MTBE / ETBE Transport over inland waterways

Guidelines

MARCH 2008

EFOA

The European Fuel Oxygenates Association

EFOA
EUROPEAN FUEL OXYGENATES ASSOCIATION

- Founded in 1985, EFOA is a non-profit, technical organisation.
- Its role is to represent the European Fuel Ether industry in a wide variety of technical and government initiatives.
- EFOA is recognised by the European Commission as a stakeholder on fuel quality and biofuels.
- We have 10 members representing the majority of the European ether capacity:

Our Mission

- EFOA, is dedicated to the responsible usage and the promotion of chemical ether fuel oxygenates as components of gasoline.
- EFOA supports and disseminates state-of-the art scientific research on the benefits and impact of ethers on health and the environment.
- EFOA believes in the application of sound scientific principles and actively promotes constructive co-operation with all stakeholders; industry, NGOs, etc.

PREAMBLE

Fuel ethers are oxygen containing petrol blending components. Their high octane ratings and clean burning characteristics means they are ideally suited to the production of high quality unleaded petrol.

For all these reasons fuel ethers have been widely used all over the world for the last 30 years.

Ether usage varies across Europe but at the current time they represent somewhere around 4% of the EU petrol pool.

Apparently random short-term concentration peaks of fuel-ethers MTBE (Methyl-tert-Butyl ether) and ETBE (Ethyl-tert-Butyl ether) are analysed regularly throughout the year in the Rhine at the International Monitoring station at the Dutch-German border in Bimmen-Lobith. The peaks last less than 24 h and vary in severity up to 60 – 70 ◂g/l, far below any health risk but in a range of magnitude causing a possible risk of taste and odour tainting of drinking water produced from Rhine water.

EFOA led analysis of the data and investigations about possible sources resulted in indications that barges transporting the substances on the Rhine are the probable source, especially after they have unloaded the product and contain liquid and vapour residues of the products only.
Deeper analysis of the measured concentration data have demonstrated that most of the incidents are happening in the Rhine from Duisburg to just north of Wesel.

EFOA believes that this problem can be solved by raising awareness of the properties of fuel ethers and the need for correct product handling and residue management. For this reason we have prepared the following code of best practice when transporting fuel ethers by barge.

DISCLAIMER

In order to address the problem of incorrect product handling and residue management EFOA has developed this code of best practice (CoP) covering the loading and unloading of fuel ethers from barges.

The CoP is based on the experience and expertise of the EFOA member companies in handling ETBE and MTBE.

Whilst it is intended to be a summary of best practice, it is recognised that other quality systems and processes may be equally effective in achieving the desired level of environmental protection.

The systems described in the CoP are entirely voluntary. Individual companies may decide to apply the CoP either in full, or in part, or not to apply it at all, according to their own judgment.

In addition, the information included in the CoP is provided without prejudice.

The CoP is freely available on our internet site **http://www.efoa.org**.

CODE OF BEST PRACTICE (CoP)
COVERING THE LOADING AND UNLOADING OF FUEL ETHERS FROM BARGES

The purpose of this code of best practice is to minimise the vapour and liquid residues that are generated during the shipment of MTBE and ETBE in order to reduce the potential for their release into water (see Annex 3).
All operations must be conducted in accordance with the relevant national regulations and the requirements of international regulations (for example ADNR regulations) as appropriate.

1 Barge selection

It is recommended that all consignors involved in the transport of MTBE/ETBE should undertake inspections of barges or participate in a common inspection scheme (e. g. European Barge Inspection Scheme). This will enable each consignor to satisfy himself of the suitability of barges employed and ensure that appropriate safety standards are maintained. Barges equipped with deep well pumps or equivalent are preferred. Barges are preferred that have separate ballast and product tanks, as well as vapor return- and efficient stripping facilities according to the latest technical standards. Barges with low-emission sampling points are preferred. Barges with previous cargo MTBE or ETBE are preferred. Efforts should be made to also ensure that the following cargo will be compatible with MTBE and ETBE.

2 Loading

These operations should be carried out according to the latest edition of the ADNR-checklist. Sampling after loading to be carried out according to the latest available ADNR-rules, by taking into consideration UN regulated waiting time between end of loading and sampling. Sampling of ships tank should be executed with lowest emission possible, ideally via a closed sampling system. Loading lines should be emptied into ship product tanks to avoid emissions or spillages.

The loading location should be able to handle barge vapour residues. Closed loading systems are preferred, i.e. vapour return facilities, incineration or vapour absorbing systems should be considered. When the previous cargo was incompatible then the barge should be presented clean, dry and odourless and at atmospheric pressure.

Barges with previous cargo MTBE/ETBE or compatible product should be accepted, without intermediate cleaning, but liquid free.

The cargo should be accompanied by EFOA handling recommendations (see Annex 1).
We recommend that the following UN numbers are used; for MTBE UN2398, hazard class 3, packing group II, for ETBE UN1179, hazard class 3, packing group II.

3 Unloading

These operations should be carried out according to the latest edition of the ADNR-checklist.
Vapour handling: barges should either to be connected to a vapour return line of the land tank in to which the product is to be discharged or land tank to be connected to an off-gas handling system i.e. vapour return facilities, incineration or vapour absorbing system.
Resting of barges: unloading facilities should always provide installations or appropriate connections to use the efficient stripping system of barges. This is in order to ensure that barges product tanks can be rested and are liquid free as far as the latest technical standards allow.

