Objectives:

• Review

• Awareness of Modern Current Atypical Oil Products

• Familiarization with Transportation

• Emerging Risks Associated with Atypical Oil Products

• Awareness of Response Operations Options

• Discussion
Gulf Strike Team
Bulletin Supplement

Responder Awareness – North American Crude Oil Shipments

The information contained in this document is advisory in nature and intended to raise awareness within the response community. It is not a standard or regulation, and it creates no new legal obligations.

Growth of North American Petroleum Production

North American crude oil production has rapidly risen over the past few years. This growth is, in part, a result of non-traditional drilling techniques used to access shale and bitumen oil reserves. The main formations currently being tapped include Canadian Tar Sand formations, the Bakken Shale formation located in North Dakota, and the Eagle Ford Shale formation located in southwestern Texas. Additional areas of exploration include northeastern Colorado, central Florida, and the Pennsylvania region.

This petroleum production growth has outpaced the carrying capacity of the nation’s current fixed infrastructure and pipelines. As a result, additional transportation capacity needs are being met by rail cars, tanker trucks, and barges to move these crude products to coastal refineries and distilleries. Areas seeing significant increases in commerce and maritime traffic include the Columbia River System, the Hudson River, and the Mississippi River and associated navigable waterways.

Unlike traditional crude oil reserves, these formations produce petroleum with varying physical properties and hazards. For example, Canadian Tar Sand Oil is so viscous that petroleum fractions are added to decrease the product’s viscosity for easier transport. In some cases, rail cars laden with Tar Sand Oil must be heated until the product reaches a sufficiently mobile form before being rolled onto a truck or barge for transport to coastal refineries. Some containers are designed to withstand the high pressure and heat generated during transport.

As this oil production continues to rise and more formations are identified through further exploration, pollution incidents involving these products may increase and consequently pose threats to responders and the environment. Area committees and response organizations are encouraged to stay informed about these products, especially those moving through their areas of responsibility.

The Gulf Strike Team (GST) recently responded to multiple train derailments and large releases involving some of these products, which included valuable lessons learned to be shared amongst the response community.

Safety Data Sheets

Companies generate and maintain copies of Safety Data Sheets (SDSs) for the crude oil they are transporting or refining. Responders should pay particular attention to SDS values that may have been “estimated” instead of measured. Oil produced in formations can vary greatly from one geographic location to the next. Companies may also use generalized SDSs for their products and may not have the physical characteristics for each shipment of crude oil they are transporting. Physical properties within each load, regardless of generalized information, may vary and pose their own unique hazards to responders.

One SDS reviewed for Bakken Crude Oil, a physical property such as the lower and upper explosive limits, auto-ignition temperature and vapor density estimates. The hazard classification section was also broad in nature. However, a SDS for Eagle Ford Shale Oil listed specific physical and detailed information on the hazard classifications. Treat each response uniquely and carefully follow the product’s SDSs.

Hazard Awareness

The following hazards are situation specific and may not represent similar events or trends for responses in the future.

Canadian Tar Sand Oil

Diuretics, a fluid used to lower viscosity, are added to bitumen based oils (Canadian Tar Sand Oil) in large enough quantities to make the original product easier to pump and transport. A diuretic frequently used in large volume is Natural Gas Condensate. Natural Gas Condensate consists of many short chain hydrocarbons, which includes various alkenes, aromatics, BTX, and long chain chemical variants. Natural Gas Condensate can have a proper shipping name of Petroleum N.O.S., which is accepted as a dangerous good under the IMDG Code. Some of the hazards include: flammability, easily ignited by heat, sparks or flame, vapors forming explosive mixtures with air, toxicity through various routes of exposure, and being volatile at room temperature. Once the diuretic is separated from the product, the original analysis should not be made unless the BTX analysis is determined to be at a level of 0.02% by weight, and it would be necessary to dilute the product to 0.02% by volume. In a marine or aquatic environment and under the right conditions, this product could break down to the bottom of the impacted waterways making recovery efforts far more challenging and time consuming than traditional recovery techniques.

