

## METHANOL SMALL QUANTITIES BULLETIN



This bulletin is about relatively small quantities of methanol or products containing methanol, such as maximum 60 gallon containers or smaller size containers (e.g., hand held) or small sized portable tanks. It describes requirements at local, state, national and international level governing methanol transportation, storage and use of methanol in occupational and consumer settings, disposal and spills of methanol. Many of the requirements discussed are drawn from specific US or North American regulations but counterpart requirements apply within other national jurisdictions. Where applicable, attention is drawn to international regulations developed by intergovernmental organizations and enforced or adopted by member nations, especially as to international transportation of dangerous goods. Consult other available Methanol

Institute guidance and bulletins for technical information about methanol safe handling, fuel blending and larger-scale storage, terminal, transfer, etc. aspects of methanol.

### Transportation of Hazardous Materials and Dangerous Goods

Methanol and many methanol-containing products are considered hazardous materials for transport purposes. Under US, Canadian and global dangerous goods regulations, no one may offer, accept or transport hazardous material not in accordance with applicable requirements. These regulations apply to any person who offers methanol for transportation, causes it to be transported, transports it or performs pre-transport functions (packaging, shipping paper, certification of proper condition for transport). Proper hazardous materials transportation employee training and recordkeeping are required. Registration with federal transportation authorities apply to offer or transport large quantities (non-bulk 5,000 pounds US) of one class of hazardous material requiring placarding. Exceptions exist for transport by individuals for non-commercial purposes in private motor vehicle, certain government agencies and US Postal Service transport.

As a practical matter, most commercial transport of methanol or methanol products requires proper hazardous materials employee training and/or use suitable commercial services that prepare materials for transport and/or transport them. Federal Express offers US commercial transport services for dangerous goods by ground. Training and compliance to US Department of Transportation (DOT) regulations is required and a Federal Express dangerous goods shipping tutorial program must be completed before being approved to offer packages for transport. Air cargo and maritime carriers offer dangerous goods transport, when in conformance to applicable air and maritime international regulations discussed as follows. The US Postal Service offers limited domestic, ground-only service for flammable liquids, discussed below.

### Jurisdictions and Regulations to Follow

Consult appropriate Safety Data Sheets (SDS) for applicable regulatory authorities for methanol dangerous goods transportation, depending on the national jurisdiction, the modes of transportation and if transportation is international. Compliance is required to the dangerous goods transportation regulations of any nations through which transit will occur, or to the regulations of any applicable intergovernmental transportation organization.

For domestic road/rail/vessel transport, comply with national transportation requirements such as US DOT Hazardous Materials Regulation, Canada Transport of Dangerous Goods Regulations or equivalent in other jurisdictions. Some nations accept compliance with requirements of a partner nation, as the US accepts shipments from Canada compliant to its Dangerous Goods regulations. EU dangerous goods transport requires conformance to RID/ADR/ADN for road/rail/inland waterway. These national and international regulations are aligned on a continuing basis with the United Nations Committee of Experts on the Transport of Dangerous Goods, Model Regulations (UN TDG), and provide largely harmonized requirements for dangerous goods transport. Generally these national regulations and UN TDG model regulations are available for free distribution and training opportunities are provided by national agencies.

Methanol dangerous goods transport by air requires conformance to the International Civil Air Organization Technical Instructions on the Safe Transport of Dangerous Goods by Air (ICAO TI). In practice this is intended by conformance to the International Air Transport Association (IATA) Dangerous Goods Regulation, the air transport industry code based on the ICAO TI. US DOT allows certification of packages to ICAO TI for air transport including the domestic ground transport incident to air shipment. Dangerous goods transport by maritime vessel requires conformance to the International Maritime Organization Dangerous Goods Code (IMDG) and national maritime authorities within their jurisdictions, which constantly align national regulations with IMO. These international agencies and organizations offer their appropriate codes for distribution and training opportunities, generally for fee.