(!) It is very important that receivers ensure sufficient time and tankage is available to achieve complete unloading.

Receivers should make every effort to remove all liquid product from the barge on-shore. Pumps and lines must also be emptied on-shore as this minimises the residual material the barge has to handle. See section on cleaning and disposal of wastes.

4 Transit

MTBE and ETBE vapours are heavier than air so will naturally go towards the river. Thus in transit, ideally vapours should not be vented. If there is no other option, venting must be done in accordance with the ADNR and the VOC Directive (94/63). In addition it is recommended to:

- Not vent when humidity levels are high e.g. raining or snowing
- Vent vapours above the deck level to minimise risk of water contact

Ballasting should always be restricted to dedicated ballast tanks. No ballast should be taken into or released from product tanks.

During transport no product movements to be made i.e. emptying of lines, swapping of product between tanks or other activities concerning ship lines, tanks, pumps etc.

5 Previous Cargoes and Cleanliness

Annex 2 details a list of compatible cargoes with ETBE and MTBE.

The tank that carries MTBE/ETBE shall not have carried substances that result in dangerous reactions/effects. Examples of such substances can be found in the EPA's Chemical Compatibility Chart or the US Coast Guard compatibility charts (Title 46, Code of Federal Regulations, part 150, October 1995).

Tanks to be loaded with MTBE/ETBE shall not be cleaned with materials which are reactive with ethers e.g. strong acids or oxidising agents (consult material safety data sheet; a specimen is included as annex 4).

6 Cleaning and Disposal of Wastes

In all circumstances barge product tanks should be drained and free of liquids after discharging by using an efficient stripping system of the barge in connection with the discharging installation to be proved by an independent inspector.

Any cleaning of barges tanks, as well as the disposal of any product residues and wash waters must be done in a proper form at authorised disposal facilities and according to the applicable laws.

It is strongly recommended that operations should be organised to minimise waste levels.

➔ ANNEXES

ANNEX 1
MTBE : HANDLING RECOMMENDATIONS FOR WATER PROTECTION

Un-No: 2398 Addendum to the Inland Waterway TREMcard Date: 28 September 2006

DANGEROUS GOOD

Methyl-Tert-Butyl-Ether: colourless liquid with strong turpentine-like odour and taste

NATURE OF HAZARD FOR WATER

- Partly soluble in water with limited evaporation from water.
- Removal from water is difficult.
- Slow biodegradation.
- Strong odour and taste even by very small concentrations means hazards to drinking water production and purification plants.

AVOIDING SPILLS

- Any risk of spill in water has to be avoided.
- Transport of MTBE compatible loads only, without tank cleaning where ever possible.
- Degassing in atmosphere not during rainfall.
- Condensate of degassed MTBE should not rinse in surface water (1000 m^3 tank may contain 150-200 kg MTBE vapour after unloading without degassing).
- Washing water from tank cleaning operations to be treated in authorized treatment stations.
- Avoid ballasting in product tanks. Ballasting only in completely cleaned product tanks from both vapour and liquid MTBE. Ballast water from product tanks which were not completely cleaned before ballasting has to be treated in authorized treatment stations.

IN CASE OF SPILLAGE

- Do not allow entrance in water.
- Take up mechanically or with an absorbent material.
- To be disposed of to authorized stations.

EMERGENCY CALL 112

FURTHER INFORMATION

Regarding other hazards than for water, please refer to the Safety Data Sheet (MSDS) or Inland Waterway Transport Emergency Card (TREMcard).

ANNEX 2

INSTRUCTIONS FOR PRODUCT LOADINGS OF ETBE/ MTBE	
accepted preload	actions needed *
Gasoline, max. 50 ppm Sulphur	1
Gasoline, max. 10 ppm Sulphur	1
Diesel, max. 50 ppm Sulphur	2
Diesel, max. 10 ppm Sulphur	2
Heating Oil, undyed	2
Heating Oil, dyed	2
Jet A-1 / Kerosene	6
AVGAS 100 LL	2 + 5 or 4 + 5
Middle distillate -components	2
Gasoline-Components	1
Light distillate fuel (LDF)	2
Alcohols (Methanol, Ethanol)	1
FAME (Bio-diesel)	2
TBA (t-butyl alcohol)	1
MTBE/ ETBE	1

* see barge remarks

INSTRUCTION FOR PRODUCT CHANGE BY MINERAL OIL PRODUCTS AND -COMPONENTS FOR INLAND WATER-, COASTER AND SEA-GOING SHIPS

In accordance with the International Transport Guidelines the degassing of barges transporting dangerous goods (ADNR – Paragraph 7.2.3.7) is authorized under certain conditions.

As of 1st January 2006 the degassing (ventilation) of gasoline is forbidden in Germany as per the 20th Emission Protection Rules (BImSchV – UN No. 1203; VK 91, VK 95 and VK 98).

For the above reasons after transporting petrol a barge should not be vented. If venting is unavoidable it must be done with a certified efficient stripping system and this system must have a current valid certificate.

