Methanol Safe Handling TECHNICAL BULLETIN

METHANOL RAILCAR AND TANKER TRUCK ACCIDENT RESPONSE

Methanol, also known as wood alcohol or methyl alcohol, is a colorless liquid with a faintly sweet alcohol odor. Methanol vapor is slightly heavier than air and is capable of traveling some distance to a source of ignition. Once ignited the vapor may flash back to the source pool.

Emergency responders need to consider the unique properties of methanol when faced by a railcar or



tank truck incident involving methanol. Chief among these considerations is the fact that methanol has a wide flammability range from 6% (LEL or Lower Explosive Limit) in air to 36.5% (UEL or Upper Explosive Limit) in air. The significance of this is that a tank could explode before the atmosphere inside gets too methanol rich to burn. As a conductive polar solvent, methanol is also highly corrosive to certain materials. Therefore, transportation tankage must take this into account in order to prevent galvanic corrosion of dissimilar metals. Finally, methanol is toxic if ingested (swallowed).

Knowing the risks associated with methanol and taking proper safety measures in a transportation incident can ensure the well-being of train crews and truck drivers as well as emergency responders and the general public. You will find information on methanol safe handling in this bulletin. Please refer to this document for guidance on methanol safety and feel free to download and distribute it to others in your industry.

	Physical Properties of Methanol
Chemical Formula	CH₃OH
CAS Registry Number	67-56-1
DOT Number	UN 1230
Boiling Point	148 °F
Freezing Point	-144 °F
pH	7.2
Solubility	100%
Vapor Density	1.11 @ 60 °F
Vapor Pressure	1.86 psia @ 68 °F
Flash Point	52 °F
Density	6.63 lb. per gallon
Purity % Weight	minimum 99.85

Methanol Institute



Bulk Transportation of Methanol

The proper shipping name for methanol is: *Methanol, 3, UN1230, PGII.* The label code is 3-Flammable Liquid for domestic shipments. For international shipments the label codes 3 and 6.1-Toxic Substances are both used.



Only the following bulk packagings are allowed by US DOT by rail: Class DOT 103, 104, 105, 109, 111, 112, 114, 115, and 120 tank car tanks; Class 106 or 110 multi-unit tank car tanks and AAR Class 206W tank car tanks.

For highway cargo tanks: Specification MC 300, MC 301, MC 302, MC 303, MC 304, MC 305, MC 306, MC 307, MC 310, MC 311, MC 312, MC 330, MC 331, DOT 406, DOT 407 and DOT 412 cargo tank motor vehicles. Cargo tanks transporting methanol must also comply with the following special requirements.

Methanol (CAS: 67-56-1, NIOSH: PC-1400000, DOT: 1230, UN-1230, NA-1230) is classified by the International Code Council (ICC) and the National Fire Protection Agency (NFPA) under the Uniform Fire Code as a "IB Flammable Liquid" and by the United Nations as a "1993 Class 3 Flammable Liquid." NFPA and U.S. Department of Transportation (DOT) rank Flammability as a 3 primary hazard, and toxicity, as a 6.1 ranked secondary hazard. Guidelines for handling IB flammable liquids are provided by codes and standards published by ICC, NFPA, and the International Fire Code.

<u>Pressure relief system</u>: Except as provided by U.S. Code §173.33(d), each cargo tank must be equipped with a pressure relief system meeting the requirements of §178.346-3 or §178.346-4 of this subchapter. However, pressure relief devices on MC 310, MC 311, and MC 312 cargo tanks must meet the requirements for a Specification MC 307 cargo tank. Pressure relief devices on MC 330 and MC 331 cargo tanks must meet the requirement in §178.337-9 of this subchapter.

<u>Bottom outlets</u>: DOT 406, DOT 407 and DOT 412 must be equipped with stop-valves meeting the requirements of §178.345-11 of this subchapter; MC 304, MC 307, MC 310, MC 311, and MC 312 cargo tanks must be equipped with stop-valves capable of being remotely closed within 30 seconds of actuation by manual or mechanic means and by a closure activated at a temperature not over 121 °C (250 F); MC 330 and MC 331 cargo tanks must be equipped with internal self-closing stop-valves meeting the requirements in §178.337-11 of this subchapter.



