriot Propulsion Harness Assembly
4. Target Acquisition Detection System (TADS) Area
5. Microelectronics (MEC) Wafer Fabrication Laboratory
6. Model Shop
7. Photomask Area
8. Bonding/Molding (Nonmetallics) Area
9. Training Center
10. Launch Test Area
11. Walleye Modification Area

The survey team visited and monitored worker exposures in the first five work areas, which constitute the major usage locations for glycol ether-containing formulations.

Hellfire Remote Area. Approximately 30 Hellfire missiles per day are spot painted by spray gun in this area over a period of two work-shifts. A total of four workers (including two preparation workers and two painters) are employed on each shift.

Six different coatings formulations containing 2-EEA may be used in this area. Quantities of each formulation used vary from two gallons per month to 40 gallons per month. One glycol ether-containing coating was being used at the time of the survey. The concentrations of 2-EEA in the two components of the coating (Deft Brown 30140 Catalyst and Deft Brown 30140 Coating) were 5 wt. % and 20 wt. %, respectively.

Painting occurs in a ventilated spray booth (approximately 12 ft x 8 ft) with a posted face velocity of 210 linear feet per minute (lfpm). Approximately five minutes are required to paint a missile. No gloves or respirators were worn by either the preparation workers or the spray painters during the survey. Organic vapor cartridge respirators and polyurethane gloves, however, were available in the area. There is some potential for inhalation and dermal exposure to the spray painters during painting from overspray. There is also some potential for dermal exposure to the preparation people during removal of the stencils. Normally, the painters use glycol ether-containing paints for less than one hour of their work shift.

The small batches of coating formulations used in the Hellfire area are also prepared here by manually mixing different components (e.g., catalyst and primer) in Styrofoam cups under a hood (approximately 3 ft. x 2 ft.) having a posted face velocity of 150 lfpm. Viscosity checks are performed on the mixture. No gloves were worn by the workers during these operations. There exists a potential for dermal exposure from accidental spills during the blending operation.

GSB Spray Painting Area. Piece parts for missile systems are spray painted in this area. A total of eight workers (including four painters and four preparation workers) are employed on each shift.

Formulations containing 2-EEA, 2-EE, or 2-MEA are used in the GSB area. Martin Marietta uses 12 formulations containing 2-EEA, 4 formulations containing 2-EE, and one 2-MEA formulation in this area; quantities used average 1 gallon per week of each formulation. The only ethylene glycol ether-containing formulation being used at the time of the survey was a Pratt & Lambert green pigmented epoxy resin containing 20-30 wt % 2-EE.

Painting occurs in ventilated spray booths having posted face velocities of 100 to 150 lfpm. The painters in this area wore organic vapor cartridge respirators and polyurethane gloves. Approximately half of their work-shift is spent performing batch blending and painting operations. Preparation workers apply and remove masking in this area. No personal protective equipment was used by the preparation workers during the survey.

Patriot Propulsion Harness Assembly. In this area, a prime coat is manually applied to the surfaces of the harness assembly using a cheesecloth. A total of six workers per shift are involved in the harness assembly priming activities.

The specific prime coat used in this area is Dow Corning 1200 Prime Coat-Red which contains 85 wt % naphtha, 5 wt % methyl cellosolve orthosilicate, 5 wt % tetrapropylorthosilicate, and a proprietary ingredient. The Material Safety Data Sheet (MSDS) for this product indicates that 2-ME may be formed upon hydrolysis. Usage of the prime coat in this area occurs daily; approximately 24 pints are used per week.

The Patriot Harness Assembly priming operations occur in an enclosed room with general ventilation and no local exhaust ventilation. The operators (referred to as nonmetallic processors) wear cotton gloves over a double layer of disposable polyurethane gloves and safety glasses during the priming operations. The gloves are disposed of after priming each harness assembly. On an average, a nonmetallic processor changes gloves six times per shift. There exists a potential for dermal exposure from accidental spills, as well as a potential for inhalation exposure because of both the absence of local exhaust ventilation over the harness assemblies and the lack of respiratory protective equipment on the workers.

TADS Area. One painter per shift is employed in this area where spray painting of the McDonnell-Douglas Apache TADS occurs. While the TADS area was initially identified as using a targeted glycol ether-containing paint, it was discovered after monitoring commenced that coatings used in this area do not contain any ethylene glycol ethers. Some of the coatings, however, contain propylene glycol ethers. An epoxy polyamide primer coating used in this area contains propylene glycol monomethyl ether, and an aircraft green polyurethane coating contains propylene glycol monomethyl ether acetate.