### Methanol Transportation Requirements

The following describes US and international transportation requirements, calling to attention similarities and differences. Consult regulations for each jurisdiction or transportation agency for detailed requirements. Generally for methanol the proper UN shipping name is “Methanol” UN 1230. Some methanol-containing materials are better described by other UN shipping names such as fuel cell cartridges containing flammable liquids or formaldehyde-methanol solution.

For UN 1230 methanol, hazard classification is 3 (flammable liquid) and packing group is II (medium risk). These aspects are applied the same across all jurisdictions. UN TDG and international transport ascribe 6.1 subsidiary risk (toxicity) to methanol due to human experience (poison by ingestion). The US DOT does not list 6.1 subsidiary risk for methanol. This is an important distinction between methanol transport US domestic-only and regulations

of Canada and most other nations, UN TDG, ICAO TI and IMDG. One result is only one label for Class 3 is required for US domestic transport while an additional label is required internationally for subsidiary risk 6.1. Another result is aqueous methanol solutions so dilute they cannot sustain a flame still retain 6.1 risk and dangerous goods status internationally.

All national and international transportation agencies specify packing instructions and requirements for Intermediate Bulk Containers and portable tanks applicable to methanol. The number/code for instructions vary by jurisdiction, such as UN P001 for liquids (the basis of international road/rail/vessel instructions) is equivalent to US 49 CFR 173.202. But the requirements including UN-specification



packaging/performance testing for methanol are essentially harmonized. US and international packing instructions require combination outer packagings meeting UN- specifications for drum, jerry can and box and suitable inner packagings. Single packagings of UN-specification drum, jerry can and receptacles are authorized except for passenger-carrying aircraft.

U.S. and national/international authorities for road/rail/vessel (UN TDG) and air transport (ICAO/IATA) authorize limited quantity exceptions for methanol. These allow combination packagings with up to 1 L (liter) inner packagings in strong outer packaging instead of UN-specification packagings and are exempt from labeling requirements and placarding, except by air (UN TDG Chapter 3.2 table/methanol, Chapter 3.4; US 49 CFR 172.101 table/methanol, 173.150).

Maximum quantities of methanol transported by air are 1 L per package for cargo on passenger-carrying aircraft or passenger-carrying railcar (US) and 60 L per package on cargo-only aircraft (ICAO/IATA 305, US 49 CFR 172.101 table/methanol). ICAO/IATA authorizes limited quantity exception for methanol up to 1 L per package in combination package with .5 L per inner package (Y305).



Besides the Limited Quantity exception at 49 CFR 173.150, the US offers three other transportation exceptions at 173.150 potentially applicable to methanol that are not offered internationally (i.e. domestic US use only). The first is Consumer Commodities, a limited quantity that is a consumer commodity can be re-classed to ORM-D until Dec. 31, 2020 for ground and vessel transport. (ORM-D by aircraft transport is no longer available; the phase out of ORM-D reflects US aligning with UN TDG and ICAO). The second is Aqueous Solutions of Alcohol, whereby an aqueous solution of 24% or less alcohol by volume and no other hazardous material may be re-

classified to Combustible Liquid, or if it contains 50% or more water, it is not subject to the US hazardous materials transportation requirements. The third is Combustible Liquids, if applicable to a methanol solution, for which transportation requirements are reduced, but not eliminated, compared to those for flammable liquid methanol.

Significant relief from transportation requirements is available for shipments of small quantities of methanol by the US and for excepted quantities of methanol by the US and UN TDG, limited to 30 ml (one ounce) per inner package/receptacle. Completed packages of US small quantities must not exceed 29 Kg (64 pounds). Outer packages aggregate limit for excepted quantities is 500 ml (liquids in Packing Group II). Requirements are specified including performance (drop) testing of completed packagings. (UN TDG Chapter 3.5; 49 CFR 173.4, 173.4a).