Nbr	Required action	Remark
1	**Normal emptying**	Tanks and pipelines have to be drained and empty. Attention should here be paid to dead ends, lows, sample lines and deck lines. No special cleaning measures are necessary.
2	**Special emptying**	Ship has to be equipped with a certified «efficient stripping system (ESS)». Tanks, pipelines, pumps and filters have to be completely emptied with an «effective stripping system». This must be documented in the cargo journal. Or, where allowed, by A1-products as pre-loading: Tanks, pipelines, pumps and filters have to be empty and gas free. «Gas free» means: certificate of one expert mentioned in the ADNR, with the remark «safe for entry but not for fire activities». Or by A3-products as pre-loading: A certificate of a surveyor must confirm that the ship is cleaned of residues. The disponent has then to decide if a product change is possible with the asserted residue quantity. In case of need ckeckings and analyses for all three cases can be requested.
3	**Not recorded**	
4	**«Dedicated»**	Direct loading only if same pre-loading.
5	**AVGAS 100 LL**	For the transport of AVGAS 100 LL only coated ships are allowed. After stripping of the previous loading complete emptying has to be guaranteed by an independent surveyor.
6	**Not permitted**	A direct product change is not allowed. Either «Dedicated» (see § 3) or another product, compatible with the list.

INSTRUCTION FOR PRODUCT CHANGE BY MINERAL OIL PRODUCTS AND -COMPONENTS FOR INLAND WATER-, COASTER AND SEA-GOING SHIPS

LOADING	PRE-LOADING ---------->														
	Gasoline max. 50 ppm Sulphur	Gasoline max. 10 ppm Sulphur	Diesel max. 50 ppm Sulphur	Diesel max. 10 ppm Sulphur	Heating Oil un-dyed	Heating Oil dyed	Jet A-1 / Kerosene	AVGAS 100 LL	Middle distillate, -compo-nents	Gasoline Compo-nents	Light distillate fuel (LDF) without bio parts	Ether (MTBE, ETBE)	Alcohols (Methanol, Ethanol)	FAME (Bio-die-sel)	TBA (t-bu-tyl alcohol)
Gasoline, max. 50 ppm Sulphur	■	1	1	1	2	2	2	2	2	1	2	1	1	2	1
Gasoline, max. 10 ppm Sulphur	1	■	1	1	2	2	2	2	2	1	2	1	1	2	1
Diesel, max. 50 ppm Sulphur	2	2	■	1	2	2	2	2	2	2	2	2	2	1	2
Diesel, max. 10 ppm Sulphur	2	2	1	■	2	2	2	2	2	2	2	2	2	1	2
Heating oil, undyed	2	2	1	1	■	1	1	2	1	2	2	2	2	2	2
Heating oil, dye	2	2	1	1	1	■	1	2	1	2	2	2	2	2	2
Jet A-1 / Kerosene	6	6	2	2	2	6	■	6	6	6	6	6	6	6	6
AVGAS 100 LL	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	■	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 OR 4+5	2+5 ODER 4+5	2+5 ODER 4+5
Middle distillate -components	2	2	1	1	1	1	1	2	■	2	2	2	2	2	2
Gasoline-Components	1	1	1	1	2	2	2	2	2	■	2	1	2	2	1
Light distillate fuel (LDF)	2	2	1	1	2	2	2	2	1	1	■	2	2	2	1
Ether (MTBE, ETBE)	2	1	2	1	2	2	2	2	2	2	2	■	1	2	1
Alcohols (Methanol, Ethanol)	2	2	2	2	2	2	2	2	2	2	2	1	■	2	1
FAME (Bio-diesel)	2	2	1	2	2	2	2	2	2	2	2	2	2	■	2
TBA (t-butyl alcohol)	1	1	1	1	2	2	2	2	2	2	2	1	1	2	■

Description of numbers see annex 2, page 12.

■ = «dedicated»

ANNEX 3

Suggested Practices to Help Prevent accidental Rhine water contamination by ethers

By Albert de Haas, Ekkehard Schulte-Körne and Graeme Wallace of the European Fuel Oxygenates Association (EFOA)

Accidental contamination of the River Rhine is suspected of having occurred as a result of practices linked to barge transport. EFOA - the Brussels based association that represents producers of clean fuel components - has developed a set of simple but effective measures which will allow barge operators to minimise the risk of this happening.

The Rhine is not only one of the world's most important arteries for inland transport but also vital to drinking water for millions of people. Since the 1970s and 1980s rigorous monitoring and cooperation between organisations in Germany and the Netherlands have greatly improved the river's water quality. Recently, however, monitoring stations have detected in the river short-term peaks of two ethers - MTBE and ETBE - that are used to improve fuel efficiency in vehicles.

Barges transport more than 500,000 tonnes of ethers on the Rhine each year. These transits normally pose little or no risk to health or the environment. However if enough material accidentally enters the Rhine it can affect the taste of drinking water. When this happens, the water authorities need to take alternative supplies to the Rhine or additionally filter the water, which could add costs.

Stepped-up controls by the river police over a limited time period led to the disappearance of the problem but, even if further investigations are continuing, practices related especially to barge fuel transport tanks are the suspected cause.

The reputation of barge transport as being environmentally beneficial is at risk, as well as potential imposition of further legal controls. To assist, and in line with its commitment to Responsible Care for the environment, EFOA has issued practical guidelines for barge operators.