Vehicle Accident or Emergency – Tank Cars and Tank Trailers

In the event of an accident or emergency involving tanks of methanol, the vehicle crew should take the following general actions, if it is safe and practical to do so:

- Apply brakes, stop engine and isolate the battery by activating the master switch.
- Avoid sources of ignition; do not smoke or switch on any electrical equipment.
- Inform the appropriate emergency services; give as much information about the incident or accident and about substances involved as possible.
- Put on a warning (reflective) vest and place selfstanding warning signs as appropriate.
- Keep the transport documents readily available for examination by responders upon arrival.
- Do not walk into or touch spilled methanol.
- Do not inhale methanol vapors, smoke, or dust generated by staying up wind.
- If safe to do so and equipment is available, use fire extinguisher(s) on small, incipient (just starting fires) on tires, brakes or engine compartments.
- Leave fires in the load compartment(s) to professional fire fighters.
- Where appropriate and safe to do so, activate on board equipment to prevent leakages into the aquatic environment or sewer system or to contain spillages.
- Move away from the vicinity of the accident or emergency at least 50 meters (150 feet); warn others about getting close to the tank car or trailer until emergency responders arrive and take over this duty.
- Remove any contaminated clothing or contaminated protective equipment you used; dispose of it safely.

	POTENTIAL HAZARDS (from Emergency Response Guide #131)
HEALT	ΓΗ ΓΕΛΟΣΤΟΛΙΑΤΑΙ ΤΗ
•	TOXIC: very dangerous irreversible effects if inhaled, in contact with skin and if swallowed. May be fatal if ingested. Symptoms may develop after several hours. Eye irritant.
•	Contact with methanol will irritate or burn the eyes.
•	Fire will produce irritating, corrosive and toxic gases.
•	Methanol vapors may cause dizziness or suffocation.
•	Runoff from fire control or dilution water may cause pollution.
FIRE O	R EXPLOSION
•	HIGHLY FLAMMABLE: Will be easily ignited by heat, sparks or flames.
•	Methanol vapors may form explosive mixture with air.
•	Vapors may travel to source of ignition and flash back.
•	Methanol vapor is heavier than air. Vapors will spread along the ground and collect in low or confined areas (sewers, basements, culverts, tanks).
•	Vapor explosion or poison hazard in indoors, outdoors or in sewers.
•	Runoff to sewer may create fire or explosion hazard.
•	Containers of methanol may explode when heated.
•	Liquid methanol is lighter than water.
NOTE:	This guide (from ERG Guide 138) has been adapted specifically for methanol.
The me	ethods used for controlling sources of ignition for liquid methanol are more or less the same as those
for gasoline. The lower flammable limit (LFL) for gasoline vapor is 1.4% v/v; the LFL for methanol vapor is	
7% v/v.	. Gasoline vapor travels further along the ground without being diluted and ignites at a much lower

concentration than methanol vapor.





International Signal Word: Danger!

International Precautionary Statements:

Danger! Poison! May be fatal or cause blindness if swallowed. Vapor harmful.

Flammable liquid and vapor. Harmful if swallowed, inhaled, or absorbed through the skin. Causes eye, skin, and respiratory tract irritation. May cause central nervous system depression. Cannot be made non-poisonous.



The third pictogram is not currently used in the United States.

Fire Safety and Emergency Response

Solutions of methanol containing up to 74% water are flammable. Methanol is harder to ignite than gasoline and burns at a slower rate with less heat intensity. The concentration of methanol vapor in air must be at least 6% to burn. This concentration may be achieved in ground depressions, ditches and culverts as well as in the tank. Methanol flames are nearly invisible in bright sunlight, but the heat generated can be detected and the flames and smoke of other materials ignited by the methanol fire. A large amount of water removes the heat and helps to dilute methanol to the point where most fires can be readily extinguished.

Rail and highway transport are considered to be safe, as long as methanol is contained within an upright tank car or tank trailer. In the event of train derailment or truck wreck in which the tank trailer is turned over, first responders should treat methanol as highly flammable and highly toxic.

Methanol tanks are known to BLEVE (Boiling Liquid Expanding Vapor Explosion), an instantaneous tank failure and catastrophic release and ignition of vapor. The risk of BLEVE increases when the tank is directly involved in flames and/or when subject to high radiant heat flux.