#### US Postal Service Ground Shipment of Flammable Liquids:

The US Postal Service offers domestic, ground-only shipment for certain flammable liquids that appear to include methanol, only if qualified to be re-classed to ORM-D (i.e., only if a limited quantity and a consumer commodity). This is an important option for shipping methanol without required hazardous materials employee training required by transportation regulatory agencies. Postal Service packing instructions must be followed, limited to 1 quart in metal/1 pint in nonmetal primary receptacle with a screw cap or equivalent closure in a secondary receptacle per each mail piece. (US Postal Service Publication 52, Domestic Mail Manual section 601).

### **Storage, Use and Fire Safety**

#### Local Fire Code and Applicable Fire Safety Regulatory Requirements

Guidance should be reviewed on safe methanol storage, use and fire safety from applicable methanol SDS, MI guidance, US Occupational Safety and Health Administration (OSHA) and other information sources. Regulations concerning flammable liquids fire safety apply by OSHA and equivalent governmental agencies. In particular, the fire code as adopted in every particular jurisdiction will govern onsite storage and use of methanol. It must be consulted and complied with, typically requiring construction and operational fire permits specific to storage, handling or use of methanol.

The International Fire Code (IFC) is a commonly referenced local fire code and can require operational permits to store, handle or use Class I liquids starting at 5 gallons (19L) in a building or 10 gallons (37.9L) outside of a building. Annual hazardous material inventory reports can be required for storage of amounts not much larger, such as 30 gallons indoor or 60 gallons outdoor. Methanol (neat) meets the classification of Class IB Flammable Liquid under IFC. Construction permits are required to install or alter equipment where flammable liquids are to be stored, handled or used. Construction and operating permits can be consolidated. Application for permits will typically require a Hazardous Materials Inventory Statement (HMIS) and a Hazardous Materials Management Plan (HMMP). Update of the HMIS is required annually and when flammable liquids quantities increase or hazardous materials of other class enter the site, and the HMMP should be revised accordingly as needed.

The HMIS reports additionally fulfill US federal requirements (SARA III, EPCRA) to report hazardous chemical inventory to fire departments for emergency planning. However, additional reporting to Local and State Emergency Planning Committees might still be required.

Chemical releases or discharges (spills) must be reported to the fire department and typically to the state environmental protection regulatory agency.

IFC sets a number of general requirements for storage, handling and using hazardous materials (Chapter 27). These include maximum quantity for Class IB flammable liquids per control area in storage and use (open and closed), 120 gallons. Use of approved storage cabinets, other containment measures and automatic sprinkler systems can increase quantity allowances.

IFC sets requirements for flammable and combustible liquids (Chapter 34), some specific to Class IB flammable liquids. The aspects covered include: General requirements, electrical and classified locations, fire protection, labeling/signage and piping systems; containers (60 gal maximum) and portable tanks (660 gal maximum) storage; liquid storage cabinets protocol; indoor storage; quantity limits per building occupancy type; specifications for liquid storage rooms and warehouses; outdoor storage of containers and portable tanks; dispensing, use, mixing and handling; and special operations, including farms and construction sites, well drilling and operating, bulk plants/terminals and bulk-process transfer using tank vehicles and cars.

### Workplace Safety Regulations

Guidance should be reviewed on safe methanol practices from applicable methanol SDS, MI guidance, US OSHA and other information sources. Requirements for occupational safety for each jurisdiction should be consulted.

US OSHA requirements at various subparts of 29 CFR 1910 cover a broad range of potential occupational hazards involved with workplaces in general and specific to use of methanol/methanol-containing products. These include Subpart H Hazardous Materials, 1910.106 Flammable Liquids, Subpart L Fire Protection, 1910.1450 Occupational Exposure to Hazardous Chemicals in Laboratories and the 1910.1200 Hazard Communication Standard. The website of OSHA offers access to guidance directed at numerous activities and occupational processes.