There are three main recommendations. First MTBE and ETBE in gaseous form may enter into water. When venting tanks to remove residual vapour the outlet pipes should be placed well above the river surface, hence flexible venting hoses should be avoided. For the same reason, barge operators should avoid releasing vent gas when it is raining.

A second possible source of contamination is taking in water as ballast to compensate for offloaded cargoes. When discharged from tanks, the ballast water could contain the two substances in higher than acceptable concentrations. Only barges that are equipped with dedicated ballast tanks, and therefore do not place ballast in cargo tanks should be used to transport MTBE and ETBE.

Third, as is standard operating practice barges should only discharge liquid residues at approved disposal stations.

ANNEX 4
(Specimen)

Material Safety Data Sheet

METHYL TERTIARY BUTYL ETHER

➔ Section 1 Identification

Product Name	METHYL TERTIARY BUTYL ETHER
Product Number	000000000000499180
Chemical Family	Alkyl ethers
CAS Number	1634-04-4
Chemical Name	t-Butyl Methyl Ether
Synonyms	Methyl t-Butyl Ether (MTBE), Tert-Butyl Methyl Ether, MTBE
Type of Use	Gasoline additive, solvent

➔ Sectie 2 Hazard identification

EMERGENCY OVERVIEW

Signal Word
DANGER.

Hazards
Highly flammable. Irritant.
Complementary Information: Unpleasant terpentine-like taste in water.

R-Phrases
R11 - Highly flammable.
R38 - Irritating to skin.

Physical State
Liquid.

Color
Clear, colorless.

Odor
Turpentine-like odor.

Odor Threshold
0.053 ppm / Odor is not an adequate warning of potentially hazardous ambient air concentrations. Some individuals find the odor of MTBE objectionable (threshold for detection in air approx. 0.0002 mg/l; 0.053 ppm). Multiple studies suggest that approximately 15ug/l of MTBE is the appropriate concentration to use as an odor threshold in water. The only study suggesting any lower threshold is a single research study concluding that the odor threshold of MTBE in water was less than 1ug/l (Campden, 1993). The results of that single study could not be replicated, even by the

original laboratory. Given both the anomaly of the Campden study result and the fact that it could not be replicated, we do not consider it to provide a valid basis for setting an odor threshold level for MTBE in water.

POTENTIAL HEALTH EFFECTS
- Signs and Symptoms of Acute Exposure
See component summary.

→ **t-Butyl Methyl Ether 1634-04-4**
Eye irritant. Moderate skin irritant. Not a skin absorption hazard. Mucous membrane irritant. Overexposure may produce anesthetic or narcotic effects. Aspiration hazard.

Skin: May cause moderate skin irritation. Not expected to be a skin absorption hazard. Not expected to be a sensitizer.
Inhalation: Vapors may cause irritation of the eyes, nose and throat as well as CNS depression (fatigue, dizziness, loss of concentration, with collapse, coma and death possible in cases of severe overexposure). High vapor concentrations may be irritating to the upper respiratory tract.
Eye: Contact with the eyes may cause irritation consisting of reversible redness, swelling and mucous discharge to the conjunctiva.
Ingestion: Ingestion may cause discomfort and irritation of the gastrointestinal tract and CNS depression (fatigue, dizziness, collapse, coma and death). Aspiration into the lung may cause fatal chemical pneumonitis.

Chronic Health Effects
See component summary

→ **t-Butyl Methyl Ether 1634-04-4**
Breathing mist or vapors may cause mucous membrane or upper respiratory tract irritation. Prolonged exposure may produce anesthetic and narcotic effects. Repeated or prolonged contact with skin may cause defatting and drying of the skin which may result in dermatitis. Chronic animal toxicity studies exposing rats and mice to MTBE have been performed. A description of these studies and an assessment of their results is presented elsewhere in this document.
See section 11.

Conditions Aggravated by Exposure
Medical information regarding special health effects is not conclusive. This material may aggravate pulmonary/bronchial disease and/or cause breathing difficulty.

→ Section 3 Composition/information on ingredients

COMPONENT NAME	CAS#	EU INVENTORY	CONCENTRATION WT %	RISK	SYMBOL
t-Butyl Methyl Ether	1634-04-4	216-653-1	<= 97.0	R 11 R 38	F Xi

Compositions given are typical values not specifications.
See section 16 for full text of risk phrases

➔ Section 4 First aid measures

General
Take proper precautions to ensure your own health and safety before attempting rescue and providing first aid. For specific information refer to the Emergency Overview in Section 2 of this MSDS. Assess rapidly and aggressively. Resuscitation may be indicated.

Skin
Promptly remove soiled clothing/wash thoroughly before reuse. Wash skin thoroughly with mild soap and water. Flush with lukewarm water for 15 minutes. If sticky, use waterless cleaner first. Seek medical attention if ill effect or irritation develops.

Inhalation
If overcome by exposure, remove victim to fresh air immediately. Give oxygen or artificial respiration as needed. Obtain medical attention if breathing difficulty persists.

Eye
Immediately flush the eyes with large amounts of clean low-pressure water for at least 15 minutes, occasionally lifting the upper and lower lids. If pain or irritation persists, promptly obtain medical attention.

Ingestion
If large quantity swallowed, give lukewarm water (pint/ 1/2 litre) if victim completely conscious/ alert. Do not induce vomiting. Risk of damage to lungs exceeds poisoning risk.
Obtain emergency medical attention.