EMERGENCY RESPONSE (from Emergency Response Guide #131)

FIRE

Caution: Methanol has a very low flash point (12°C, 54°F).

Small Fire

• Dry chemical, CO₂, water spray or alcohol-resistant foam¹.

Large Fire

- Water spray, fog or alcohol-resistant foam¹.
- Move containers from fire area if you can do it without risk.
- Dike fire-control water for later disposal; do not scatter the material.
- Use water spray or fog; do not use straight streams.

Fires Involving Tanks or Car/Trailer Loads

- 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.
- Withdraw immediately in case of rising sound from venting safety devices or discolor 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.

SPILL OR LEAK

- Fully encapsulating vapor protective clothing should be worn for methanol spills and leaks with no fires.
- ELIMINATE all ignition sources (no smoking, flares, sparks or flames in immediate area of liquid or vapor methanol).
- All equipment used when handling methanol must be grounded.
- Do not touch or walk through spilled methanol.
- Stop leak if you can do it without risk.
- Prevent entry of methanol liquid or vapor into waterways, sewers, basements or confined areas.
- A vapor suppressing foam may be used to reduce vapors.

SMALL SPILL

- Absorb methanol with earth (soil), sand, cat litter, or other non-combustible material and transfer to containers for later disposal.
- Use clean, non-sparking tools to collect absorbed material.

LARGE SPILL

- Dike far ahead of liquid methanol spill for later disposal.
- Water spray may reduce vapor; but may not prevent ignition in closed spaces.

FIRST AID

- Move victim to fresh air.
- Call 911 or emergency medical service.
- Give artificial respiration if victim is not breathing.
- Do not use mouth-to-mouth method if victim ingested or inhaled methanol; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.
- Administer oxygen if breathing is difficult.
- Remove and isolate contaminated clothing and shoes.
- In case of contact with methanol, immediately flush skin or eyes with running water for at least 20 minutes.
- Wash skin with soap and water.
- In case of burns, immediately cool affected skin for as long as possible with cold water.
- Do not remove clothing if adhering to burnt skin.
- Keep victim warm and quiet.
- Effects of exposure (inhalation, ingestion or skin contact) may be delayed.
- Ensure that medical personnel are aware that methanol is involved and take precautions to protect themselves.

NOTE: This guide (from ERG Guide 138) has been adapted specifically for methanol.



Note 1: Alcohol resistant fire fighting, fire extinguishing foam (AR-AFFF).

While public emergency responders may have the Emergency Response Guidebook, the pertinent Guide 131 for Public Safety has been modified specifically for methanol:

	PUBLIC SAFETY (from Emergency Response Guide #131)
•	CALL EMERGENCY RESPONSE Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, emergency responders should refer to appropriate telephone number listed on the inside back cover of the Emergency Response Guidebook.
•	As an immediate precautionary measure, isolate spill or leak area for at least 50 meters (150 feet) in all directions
•	Keen unauthorized personnel away
•	Stay upwind
•	Keep out of low areas
•	Ventilate closed spaces before entering
PROTE	CTIVE CLOTHING
•	Wear positive pressure self-contained breathing apparatus (SCBA).
•	Wear chemical protective clothing that is specifically recommended by the manufacturer for methanol. It may provide little or no thermal protection.
•	Structural firefighters' protective clothing provides limited protection in fire situations ONLY; it is not effective in spill situations where direct contact with methanol is possible.
EVACU Spill	IATION
•	Upwind 50 meters (150 feet)
٠	Increase this distance as necessary in the downwind direction.
Fire	
•	If railcar or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also consider initial evacuation for 800 meters (1/2 mile) in all directions.
NOTE:	This guide (from ERG Guide 131) has been adapted specifically for methanol.

Spill Response

Initial response by train crew or truck driver:

- Contact local fire department.
- Contact your dispatcher or company emergency number.
- Contact the National Response Center (NRC: 1-800-424-8802) if a reportable quantity is released (RQ for methanol: 5,000 pounds or 2,270 kilograms; this is approximately 760 gallons of pure methanol). If in doubt, contact NRC.

