SIDS INITIAL ASSESSMENT REPORT
For 15th SIAM

Boston, USA
October 22-24, 2002

Category Name: High Boiling Ethylene Glycol Ethers Category

Category Members: Triethylene glycol butyl ether, CAS No. 143-22-6
Tetraethylene glycol methyl ether, CAS No. 23783-42-8
Tetraethylene glycol butyl ether, CAS No. 1559-34-8

2.0 GENERAL INFORMATION ON EXPOSURE

Manufacture

Members of the High Boiling Ethylene Glycol Ethers Category (and the surrogates) are manufactured in closed, continuous equipment by the reaction of ethylene oxide with methyl alcohol or butyl alcohol. This reaction can produce glycol ethers of varying chain length depending on the molar ratio of reactants and the temperatures and pressures used in the reaction. Milder conditions and lower molar ratios of ethylene oxide to alcohol will produce the ethylene glycol mono-alkyl ethers. Using more ethylene oxide and higher temperatures and pressures produces diethylene glycol ethers, triethylene glycol ethers, tetraethylene glycol ethers and higher homologues. The products are purified by distillation. Triethylene glycol butyl ether (TGBE) is a relatively pure product (purity 85-100%). The most common chain length of tetraethylene glycol methyl ether (TetraME) and tetraethylene glycol butyl ether (TetraBE), is four ethylene glycol units; however these materials also contain tri-, penta-, hexa- and higher polyethylene glycol units end-capped with a methyl or butyl ether group.

In the United States, 20,900 metric tons (46 million pounds) of TGBE were produced in 1999 by three manufacturers. In the United States in 1998, > 454 - 4,540 metric tons (> 1-10 million pounds) of TetraME and > 4,540 - 22,700 metric tons (> 10-50 million pounds) of TetraBE were produced (U.S. EPA, 1998).

Regions other than Japan and the United States (including Canada, Mexico, South America and Eastern Europe) do not produce significant commercial amounts of TGBE (CEH 2000). Production is projected to increase slightly to 22.3 thousand metric tons (49 million pounds) by the Year 2004 (CEH, 2000). In Western Europe, consumption of triethylene glycol ethers (total methyl, ethyl and butyl ethers) was 40 thousand metric tons (88 million pounds) (CEH, 2000). The volumes of the individual triethylene glycol ethers were not broken out for Europe. The manufacturing volumes for triethylene glycol ethers in Japan individually or combined are not available.

Uses

The most significant current use of the category members and surrogates is as components of automotive hydraulic brake fluids (CEH, 2000). No other major uses are reported. Manufacturers transport TGBE in tank cars and tank trucks to processors of brake fluids. The processors blend the TGBE, TetraBE or TetraME in enclosed equipment with other components to produce formulations that meet performance specifications for brake fluids. These formulations may be further treated or blended with additives to make the hydraulic fluids non-corrosive and stable to decomposition during use. A typical brake fluid formulation contains a mixture of glycol ethers and sometimes polyethylene glycols, as well as additives. An example of a brake fluid is Shell DOT 4, which is described in Table 2.

In the United States, the brake fluids must meet Department of Transportation (DOT) standards. One important performance need is low volatility. The resulting brake fluids are sold to vehicle manufacturers and automotive and truck garages in drums or smaller containers for addition to brake systems. Some brake fluids containing high boiling ethylene glycol ethers (typically in pint and quart cans) are sold by automotive stores to consumers.

Triethylene glycol butyl ether (TGBE) also has been used as a plasticizer intermediate (Hawley's Condensed Chemical Dictionary 12th ed. 1993); a chemical intermediate for reaction products with aluminum isopropoxide (SRI); and in various solvent applications (Ullman's Encyclopedia of Industrial Chemistry). These reported uses (if still active) are believed by the manufacturers to be minor uses compared to use as brake fluid components.