The OSHA methanol occupational air exposure Permissible Exposure Level (PEL) is 200 ppm/8 hr (260 mg/m<sup>3</sup>). (29 CFR 1910.1000). American Council of Governmental Industrial Hygienists (ACGIH) 8 hr Time Weighted Average (TWA) is 200 ppm and Short Term Exposure Level (STEL) is 250 ppm. Equivalent exposure values are typical among agencies and organizations globally.

### Methanol Hazard Communication in Workplaces



Hazardous substances labeled and marketed solely for industrial use are generally governed under workplace safety regulations. These set out general requirements and specify hazard criteria that require warnings, SDS/Safety Data Sheets, specific hazard warnings on containers according to hazard criteria and employee training. Receipt and utilization of containers of methanol in the workplace are subject to such requirements as to flammable

liquid hazard and one or more hazards of toxicity, depending on jurisdiction.

Appropriate SDS should be consulted for workplace labeling and hazard communication for methanol products required in any particular jurisdiction. Methanol is regulated under the US OSHA Hazard Communication Standard at 29 CFR 1910.1200, Canadian Consumer Chemicals and Containers Regulations (CCCR) and Workplace Hazardous Materials Information System (WHMIS) controlled product regulations and similar EU Directive. These are among requirements in effect globally and aligned by nations with the UN Globally Harmonized System for Classification and Labeling of Chemicals (GHS). The OSHA hazard communications standard was revised recently to align with GHS Rev. 3 as to SDS requirements and hazard label elements.

Proper labeling will include specific pictograms, signal words and statements of hazard and precautions for the flammable liquid and toxicity hazards. Original containers with labels provided by commercial suppliers should be maintained or replaced with up-to-date equivalent, provided by the supplier if possible. Transfer of methanol product to other or new containers requires new labels. Products made with methanol but meeting different hazard criteria require new warnings and potentially SDS and employee training appropriate for such criteria.

#### Consumer Safety for Products Containing Methanol

Consumer hazardous substances generally are intended or packaged in a form suitable for use in the household and are regulated unless without foreseeable risk of consumer exposure. Consumer products containing methanol are typically required to have warning symbols and statements specific to methanol toxicity and as to flammability, defined by each jurisdiction, and to be in child-resistant packaging. Consult consumer safety requirements for products containing methanol in any particular jurisdiction.

The US Consumer Product Safety Act prohibits consumer products presenting an unreasonable risk of serious injury or death. US Consumer Product Safety Commission (CPSC) regulations identify methanol among products requiring special labeling, due to human experience when containing 4% or more by weight methanol, at 16 CFR 1500.14. Specific warnings are required for methanol as to label symbol, signal words and statements of hazard and precaution. Methanol is also identified among substances requiring special packaging when containing 4% or more weight methanol, at 16 CFR 1700.14. Packaging must be in accordance with child resistant/poison prevention packaging standards at 16 CFR 1700.15. The state of California requires additional warning statements for methanol for reproductive toxicity.

Canadian CCCR regulations define methanol, under Toxic Products, as a substance of special concern based on human experience as to toxicity (at/over 1% and 5 ml). Required warning information for methanol toxicity is set out at CCCR Section 39 and child resistant containers in accordance with section 40 are required unless over 5L capacity. Methanol is also subject to required warning information for flammability at CCCR Section 54 (exception provided for over 50% water/methanol solution that does not sustain combustion). Required warnings for toxicity and flammability of methanol are specified, including symbols, signal words, and statements of hazards and instructions.

## California Office of Environmental Health Hazard Assessment (OEHHA), Proposition 65

The OEHHA office of California Environmental Protection Agency maintains a list of over 800 chemicals determined by the state to cause cancer or reproductive toxicity, under Title 27, commonly called Proposition 65. (Safe Drinking Water and Toxics Enforcement Act of 1986). Methanol was determined in March 2012 to exhibit toxicological endpoint “developmental toxicity” based on authoritative bodies of reference. Exception was provided for foods and beverages containing methanol or digested to naturally create methanol from their consumption. “Safe harbor” values were issued for exposures below Maximum Allowable Dose Levels of 47 mg/day for inhalation and 23 mg/day by ingestion (1/1000<sup>th</sup> of NOEL/No Observable Effects Level). Businesses are to provide state residents “clear and reasonable” warnings about significant amounts of listed chemicals released in the environment from products they purchase, in homes and in workplaces. Warnings may be by consumer product label, signs at workplaces and rental units, or other means.