Painting occurs in a ventilated spray booth (approximately 12 ft x 8 ft) having a posted face velocity of 200 lfpm. The spray painter wears an organic vapor cartridge respirator and vinyl gloves during the painting operation, spending approximately one-third of the shift performing painting operations and the remainder of the time masking the aircraft component to be painted. There exists a potential for dermal exposure when cleaning up accidental spills.

MEC Wafer Fabrication Laboratory. A positive photoresist, Shipley Microposit S1400-31 D1 photoresist containing 82 wt % 2-EEA, is used in this area in the fabrication of silicone wafers. The photoresist is applied by syringe onto spinning discs for application to the wafer, and the wafer is subsequently inspected for tears and touched-up with photoresist if necessary. A total of four workers (including two wafer processors and two wafer inspectors) are employed on each shift. Usage of photoresist in this area is sporadic; approximately two quarts are used per week.

All wafer fabrication operations occur in temperature- and humidity-controlled Class 10000 "clean rooms." The general clean room area has a ventilation rate of one air change per minute while the wafer processing and inspection areas have ventilation rates of two air changes per minute. Workers wear Tyvek® suits with hoods, booties, dust masks, and antistatic vinyl gloves in the wafer fabrication laboratory to minimize contamination of the wafer. The wafer fabrication process is highly controlled to maintain the integrity of the product. There exists little potential for inhalation or dermal exposure.

Other Areas. There is very minimal usage of glycol ether-containing formulations in the remaining six work areas. The model shop and photomask areas use formulations containing 2-EEA, 2-EE and 2-MEA; quantities used range from one pint to two gallons per year.

B. EAST SITE Electronic Systems Facility (Orlando, FL)

There are nine work areas at the East Site Electronic Systems facility where formulations containing glycol ethers are currently used:

1. VHSIC Wafer Fabrication Laboratory
2. LANTIRN A Final Assembly/Optics
3. F-18 Small Parts Assembly (SPA)
4. Graphics Department
5. Touch-up Painting Area
6. FAADS Demo Area
7. Tracker Lab (Image and Signal Processing)
8. LANTIRN Support Equipment Area
9. Stingray Area

The survey team monitored worker exposures in the first four work areas, which constitute the top usage locations for glycol ethers at this site.

VHSIC Wafer Fabrication Laboratory. The VHSIC wafer fabrication laboratory represents by far the highest consumption area at this site for glycol ethers. Unlike the MEC wafer fabrication laboratory at the Sand Lake

facility, where four circuit layers are applied on each chip, 16 different circuits are applied on each chip at this site. The photoresist is pumped from a remote storage area and automatically dispensed at this location, instead of the syringe application used at the Sand Lake facility. Approximately 12-15 people per shift are employed in this area.

The only photoresist used in this area is Microposit S1400 Photo Resist, containing 82 wt % 2-EEA. Unlike the Sand Lake facility, photoresist usage occurs daily at this site, with approximately 10 gallons being used per month.

All wafer fabrication operations at the East Site occur in Class 100 clean rooms with a very high degree of ventilation. All operators (referred to as product technicians in this area) wear Tyvek® suits with hoods, booties, safety glasses, dust masks, and gloves. Since the workers have no direct contact with the photoresist, there is extremely low potential for exposure to 2-EEA in this area.

LANTIRN A Final Assembly/Optics. The production of LANTIRN, an advanced navigation and targeting fire control system, commenced at Martin Marietta in 1985. The LANTIRN system consists of two pods, a navigation pod and a targeting pod.

Parts for the navigation pod are assembled and primed in this area. The purpose of the coating is to control moisture and insulate the assembly from the outside environment. One operator per shift works in this area. The glycol ether-containing coating used in this area is Primer 1204 containing 5 wt % 2-ME; approximately one pint is used per month. The primer is handled under a hood and applied by means of a brush. Gloves are worn during priming, which generally requires only about five minutes of the workshift.

F-18 Small Parts Assembly. Touch-up priming occurs here on small parts for the F-18 aircraft. Very small amounts of primer are applied to the small parts by Q-tip, and the parts are subsequently air-cured. One operator usually works in this area.

Two coating formulations containing 2-ME are used: Dow Corning Prime Coat Red 1200 and Primer 1204. Approximately one pint per month of each is consumed in this department.