Note to Physician
There is no specific antidote. Do not induce vomiting. However, if vomiting occurs spontaneously, maintain open airway. Gastrointestinal decontamination in accidental petroleum distillate ingestions is not recommended, because of the severe aspiration hazard. All contaminated clothing should be removed, and contaminated skin areas washed with lipophilic soap, or green soap, and water. Gastric lavage is indicated in those patients who require decontamination. Be sure that an endotracheal tube is in place prior to lavage; use cuffed tubes in patients over 7 years of age. Although activated charcoal does not bind petroleum distillate products and may induce vomiting, charcoal may be administered when the physician feels the charcoal may absorb a toxic additive. A chest x-ray should be taken immediately after stabilization of breathing and circulation to document aspiration and detect the presence of pneumothorax. Treatment of overexposure should be directed at the control of symptoms and the clinical condition of the patient.

➔ Section 5 Fire fighting measures

FLAMMABLE PROPERTIES
Classification: Highly flammable liquid
Flash Point: ~ -29 °C (-20,2 °F) (SETA)
Auto-Ignition Temperature: ~ 374 °C (705,2 °F)
Lower Flammable Limit: ~ 2,5 vol%
Upper Flammable Limit: ~ 15,1 vol%

EXTINGUISHING MEDIA
Suitable: SMALL FIRE: Use dry chemicals, CO_2, water spray or alcohol-resistant foam. LARGE FIRE: Use water spray, water fog or alcohol-resistant foam.

Unsuitable: Do not use solid water stream/may spread fire.

PROTECTION OF FIREFIGHTERS
Protective Equipment/Clothing: Wear positive pressure self-contained breathing apparatus (SCBA). Structural firefighters protective clothing will only provide limited protection.

Fire Fighting Guidance: Releases flammable vapors below normal ambient temperatures. Flammable vapors may be heavier than air. May travel long distances along the ground before igniting and flashing back to vapor source. When mixed with air and exposed to ignition source, vapors can burn in open or explode if confined. Move containers from fire area if you can do it without risk. Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
Cool containers with flooding quantities of water until well after fire is out. Do not use straight streams. Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank. Always stay away from tanks engulfed in fire. For massive fire, use unmanned hose holders or monitor nozzles; if this is impossible, withdraw from area and let fire burn.

Hazardous Combustion Products: Thermal decomposition may produce carbon monoxide and other toxic vapors.

➔ Section 6 Accidental release measures

Release Response
Extremely flammable liquid. Release can cause fire or explosion. Eliminate all sources of ignition. All equipment used when handling this product must be grounded. Do not touch or walk through spilled material. Stop leak if you can do it without risk. Prevent entry into waterways, sewers, basements or confined areas. A vapor suppressing foam may be used to reduce vapors. Absorb or cover with dry earth, sand or other non-combustible material and transfer to containers.
Use clean non-sparking tools to collect absorbed material. Water spray may reduce vapor; but may not prevent ignition in closed spaces. Dike large spills and place materials in salvage containers.

MTBE is highly volatile, partially water soluble and has only a minimal tendency to adhere to soil particles. Even small volumes can pose a threat to the environment and nearby water resources. Surface spills can reach groundwater through porous soil or cracked surfaces. All efforts should be made to prevent any leaks or spills, and to protect water resources. Where spills are possible, a comprehensive spill response plan should be developed and implemented. If a leak or spill reaches the groundwater, the groundwater may become contaminated. If the groundwater is a source of drinking water, the associated drinking water well(s) could become contaminated. MTBE can impart an unpleasant taste and odor to water at very low concentrations.

➔ Section 7 Handling and storage

Handling
For industrial use only. Keep container tightly closed when not in use. Extinguish all ignition sources. Wear recommended personal protective equipment. Containers must be properly grounded before beginning transfer. All electrical equipment should be grounded and conform to applicable electric codes and regulatory requirements. Check atmosphere for explosiveness and oxygen deficiencies. Observe precautions pertaining to confined space entry. Use only non-sparking tools. Carefully vent any internal pressure before removing closure. Isolate, vent, drain, wash and purge systems or equipment before maintenance or repair. Handle empty containers with care; vapor/residue may be flammable. Avoid contact with incompatible agents.

Storage
Store only in tightly closed, properly vented containers away from heat, sparks, open flame and strong oxidizing agents.
Soft steel; avoid most plastics, Viton and Flourel. Store closed drums with bung in up position. Vapor space above stored liquid may be flammable/explosive unless blanketed with inert gas.

➔ Section 8 Exposure controls and personal protection

Engineering Controls
Both local exhaust and good general room ventilation must be provided not only to control exposure but also to prevent formation of flammable mixtures.

Personal Protection
Inhalation: If exposure can potentially exceed the exposure limit(s),respiratory protection recommended or approved by appropriate local, state or international agency must be used.
Skin: Wear chemical resistant gloves such as: Nitrile. or Polyvinyl Alcohol. Depending on the conditions of use, protective gloves, apron, boots, head and face protection should be worn.
Eye: Wear safety glasses as minimum eye protection. Conditions may warrant the use of chemical goggles and possibly a face shield. Consult your standard operating procedure or safety professional for advice. Use protective eye and face devices that comply with ANSI Z87.1-1987.