## Oil & Gas Drilling Activities using Methanol

Use of methanol in oil & gas activities including hydraulic fracture additives are subject to a range of regulatory authorities depending on location and types of activity. Consult appropriate SDS and regulatory authorities for each jurisdiction as to local fire code for storage and processing before being brought to oil & gas location, transportation to and from oil & gas locations and local fire code for storage and use at such locations. Transportation of methanol/water solutions may take note of US exceptions for Class 3 flammable liquids, 24% or less aqueous solutions of alcohol (49 CFR 173.150) that offer opportunity to reclassify solutions to combustible liquid or to non-hazardous transport status. There are IFC chapters and OSHA occupational safety requirements directed specifically at oil & gas activities.

Follow state/provincial or equivalent oil and gas regulations including management of exploration & production (E&P) wastes for hydraulic fracture fluids and chemical disclosure of fracture additives (methanol), if applicable. The US Environmental Protection Agency (EPA) is conducting a comprehensive study on impacts of hydraulic fracturing expected to conclude in 2014. More comprehensive federal regulation of the treatment of produced waters and wastes is also likely in 2014.

## **Environmental Considerations**

Guidance should be reviewed on environmental safety, protection and recovery/disposal from applicable methanol SDS, Methanol Institute, US OSHA, US EPA, Environment Canada and other information sources. These provide extensive guidance on methanol spills/releases and environmental fate of methanol. This bulletin is confined more towards practical considerations onsite of having and using methanol with the potential for end use/disposal of methanol and methanol products. Regulations should be consulted for each jurisdiction as to applicable requirements.

Where appropriate, options that reduce, reuse and recycle methanol, particularly commercially, can reduce or eliminate volumes of methanol waste disposal, described generally as hazardous waste.

US EPA Resource and Conservation Recovery Act (RCRA) regulations identify methanol as a hazardous waste and requires restricted land disposal, notification of hazardous waste generation, and regulated treatment, storage and disposal. Hazardous waste spill/release notification and cleanup activities are required. The RCRA ID number for methanol hazardous waste is U154, identified as ignitable (I), defined at 40 CFR 261.21, and toxic (T), discarded commercial chemical compounds, 40 CFR 261.33(f). Methanol is a Domestic Product under the Canadian Environmental Protection Act (CEPA), with similar regulation as under EPA in the US being applicable in Canada.

RCRA provides reduced requirements for small quantity (SQ) hazardous waste generators at or less than 100 kg/month at 40 CFR 261.5. Above this amount, hazardous waste transfers require notification and periodic reporting of hazardous waste transfers to the EPA or delegated state program.

Residue of hazardous waste in empty containers is exempted from US hazardous waste regulation at 40 CFR 261.7. It requires that containers of hazardous materials be emptied using commonly employed means, with no more than 1-inch residue, or residue of 3% net capacity (0.3% residue over 119 gallons net capacity) remaining. Furthermore, household waste from residences is exempted from US hazardous waste regulation at 40 CFR 261.4(b). However, local waste management authority's requirements may be applicable to household waste, such as prohibiting flammable liquids from being discarded in trash. Exceptions and requirements similar to these may apply in other jurisdictions.

In cases of spills or releases of methanol or methanol hazardous waste, notification is typically required to the local fire department and to the EPA or state-delegated RCRA program. Depending on the severity of the incident, both agencies may become involved in the response. Follow-up reporting may be required as to clean up/correction of conditions. The US Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) reportable quantity for methanol is 5,000 lbs., requiring additional notification to The National Response Center (NRC).

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