General ventilation is employed in this area. The operator wears gloves during painting. The coating containing 2-ME is usually handled only once per shift for 2-3 minutes.

Graphics Department. The photographic developer used in this department consists of Startone Developer (Part B) containing 90 wt % 2-ME and a second part (Part A) that does not contain any 2-ME. The developer solution containing ten gallons of Part B in a closed system is replaced once every month. During developing, an operator inserts a canister into the machine, leaves the area, and returns to pick up the print in about ten minutes. The rollers in the developing machine were reported to be scrubbed once every two weeks with a pad and cleanser. One operator normally is responsible for the cleaning and maintenance of the developer. The graphics department has general ventilation but no local exhaust over the developer. No personal

protective equipment is used during developing. During roller cleaning operations, however, the following personal protective equipment was reported to be used: apron, face mask, goggles, and disposable rubber gloves.

Other Areas. Very small quantities of glycol ether-containing formulations are handled in the remaining five areas. Martin Marietta also reported that the touch-up painting operation was being phased out.

C. OCALA Missile Systems Facility (Ocala, FL)

Although this facility was not visited, information was obtained from the plant Safety and Industrial Hygiene Manager regarding the extent of use of glycol ether-containing formulations. The major glycol ether consumption operation at this facility is the lamination of circuit boards. A solid laminate containing 25 wt % 2-ME is used. The production rate is approximately 4500 circuit boards per week, or 88,000 ft^2 per year. The laminating presses have local exhaust hoods with face velocities of 100 lfpm.

DESCRIPTION OF THE WORKFORCE

A breakdown by gender of the number of workers potentially exposed to each of the four ethylene glycol ethers at the three facilities is provided in Table 5. The numbers shown include personnel categories such as production workers, assembly technicians, maintenance workers and management personnel.

TABLE 5

NUMBER OF WORKERS POTENTIALLY EXPOSED TO EACH OF THE FOUR ETHYLENE GLYCOL ETHERS

Facility	Total # Employees	Glycol Ether 2-ME	2-MEA	2-EE	2-EEA
Sandlake Road	5,865	436m, 251f	104m, 45f	264m, 88f	650m, 232f
East Site	6,599	130m, 102f	46m, 13f	123m, 119f	122m, 115f
Ocala	1,598	176m, 175f	19m, 48f	0m, 0f	57m, 62f

m = males; f = females

(Note: Martin Marietta did not provide individual job titles due to the diversity of products and job categories).

MEDICAL AND INDUSTRIAL HYGIENE PROGRAMS

Martin Marietta employees receive annual medical exams which include an X-ray (optional), SMAC blood test, CBC, urinalysis, audiogram, optical exam, pulmonary function test, and physical exam.

The Orlando facilities employ full-time industrial hygienists and safety professionals. In addition, the corporate staff (in Baltimore, MD) provides technical assistance, as needed, and conducts periodic audits of the plant safety and health programs.

Martin Marietta does not routinely monitor exposures to ethylene glycol ethers at either of the two facilities surveyed (Sand Lake or East Site). Baseline measurements were taken in 1986 at the Sand Lake facility and personal TWA_8 (8-hour time-weighted-average) results ranged from 0.26 to 0.69 ppm for 2-ME in the Patriot Harness Assembly area. No subsequent sampling has been performed because of these low exposures indicated in 1986. No company samples have ever been collected for any glycol ethers at the East Site facility.

More extensive monitoring has been conducted by the company at the Ocala Missile Systems facility (not surveyed). Approximately 20 samples for the four targeted chemicals have been collected between 1985-88 with detectable results ranging from 0.006 ppm (2-MEA) to 0.11 ppm (2-EEA). The increased sampling at this facility has been the result of greater usage of these glycol ethers.

SAMPLING STRATEGY AND METHODS

A one-shift sampling survey was conducted at both the Sand Lake and East Site facilities to measure the extent of exposures associated with typical usage of the four targeted chemicals. Both personal and area long-term (5-8 hours) and short-term (15-minute) samples were collected; long-term samples evaluated full-shift exposures whereas short-term samples measured peak exposures.

Initially, work areas using any of the four subject chemicals were identified from material safety data sheets and chemical inventory information. Because very minimal quantities of these chemicals are only intermittently used, supervisors were then questioned concerning their expected usage during the scheduled survey period. In those areas where any significant usage was anticipated, at least one worker in each job category with potential exposure was monitored for a full shift. Additionally, short-term samples were ocassionally collected during those periods when glycol ethers were actually handled.