2.1 Environmental Exposure and Fate

The high boiling ethylene glycol ethers typically enter the environment through slow escape and evaporation from automotive brake systems. Spills of brake fluids can also occur during brake repair or service in garages and service stations. Typically such spills would be a few drops to under a liter of liquid. Emissions to the atmosphere or surface water occurring via industrial wastes or effluents during manufacture or processing are limited by predominately enclosed processing and low volatility. TGBE entering the atmosphere from industrial air emissions or evaporation from brake systems may be washed out of the atmosphere by rainfall (Staples et al., 1988). It is likely that the same process will occur with TetraME and TetraBE.

2.1.1 Photodegradation

Estimated photodegradation hydroxyl radical rate constants (Table 4) for category members are in close agreement. Photodegradation half-lives of TGBE, TetraME, and TetraBE (estimated using the EPIWIN/AOP model) have atmospheric photodegradation half-lives of 2.5, 2.4 and 2.0 hours respectively.

2.1.2 Stability in Water

The category members are not expected to hydrolyze readily. No hydrolysis studies could be located, and the EPIWIN/HYDROWIN model cannot predict hydrolysis rates for the ether function

[R-O-R, where R=organic alkyl group]. However, ether groups are generally stable to water under neutral conditions and ambient temperatures. The ether function is hydrolyzed by heating in the presence of halogen acids, particularly hydrogen iodide (Fieser and Fieser, 1960).

2.1.3 Volatilization

As can be seen from Table 3, the category members are highly soluble to miscible in water, possess high boiling points (between 235-350 °C) and low vapor pressures. The estimated Henry's Law Constants, falling in the narrow range of 3.54 E-14 to 3.67 E-13 m^3* atm/mol @ 25° C (Table 4), point to a limited volatilization potential.

2.1.4 Transport and Distribution

The potential distribution of TGBE has been estimated using the Mackay Level III fugacity modeling approach (EPIWIN). Such modeling estimates relative distribution within different environmental compartments, based on key physical property parameters. The Level III estimated mass balances for category members, shown in Table 4, lend further weight to limited volatilization and a preference for partitioning to water and soil. The ethers in this category possess physical properties that suggest that once they enter the aqueous compartment, they tend to remain dissolved in water. Soil/sediment partition coefficients (Koc) of 10 have been estimated for TGBE, TetraME and TetraBE using the EPIWIN/PCKOCWIN (Table 4). These results suggest that the category members have uniformly high soil mobility. Thus, these products can leach from soil deposits to groundwater, but can also be transported to environments where aerobic biodegradation can take place.

Table 4. Comparison of Environmental Fate Parameters for Category Members and Surrogates[a]

Chemical	Henry's Law Constant[b] (atm-m^3/mole)	Photodegradation OH radical rate constant[b] (cm^3/molecule-sec)	Koc[c]	Predicted Environmental Distribution (Mackay III fugacity model)[b]			
				Air (%)	Water (%)	Soil (%)	Sed. (%)
TGBE 143-22-6	9.52 E-14	51.5 E-12	24 [d]	0.0608	44.7	55.1	0.0766
TetraME 23783-42-8	1.57 E-13	54.0 E-12	10 [b]	2.45 E-9	45.3	54.6	0.0755
TetraBE 1559-34-8	3.67 E-13	63.0 E-12	10 [b]	6.59 E-9	45.1	54.8	0.0755
TGME 112-35-6	3.54 E-14	40.0 E-12	4 [d]	0.0501	45.8	54.1	0.0763
TGEE 112-50-5	4.77 E-14	45.4 E-12	7 [d]	0.0538E-6	45.8	54.0	0.0764
MPEG350 9004-74-4	No data	No data	No data	No data	No data	No data	No data
DOT4 Brake Fluid	No data	No data	No data	No data	No data	No data	No data
Polyethylene	No data	No data	No data	No data	No data	No data	No data

glycol monobutyl ether 9004-77-7							

[a] Bolded chemicals are category members. See robust summaries for study details and references
[b] Calculated using EPIWIN or earlier Syracuse Research Corporation Interactive Calculation Program. In running EPIWIN, normal defaults were used as inputs, except in those cases where measured values exist for melting point, boiling point, water solubility. In those cases the measured values were inputs to the program.
[c] soil/ sediment coefficient
[d] log Koc = 0.544 log K_{ow} + 1.377 [Staples (1988); Howard (1993); Lyman et al. (1982)].