When reporting a release to the NRC, the person making the report should provide as much of the following information as possible:

- Name, address, and telephone number of the person reporting and the responsible party;
- Specific location of the incident;
- Date and time the incident occurred or was discovered;
- Name of the chemical/material released: in this case, methanol;
- Source and cause of the release;
- Total quantity discharged;
- Medium into which the substance was discharged (air, water, soil);



- Amount spilled into water;
- Weather conditions;
- Name of the carrier or vessel, the railcar/truck number, or other identifying information;
- Number and type of injuries or fatalities;
- Whether an evacuation has occurred;
- Estimation of the dollar amount of property damage;
- Description of current and future cleanup actions; and
- Other agencies notified or about to be notified.

Some of this information may not be available at the time of the incident. Control of the spill is handed over to the fire department upon arrival. After the fire department determines whether or not an evacuation is necessary and certifies that the area contains no fire or explosion hazards, site control passes to environmental authorities for cleanup and management. Liquid methanol accumulations may be picked up by vacuum truck. Rainwater and melted snow contaminated with methanol may be picked up by the same method. Store excavated soil in a lined berm area until removed from the site. Soil excavation should continue until the cleanup standard of 39,100 ppm (mg/Kg) is reached. Note: This is a typical brownfield unrestricted cleanup target and may vary from state to state, country to country. Use a cleanup target acceptable to local authorities.

Used or waste methanol is considered a hazardous waste in the United States. Waste methanol in concentrations equal to or greater than 24% by weight meets the US Environmental Protection Agency's definition of an ignitable hazardous waste. Product grade methanol, when disposed, is a listed hazardous waste. Waste methanol, or water contaminated with methanol, is considered a hazardous waste and must never be discharged directly into sewers or surface waters. It may only be disposed of at a licensed facility permitted to handle hazardous waste. Contaminated product, soil, or water with methanol must be moved only by registered transporters in approved, properly labeled containers. The recommended disposal method for methanol is incineration for heating value recovery. Concentrated liquid methanol can be used as secondary fuel in systems compatible with water-soluble waste. Waste methanol is also amenable to reclaiming by filtration and distillation. For more information on methanol waste treatment and disposal consult Chapter 8.6 of the Methanol Institute's Methanol Safe Handling Manual.

Transferring Methanol: Loading and Unloading



Methanol does not accumulate static electricity; therefore, the possibility of spark generation due to accumulation of static electricity is less when loading and unloading methanol compared to loading and unloading materials such as diesel fuel.



Nevertheless, protect methanol from accidental ignition by discharge of static electricity. Grounding straps equipped with carbide-tipped clamps are recommended, to ensure electrical contact through nonconductive surface coatings, such as paint.

Bonding helps dissipate static electricity generated during fluid transfer through a conductive or nonconductive material. The practice involves making a connection between a grounded object and an ungrounded object.

Transfer methanol to storage vessels fitted with dip-tube-filling to guard against ignition from static electricity generated as a result of liquid falling through air. Electrical conductivity of methanol is relatively high compared to most fuel materials. Therefore, velocity limits should be placed on transfer operations that involve high pressure drop, hydraulic impacts, and erosion concerns. When filling storage vessels, the vessel and associated fill equipment pump should be bonded together and grounded. Fill pipes or hoses should be conductive and should be bonded to the filling system. Bond with a 1/8-inch bare stainless steel cable connected to a clamp with hardened steel points and screws or a strong spring (see Methanol Safe Handling Manual).

Reference Guidelines and Standards

American Petroleum Institute (API) Recommended Practice (RP) 2003, Protection against Ignitions Arising out of Static, Lightning and Stray Currents.

- Intergovernmental Organization for International Carriage by Rail, Regulations concerning the International Carriage of Dangerous Goods by Rail.
- Laubenheimer, Laura, Jacqueline Ayer and Timothy Hofseth, "Spill Response, Cleanup and Environmental Issues Associated with a Methanol Spill in Alaska." Prepared for California Energy Commission, Sacramento, California by Acurex Corporation Environmental Systems Division, Mountainview, California, March 29, 1991.
- Methanol Institute, Methanol Safe Handling Technical Bulletin: Precautions for Loading, Unloading, Transport and Storage of Methanol.

Methanol Institute, Methanol Safe Handling Manual.

U. S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration, 2012 Emergency Response Guidebook: A Guidebook for First Responders during the Initial Phase of a Dangerous Goods Hazardous Materials Transportation Incident.

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