OSHA Method 53 was used for sampling and analysis. Airborne samples were collected on charcoal, desorbed with methylene chloride/methanol and analyzed by gas chromatography using a flame ionization detection (GC/FID). A brief description of the sampling and analytical procedures follows:

Long-term samples were taken with Gilian Model LFS-113DC portable low-flow air sampling pumps calibrated at a flow rate between 0.1-0.2 liters per minute (Lpm). Targeted sample volumes were generally between 30-70 liters.

Short-term samples were collected with SKC Model 224 sampling pumps calibrated at approximately 1.0 Lpm; sample volumes were nominally 15 liters.

All samples were collected on SKC No. 226-01 coconut charcoal tubes (100 mg primary/50 mg backup sections) connected to sampling pumps with tygon tubing. Personal samples were attached near the breathing zone of the worker while area samples were positioned in the immediate vicinity of typical work stations. Samples were refrigerated between sample collection and analysis. Sample analyses were performed by DataChem (Salt Lake City, UT). Charcoal tube samples were desorbed with 95/5 (v/v) methylene chloride/methanol and analyzed using a Hewlett-Packard Model 5890A gas chromatograph equipped with a flame ionization detector.

Table 6 presents the analytical limit of detection (LOD) and limit of quantitation (LOQ) for each of the four ethylene glycol ethers. The LOD is that level at which an instrument response can confidently be attributed (95% probability) to the presence of the compound being measured; the LOQ indicates the point at which an indicated response is within acceptable confidence limits. Table 6 also shows the equivalent LOD and LOQ concentrations for an 8-hr TWA sample collected at 0.2 Lpm and a 15-minute short-term sample collected at 1.0 Lpm.

TABLE 6

LIMIT OF DETECTION (LOD) AND LIMIT OF QUANTITATION (LOQ) FOR THE FOUR ETHYLENE GLYCOL ETHERS

Specific Glycol ether	Analytical Limits (mg/sample)		Sampling Limits (ppm/sample) TWA8[a]		Peak[b]	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
2-EE	0.03	0.07	0.08	0.19	0.55	1.28
2-EEA	0.03	0.08	0.06	0.16	0.37	0.99
2-ME	0.03	0.08	0.10	0.27	0.64	1.71
2-MEA	0.01	0.02	0.02	0.04	0.14	0.28

[a] 8-hour time-weighted average sample collected at 0.2 Lpm.
[b] 15-minute short-term sample collected at 1.0 Lpm.

MONITORING RESULTS

Thirty-eight field samples were collected and analyzed for each of the four target ethylene glycol ethers. Only nine field samples indicated the presence of any of the ethylene glycol ethers; one sample indicated more than one glycol ether present. The analytical results of all field samples are shown in Table 7. Of the ten detectable results, six were between the LOD and the LOQ.

Long-term Sampling. A total of 32 long-term (5-8 hours) samples were collected during the two shifts surveyed. Of the eight different areas/processes sampled for full-shift exposures at the two sites, only 2-MEA was detected and only in the Patriot Harness Assembly area. Individual sample results are reported in Table 7 as time-weighted-averages (TWAs) over the respective sampling duration. (as shown in Table 7). All five samples collected in this area had detectable full-shift concentrations of 2-MEA; the arithmetic mean concentration for all five samples was 0.13 ppm. These results are suspect since 2-ME (rather than 2-MEA) was expected based upon the material safety data sheet information provided for Dow Corning Primer 1200. The uncertainty in the results was attributed to two factors by the laboratory performing the analyses: 1) the LOD for 2-MEA is three times lower than that for 2-ME, and 2) a high level of interferences surrounded the 2-MEA peak on the chromatograph during the analysis, making positive qualitative

identification difficult. The low-level results reported for 2-MEA must therefore be considered suspect. None of the other ethylene glycol ethers were found from long-term samples collected in any other areas.

Short-term Sampling. Six samples were collected to evaluate short-term (peak) exposures; results are shown in Table 7. The two 15-minute samples in the Hellfire area had measurable levels of 2-EEA (arithmetic mean of 0.64 ppm); 2-MEA was measured in short-term samples collected in both the Patriot Harness Assembly and F-18 SPA (Small Parts Assembly) areas; concentrations were 0.14 and 0.67 ppm, respectively. The F-18 SPA sample also indicated the presence of 2-ME at 1.04 ppm.