2.1.5 Biodegradation

When released to water, some studies show that biodegradation of category members is reasonably rapid (Table 5). OECD guideline studies indicate biodegradability (> 90%) for TGBE (ready or inherent) and TetraME (inherent). However, the APHA comparative biodegradation study of TGME, TGEE and TGBE indicate slower rates of biodegradation (from 47-71%). Altogether, the data suggest that different study methodologies provide variable results for the tri- and tetraethylene glycol ethers. No category members or surrogates that were tested demonstrate marked resistance to biodegradative processes.

Table 5. Comparison of Biodegradation Rate Ranges for Category Members and Surrogates*

Category Member	Biodegradation Rate Ranges
TGBE 143-22-6	47% after 20 days (APHA) (ready) 88% after 14 day (OECD) (ready)** 92% after 21 days (OECD) (ready)** 100% after 9 days (OECD) (inherent)**
TetraME 23783-42-8	99% after 8 days (OECD) (inherent)**
TetraBE 1559-34-8	Data for all chemicals are used
TGME 112-35-6	71% after 20 days (APHA) (ready)
TGEE 112-50-5	71% after 20 days (APHA) (ready)
MPEG 350 9004-74-4	No data
DOT4 Brake Fluid	No data
Polyethylene glycol monobutyl ether 9004-77-7	No data

* Bolded chemicals are category members. See robust summaries for study details and references.
**Original reference was not available. The study was described in a previous IUCLID data set produced by the European Chemicals Bureau and given a reliability rating of 2 (valid with restrictions). According to the OECD Secretariat, this study should be assigned a reliability rating of 4 for this submission (since it was not reviewed).

2.1.6 Bioaccumulation

The category members have a limited potential to bioaccumulate (based on log K_{ow}s ranging from –1.73 to +0.51@ 20^{o}C), and predicted bioconcentration factors, log BCF = ca. 0.50 (EPIWIN/BCF Program).

2.2 Human Exposure

The most likely routes of human exposure to category members are via inhalation or dermal contact. While exposure may occur during manufacture or processing, greater exposure potential is associated with use of brake fluids containing category members.

2.2.1 Workplace Exposure

Exposure during manufacture is limited by the use of enclosed equipment, necessitated by the highly hazardous properties of the reactant ethylene oxide. Bulk storage, handling and transport of product further limits exposure potential. Processors use enclosed equipment for the formulation of brake fluids containing category members. Worker exposure is more likely to occur while adding brake fluids containing high boiling ethylene glycol ethers to automotive brake systems, i.e. when charging, servicing and repairing brakes in automotive factories and garages. Dermal contact is an expected exposure route (rather than inhalation), based on the low volatility of the high boiling glycol ethers.

2.2.2 Commercial Product Exposure

Home automobile mechanics may be occasionally exposed to high boiling glycol ethers in brake fluids when topping off the brake fluid level in the brake master cylinder. Dermal contact through minor spills is a greater source of exposure than inhalation, since high boiling glycol ethers are not volatile and the operation is of short duration.

2.2.3 Environmental Exposure

General population exposure is also possible through inhalation of ambient air containing low concentrations of high boiling ethylene glycol ethers that may be released from industrial processes or through evaporation of brake fluids containing them. Ingestion of drinking water containing category members as contaminants is also possible. No public monitoring studies or data have been identified that report the presence of TGBE, TetraME or TetraBE in ambient air or groundwater. However, TGBE was listed as a contaminant found in advanced treatment water in lake Tahoe, CA, Pomona CA and Orange County CA (Lucas, 1984).