Additional Remarks
Selection of appropriate personal protective equipment should be based on an evaluation of the performance characteristics of the protective equipment relative to the task(s) to be performed, conditions present, duration of use, and the hazards and/or potential hazards that may be encountered during use. Emergency eye wash fountains and safety showers should be available in the immediate vicinity of any potential exposure. Use good personal hygiene practices.
Wash hands before eating, drinking, smoking, or using toilet facilities. Promptly remove soiled clothing/wash thoroughly before reuse.

OCCUPATIONAL EXPOSURE LIMITS				
Component Name	Source	Type	Value	Notation
t-Butyl Methyl Ether	US (ACGIH)	TWA	50 ppm	None
	OEL (AU)	STEL	100 ppm - 360 mg/m³	None
	OEL (AU)	MAK	50 ppm - 180 mg/m³	None
	OEL (BE)	TWA	40 ppm - 146 mg/m³	None
	SUVA (CH)	STEL	75 ppm - 270 mg/m³	None
	SUVA (CH)	MAK	50 ppm - 180 mg/m³	None
	OEL (CZ)	CEILING	200 mg/m³	None
	OEL (CZ)	TWA	100 mg/m³	None
	TRGS 900 (DE)	TWA	50 ppm - 180 mg/m³	None
	OEL (DK)	TWA	40 ppm - 144 mg/m³	None
	OEL (EE)	STEL	75 ppm - 250 mg/m³	None
	OEL (EE)	TWA	50 ppm - 180 mg/m³	None
	OEL (ES)	VLA-ED	40 ppm - 147 mg/m³	None
	HTP (FI)	TWA	50 ppm - 180 mg/m³	None
	OEL (LT)	TPRV	75 ppm - 250 mg/m³	None
	OEL (LT)	IPRV	100 mg/m³	None
	OEL (LT)	IPRV	50 ppm - 180 mg/m³	None
	OEL (NL)	STEL	100 ppm - 360 mg/m³	None
	OEL (NL)	MAC	50 ppm - 180 mg/m³	None
	OEL (PT)	TWA	50 ppm	None
	OEL (RU)	STEL	300 mg/m³ - Vapour	None
	OEL (RU)	TWA	100 mg/m³ - Vapour	None
	OEL (SE)	STV	60 ppm - 220 mg/m³	None
	OEL (SE)	LLV	30 ppm - 110 mg/m³	None
	WEL (GB)	STEL	75 ppm - 275 mg/m³	None
	WEL (GB)	TWA	25 ppm - 92 mg/m³	None

➔ **Section 9** Physical and chemical properties

Appearance: Liquid. Clear, colorless.
Odor: Turpentine-like odor.
Odor Threshold: 0.053 ppm Odor is not an adequate warning of potentially hazardous ambient air concentrations. Some individuals find the odor of MTBE objectionable (threshold for detection in air approx. 0.0002 mg/l; 0.053 ppm). Multiple studies suggest that approximately 15ug/l of MTBE is the appropriate concentration to use as an odor threshold in water. The only study suggesting any lower threshold is a single research study concluding that the odor threshold of MTBE in water was less than 1ug/l (Campden, 1993). The results of that single study could not be replicated, even by the original laboratory. Given both the anomaly of the Campden study result and the fact that it could not be replicated, we do not consider it to provide a valid basis for setting an odor threshold level for MTBE in water.

pH	Not applicable
Boiling Point/Boiling Range	~ 55 °C (131 °F) @ 760 mm Hg
Freezing Point/Melting Point	~ -109 °C (-164.2 °F)
Flash Point	~ -29 °C (-20,2 °F) (SETA)
Auto-ignition	~ 374 °C (705.2 °F)
Flammability	Highly flammable liquid
Lower Flammable Limit	~ 2,5 vol%
Upper Flammable Limit	~ 15,1 vol%
Explosive Properties	Not applicable
Oxidizing Properties	Not applicable
Vapor Pressure	~ 245 mm Hg @ 25 °C (77 °F)
Evaporation Rate	No Data Available
Relative Density	~ 0,74 @ 20 °C (68 °F) (Water = 1,0 at 4°C (39,2°F))
Relative Vapor Density	~ 3 @ 20 °C (68 °F) (Air = 1,0)
Viscosity	~ 0,3 mPa.s @ 25 °C (77 °F) 0,472 mm2/s @ 20 °C (68 °F)
Solubility (Water)	Moderate (1 to less than 10 Percent)
Partition Coefficient (Kow)	Log Pow = -0,8 to -1,33
Additional Physical and Chemical Properties	Additional properties may be listed in Sections 2 and 5.

➔ Section 10 Stability and reactivity

Chemical Stability
This material is stable when properly handled and stored.

Conditions to Avoid
Heat, sparks, open flame, other ignition sources, and oxidizing conditions.

Substances to Avoid
Contact with strong acids can decompose this material and generate extremely flammable isobutylene. Strong oxidizing agents.

Hazardous Polymerization
Not expected to occur.

Reactions with Air and Water
May react with oxygen to form peroxides.