DISCUSSION

Results clearly indicate that exposures to the regulated ethylene glycol ethers and acetates are quite low at the two Martin Marietta facilities surveyed. Seventy-three per cent of the field samples had non-detectable results. Only three different areas (Patriot Harness, Hellfire Remote, and F-18 Small Parts Assembly) indicated any detectable exposures to either 2-ME, 2-MEA, or 2-EEA; no measurable exposures to 2-EE were found.

The TWA exposures to 2-MEA in the Patriot area resulted from the repetitive application of a primer material (Dow Corning 1200) by hand to a piece of propulsion harness assembly. The potential for exposures resulting from accidental spills of the liquid primer existed in this area. Although some skin protection was afforded by polyurethane gloves, the workers wore only street clothes with no outer protection. No respirators were worn in a totally enclosed room with only general ventilation.

Peak exposures to 2-EEA in the Hellfire area occurred during the spray painting of missiles. A spray gun was used to intermittently spot paint missiles in a ventilated spray booth. Although respirators and gloves were clearly available in this work area, they were not worn during the survey period.

The short-term exposures to 2-ME and 2-MEA in the F-18 machine shop area occurred while a worker applied primer (Dow Corning 1200) using a Q-tip to the surface of an assembly part which had been reworked; this recoating took about three minutes and occurred only once during the shift. The work area was in a large room with only general ventilation. The worker wore disposable polyurethane gloves; no respirator was worn.

CONCLUSIONS AND RECOMMENDATIONS

Overall, the two Martin Marietta Missiles and Electronics Group facilities surveyed have well-controlled operations in areas where glycol ether formulations are used. The monitoring results indicate that airborne concentrations of the subject ethylene glycol ethers and acetates are nondetectable in most areas; this is generally attributable to the infrequent usage of small quantities of glycol ether-containing materials and the effectiveness of the engineering controls designed to both ensure product quality and to minimize worker exposures. The only area where detectable

full-shift concentrations for any of the ethylene glycol ethers were measured was the Patriot area; inhalation exposures are controlled only by general ventilation in this area. Although peak exposures were detected in the Hellfire, Patriot, and F-18 Small Parts Assembly areas, none of the results were above the limits of quantitation for the ethylene glycol ethers. The potential for dermal exposure to the glycol ethers is highest at the Sand Lake facility in the Hellfire and Patriot areas due to the frequent manual handling of glycol ether formulations; gloves were worn only in the Patriot area.

Efforts to further minimize exposures in these areas should focus on 1) installing local exhaust ventilation at work stations in the Patriot area, and 2) providing impermeable coveralls to workers in the Hellfire and Patriot areas.

TABLE 7

MONITORING RESULTS FOR THE FOUR ETHYLENE GLYCOL ETHERS AT THE MARTIN MARIETTA MISSILE SYSTEMS (SAND LAKE) AND ELECTRONIC SYSTEMS (EAST SITE) FACILITIES, ORLANDO, FLORIDA
APRIL 26-27, 1988

Date	Sample ID[a]	Job/area	Time Start	Time Stop	Flow (cc/min)	Duration (min)	Air volume (L)	Concentration[b] (ppm) 2-EE	2-EEA	2-ME	2-MEA
4/26/88	MM-SL-35[a]	Hellfire:painter	7:54	13:32	170.0	338.00	57.5	-	<0.10[c]	-	-
4/26/88	MM-SL-8	Hellfire:prep	7:56	13:32	167.0	336.00	56.1	-	<0.10[c]	-	-
4/26/88	MM-SL-54	Hellfire:painter	8:01	13:50	100.0	349.00	34.9	-	<0.16[c]	-	-
4/26/88	MM-SL-48	Hellfire:prep	7:56	13:33	102.0	337.00	34.4	-	<0.16[c]	-	-
4/26/88	MM-SL-5	Hellfire:prep	8:00	13:36	104.0	336.00	34.9	-	<0.16[c]	-	-
4/26/88	MM-SL-6	GSB Paintshop:painter	8:22	14:20	166.0	358.00	59.4	<0.14[c]	-	-	-
4/26/88	MM-SL-57	GSB Paintshop:prep	8:22	14:30	171.0	368.00	62.9	<0.13[c]	-	-	-
4/26/88	MM-SL-2	GSB Paintshop:painter	8:22	14:25	100.0	363.00	36.3	<0.22[c]	-	-	-
4/26/88	MM-SL-43	GSB Paintshop:prep	8:22	14:30	101.0	368.00	37.2	<0.22[c]	-	-	-
4/26/88	MM-SL-33	GSB Paintshop:area	8:22	14:20	104.0	358.00	37.2	<0.22[c]	-	-	-
4/26/88	MM-SL-27	Patriot:processor	8:52	14:37	168.0	345.00	58.0	-	-	<0.17[c]	0.14
4/26/88	MM-SL-11	Patriot:processor	8:52	14:35	104.0	343.00	35.7	-	-	<0.27[c]	0.12[d]
4/26/88	MM-SL-30	Patriot:processor	8:52	14:35	103.0	343.00	35.3	-	-	<0.27[c]	0.12[d]
4/26/88	MM-SL-53	Patriot:area	8:52	14:38	102.0	346.00	35.3	-	-	<0.27[c]	0.23
4/26/88	MM-SL-25	TADS:painter[e]	9:15	14:50	173.0	335.00	58.0	-	-	-	-
4/26/88	MM-SL-17	TADS:painter[e]	9:10	14:50	197.0	340.00	67.0	-	-	-	-
4/26/88	MM-SL-7	MEC:wafer processor	9:34	15:05	186.0	331.00	61.6	-	<0.09[c]	-	-
4/26/88	MM-SL-40	MEC:wafer inspector	9:32	15:05	106.0	333.00	35.3	-	<0.16[c]	-	-
4/26/88	MM-SL-41	MEC:area	9:34	15:05	170.0	331.00	56.3	-	<0.10[c]	-	-
4/26/88	MM-SL-47	Patriot:area[f]	12:20	12:35	990.0	15.00	14.9	-	-	<0.65[c]	0.14[d]
4/26/88	MM-SL-23	Hellfire:painter[f]	12:59	13:14	1000.0	15.00	15.0	-	<0.86[d]	-	-
4/26/88	MM-SL-39	Hellfire:painter[f]	13:14	13:32	1000.0	18.00	18.0	-	<0.41[d]	-	-
4/27/88	MM-ES-52	VHSIC:technician	7:25	11:30	170.0	245.00	41.7	-	<0.13[c]	-	-
4/27/88	MM-ES-46	VHSIC:technician	7:25	11:30	168.0	245.00	41.2	-	<0.14[c]	-	-
4/27/88	MM-ES-26	VHSIC:technician	7:40	11:38	100.0	238.00	23.8	-	<0.23[c]	-	-
4/27/88	MM-ES-16	VHSIC:area	7:28	11:39	186.0	251.00	46.7	-	<0.12[c]	-	-
4/27/88	MM-ES-55	VHSIC:area	7:28	11:29	104.0	251.00	26.1	-	<0.21[c]	-	-
4/27/88	MM-ES-19	VHSIC:area	7:40	11:39	184.0	239.00	44.0	-	<0.13[c]	-	-
4/27/88	MM-ES-28	VHSIC:area	7:40	11:39	104.0	239.00	24.9	-	<0.22[c]	-	-
4/27/88	MM-ES-50	LANTIRN:optics tech	8:09	12:05	102.0	236.00	24.1	-	-	<0.40[c]	-
4/27/88	MM-ES-63	LANTIRN:optics tech	8:11	12:05	197.0	234.00	46.1	-	-	<0.21[c]	-
4/27/88	MM-ES-14	LANTIRN:area	8:11	12:05	104.0	234.00	24.3	-	-	<0.40[c]	-
4/27/88	MM-ES-38	F-18SPA:area	8:38	12:28	171.0	230.00	39.3	-	-	<0.25[c]	<0.05[c]
4/27/88	MM-ES-21	Graphics:area[f]	8:58	9:13	990.0	15.00	14.9	-	-	<0.65[c]	-
4/27/88	MM-ES-20	VHSIC:area[f]	11:33	11:50	1000.0	17.00	17.0	-	<0.33[c]	-	-
4/27/88	MM-ES-36	F-18SPA:area[f]	12:18	12:33	1030.0	15.00	15.5	-	-	1.04[d]	0.67

a SL-Sand Lake; ES-East Site.
b Samples were not time-weighted to 8-hour concentrations.
c Laboratory analysis of analyte was below limit of detection.
d Laboratory analysis of analyte was below limit of quantitation.
e No ethylene glycol ethers used in this area; none detected in the analysis.
f Short-term samples.

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