➔ Section 11 Toxicological information

PRODUCT INFORMATION
Product Summary
MTBE is of slight acute toxicity, although inhalation exposure to high concentrations may cause dizziness, CNS depression, loss of consciousness and irritation to the eye and upper respiratory tract. Some individuals find the odor of MTBE objectionable. Skin contact with undiluted product may lead to moderate irritation, while repeated exposure can cause cracking due to defatting of the dermis. It is not a skin sensitizer. Neat liquid MTBE may cause mild, reversible eye irritation. Liver enlargement, without evidence of structural organ damage, is commonly seen in rats and mice after repeated exposure, while male rats exhibit a sex- and species-specific accumulation of protein droplets in proximal tubules of the kidney. Changes in estrogen-sensitive tissues were reported in female mice exposed to high concentrations of MTBE vapor, however serum estrogen levels and estrogen receptor functions were unaffected. MTBE has no adverse effect on reproduction and is not selectively toxic to the fetus. Although formaldehyde is a possible metabolite that may be formed in simple in vitro systems, results from in vivo genotoxicity tests are consistently negative. Long term inhalation exposure to very high doses was associated with an increased incidence of liver tumors in female mice and kidney- and testis tumors in male rats.

COMPONENT INFORMATION
→ t-Butyl Methyl Ether 1634-04-4

Acute Toxicity - Lethal Doses

LC50 (Inhl) →	Rat →	23.800 – 39.800 PPM →	4 hours
LD50 (Oral) →	Rat →	3800 MG/KG BWT	
LD50 (Skin) →	Rabbit →	>10.000 MG/KG BWT	

Acute Toxicity - Effects
Inhalation: Vapors may cause irritation of the eyes, nose and throat as well as CNS depression (fatigue, dizziness, loss of concentration, with collapse, coma and death possible in cases of severe overexposure). High vapor concentrations may be irritating to the upper respiratory tract.
Ingestion: Ingestion of high doses may cause discomfort and irritation of the gastrointestinal tract and CNS depression (fatigue, dizziness and possibly loss of concentration, with collapse, coma and death in cases of severe over-exposure).
Skin Contact: Prolonged or repeated contact may cause skin to become dry or cracked.

Irritation
Skin: Neat liquid is moderately irritating to skin.
Eye: Neat liquid may produce minimal, reversible eye irritation.

Sensitization
Not expected to cause sensitization by skin contact.

Target Organ Effects
Skin. Eye. Respiratory system. CNS depressant.

Repeated Dose Toxicity
No evidence of adverse systemic effects was seen in rodents exposed repeatedly to low concentrations of MTBE vapor, however higher exposures were associated with an accumulation of protein droplets in the kidney of male rats (a male rat-specific response), with liver enlargement (but no adverse histopathological lesions) in rats and mice of both sexes. A decreased incidence of cystic endometrial hyperplasia and changes in other estrogen-sensitive tissues were reported in female mice exposed to28.6 mg/l (8,000 ppm) MTBE vapor, however serum estrogen levels and estrogen receptor functions were unaffected. There are inconsistent reports of minor subjective neurological symptoms in humans regularly exposed to low levels of MTBE vapor. It is unclear, however, if these are causally-related to MTBE or where triggered by its odor. Some individuals find the odor of MTBE objectionable (threshold for detection 0.0002 mg/l; 0.053 ppm).

Reproductive Effects
No adverse effect on reproductive function or gonad histopathology seen in male and female rats exposed to 28.6 mg/l (8,000 ppm) MTBE vapor over two generations.

Developmental Effects
MTBE is not selectively toxic to the fetus. No adverse developmental effects were reported in rabbits exposed to high concentrations during pregnancy, despite the occurrence of maternal toxicity (CNS effects, significantly lower food intake, significantly lower maternal body weight). Similar maternal signs were noted in mice exposed under similar conditions, however in this instance an increased incidence of cleft palate was apparent in the offspring. Cleft palate is a stressrelated phenomenon in the mouse hence this observation was considered secondary to maternal toxicity in this species.

Genetic Toxicity
MTBE has been tested extensively for genotoxic activity in a range of in vitro and in vivo tests. While the majority of results are negative, weak positive findings (consistent with the metabolism of MTBE to formaldehyde by S9 fraction in vitro) have been obtained with Salmonella typhimurium TA102 and L5178Y TK+/- mouse lymphoma cells. The findings in Salmonella typhimurium strain TA 102, however, have not been replicated. Also consistently negative results have been obtained from in vivo tests, indicating that formation of free formaldehyde in the body is negligible. Overall, the weight of evidence indicates that MTBE is not a genotoxin.

Carcinogenicity
Studies in experimental animals have found only limited evidence for the carcinogenicity for MTBE, with tumors occurring in tissues or via mechanisms considered not relevant to humans. Female mice exposed by inhalation to up to 28.6 mg/l (8,000 ppm) MTBE vapor responded with an increased incidence of liver tumors, while male rats developed tumors in testis and kidney under similar conditions. Mechanistic studies have shown important differences in the disposition and fate of MTBE in rodents and humans, suggesting that these findings after long-term inhalation exposure are not indicative of a risk to health. Results are also available from a life-time study of non-standard design, which reported an increased incidence of combined lymphoma/leukemia in female rats given MTBE by gavage, however inadequacies in the design and reporting of this investigation limit confidence in the result. Critically, MTBE is not genotoxic indicating that a direct effect on DNA is unlikely. Listed by IARC as not classifiable as to its carcinogenicity to humans (Group 3). This listing is based on inadequate evidence in humans and limited evidence of carcinogenicity in experimental animals.

→ Section 12 Ecological information

PRODUCT INFORMATION
Ecotoxicity
This material is expected to be non-hazardous to aquatic species. See component summary.

WGK
1 (Slightly water-endangering)

Environmental Fate and Pathway
See component summary

COMPONENT INFORMATION
→ t-Butyl Methyl Ether 1634-04-4

Ecotoxicity
This material is expected to be non-hazardous to aquatic species.

Acute toxicity to fish

LC50 / 96 hours	fathead minnow 672 - 980 mg/l
LC50 / 96 hours	rainbow trout. - 887 mg/l
LC50 / 96 hours	rainbow trout. - 887 mg/l
LC50 / 96 hours	silverside minnow. - 574 mg/l
LC50 / 96 hours	sheepshead minnow. - 1,358 mg/l

Acute toxicity to aquatic invertebrates

EC50 / 48 hours	Daphnia magna. 472 - 681 mg/l
LC50 / 48 hours	waterflea. 340 mg/l
EC50 / 96 hours	saltwater mysid. 136 - 187 mg/l

Toxicity to aquatic plants

IC50 / 96 hours	green algae (Selenastrum) 491 mg/l

Toxicity to microorganisms
Summary: No Data Available.

Chronic toxicity to fish
IC50 / 31 day fathead minnow 279 mg/l

Chronic toxicity to aquatic invertebrates
NOEC50 / 28 DAY saltwater mysid. 26 mg/l
Summary: May pose slight chronic toxicity in specific invertebrates

Environmental Fate and Pathway
MTBE presents a potential concern to groundwater supplies. If released to the environment, relatively small amounts of MTBE may impart an unpleasant and distasteful odor and taste to groundwater which can render such groundwater unsuitable for consumption. Therefore, care should be used when handling, storing or transferring MTBE or gasoline blended with MTBE to insure that such product is not released into the environment and is not allowed to migrate to groundwater. Because of its solubility in water (4.3%) and relatively low organic carbon partitioning coefficient (Koc=11), MTBE is mobile in soil and, accordingly, every release into the environment has the potential for damaging groundwater supplies. Once in the groundwater, MTBE may migrate faster and farther than most other hydrocarbons and may be present at the leading edge of a groundwater contaminant plume. MTBE may not biodegrade as promptly as other gasoline constituents and may require additional and more costly remediation procedures. Other information regarding MTBE is available through the Chemical Abstracts Service, American Petroleum Institute publications, the U.S. Environmental Protection Agency and elsewhere.

Mobility
Transport between environmental compartments: The atmosphere is the main environmental compartment for releases of MTBE. In water, volatilization will result in substantial losses to the atmosphere with a half-life of 5-6 days.

Persistance and Degradability
Biodegradation: Two OECD 301D studies (closed bottle test) showed negligible (0-2%) biodegradation after 28 days. Not readily biodegradable under aerobic conditions. However, degradation has been observed in non-standard tests using pure- and mixed bacterial cultures.

Bioaccumulation: Log Kow (Fish) <3 This material is not expected to bioaccumulate.

Other Adverse Effects
As a VOC, MTBE can contribute to the formation of photochemical smog in the presence of other VOC's.

➔ Section 13 Disposal considerations

Contaminated product, soil or water may be hazardous waste due to potentially low flash point. Comply with applicable local, state or international regulations concerning solid or hazardous waste disposal and/or container disposal. Assure effluent complies with applicable regulations. Landfill solids at permitted sites. Use registered transporters. Burn concentrated liquids in systems designed for low flash point material. Avoid flame-outs. Assure emissions comply with applicable regulations. Avoid overloading/poisoning plant biomass. Dilute aqueous waste may biodegrade.

➔ Section 14 Transport information

SPECIAL REQUIREMENTS
If you reformulate or further process this material, you should consider re-evaluation of the regulatory status of the components listed in the composition section of this sheet, based on final composition of your product.

Proper Shipping Name	METHYL tert-BUTYL ETHER
ID No.	UN2398
Hazard Class	3
PG	II

➔ Section 15 Regulatory information

REGULATORY STATUS		
Country	Inventory	
Australia	AICS	X
Canada	DSL	X
Canada	NDSL	
China	IECS	X
European Union	EINECS	X
European Union	ELINCS	
European Union	NLP	
Japan	ENCS	X
Korea	ECL	X
Philippines	PICCS	X
United States	TSCA	X

X = All components are included or are otherwise exempt on this inventory

Labeling Information
Symbol
Highly flammable. Irritant.

R-Phrases
R11 - Highly flammable.
R38 - Irritating to skin.

S-Phrases
S16 - Keep away from sources of ignition - No Smoking.
S23 - Do not breathe gas/fumes/vapor/spray.
S24 - Avoid contact with skin.
S29 - Do not empty into drains.
S33 - Take precautionary measures against static discharges.

Other
EU Labeling Information

➔ Section 16 Other information

LATEST REVISION(S)
Revised Section(s): 1 Revised Section(s): 1 Revised Section(s): 1

All Relevant Risk Phases
R11 - Highly flammable.
R38 - Irritating to skin.

Law depot D/3158/2008/2

EFOA

The European Fuel Oxygenates Association

EFOA represents the fuel ether producers in Europe.

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EFOA is a sector group of Cefic, the European Chemical Industry Council.

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