Bakken Crude Oil

The GST recently responded to a spill of Bakken Crude Oil into the Mississippi River after a tank barge was breached during a collision. This specific case the product was very volatile. Even under cool atmospheric conditions (approximately 45°F), the oil was venting around the damaged barges were registering Volatile Organic Compounds (VOCs) consistently at 20-30 ppm. Benzene was detected directly adjacent to the leaking oil with containment boom and measured at 40.2 ppm, which significantly exceeded USHA’s Short Term Exposure Limit (STEL) and Ceiling of 5.0 ppm and the ACGIH’s Threshold Limit Value of 0.5 ppm, which is the occupational exposure limit for Coast Guard personnel. These atmospheric hazards were detected by the GST upon arrival approximately 12 hours after the incident occurred, and elevated levels of benzene persisted for several days into the response. In addition to physical measurements, subsequent laboratory analysis of the Bakken Crude Oil found naphthalene, a highly toxic polycyclic aromatic hydrocarbon, to be at 2000 ppm.

Eagle Ford Shale Oil

Eagle Ford Shale Oil is reported as having similar physical properties and hazards as Bakken Crude Oil with the addition of an ignitable potential through static discharge. A visual comparison of these oils revealed both have low viscosity (slightly more than gasoline but less than motor oil) with Bakken Crude Oil being dark brown and Eagle Ford Shale Oil light to medium brown in color.

Steps to Protect Responders

VOCs, including BTX, can pose a direct hazard to the health of responders. Each type of oil presented above is known to contain these compounds, which, during a response, present at a minimum an inhalation hazard to responders. One way to mitigate the hazard is to have the appropriate detection capabilities deployed properly and quantify the hazard prior to impacting response personnel. Once quantified, appropriate personnel protective strategies can be implemented, such as the wearing of an air purifying respirator or self-contained breathing apparatus. It is also equally important to have Joint Protective Room (JPR) capabilities deployed by responders, the BW Technologies GasAlert Quattro Multigas Monitors, do NOT directly measure for BTX. Special air monitoring equipment may be required to properly identify BTX hazards. Should a response event involve any of the above detected oils, ensure that appropriate equipment is a part of the planning phase of a deployment to alert responders to a potential hazard.

Recommendations

Cautionary consideration products, their hazardous properties and values; recognize that hazard variations may exist. Do not assume to any generalization for a product; fully understand the data provided through the products SDSs. Property, density, identity, and quantity hazards before taking action; use appropriate air monitoring equipment. Develop effective protection strategies and mitigate hazards through safely protocols.

National Strike Force Resources

Each Strike Team maintains air monitoring equipment which can quantitatively and qualitatively identify BTX hazards. Additionally, each Strike Team and the National Strike Force Coordination Center have a staff industrial hygienist who can help responders personnel evaluate unknown and unknown risks, interpret SDS information, and help in the development and review of site safety plans.

FOSCO5565 can contact the Gulf Strike Team’s 24 hour emergency line at (251) 441-6691 should a need arise for air monitoring equipment, responses personnel or consultation on safety protocols and response tactics.
Vapor Pressure and Volatility

- **Vapor Pressure**  
  Force exerted by the gas or vapor released by a liquid or solid substance in a closed container or space.
- **At or below the vapor pressure, there is no net evaporation.**

- A substance with a high vapor pressure at normal temperatures is often referred to as *volatile*.

As the *temperature* of a liquid or solid increases its *vapor pressure* also increases.

- **Reid Vapor Pressure**  
  It is defined as the absolute vapor pressure exerted by a liquid at 100 °F

- **Volatility**  
  in this instance refers to petroleum’s evaporation characteristics. The New York Mercantile Exchange (NYMEX) specifications for crude oil futures contracts restrict Reid Vapor Pressure (RVP) to less than 9.5 psi at 100° F. Bakken crude oil has an RVP of at least 8.75 Eagleford up to 15PSI

- **RVP gasoline**  
  Max 9.0 psi summer and below 14.7 PSI for winter Gasoline
Flammability and Flash Point
**Flammability and Flash Point**

**Lower explosive limit**
*Lower explosive limit* (LEL): The lowest concentration (percentage) of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arc, flame, heat).

**Upper explosive limit**
*Upper explosive limit* (UEL): Highest concentration (percentage) of a gas or a vapor in air capable of producing a flash of fire in presence of an ignition source (arc, flame, heat).

**Flammable (Explosive) Range**
This is the range between the lowest explosive limit (LEL) and the upper explosive limit (UEL)

Examples
- Bakken/Eagle Ford: 0.8-8.0 %
- Gasoline: 1.4-7.6%

**Flash Point**
This is the lowest temperature of the liquid at which it gives off enough vapor to form an ignitable mixture of vapor and air immediately above the liquid surface.
- Bakken/Eagle Ford: <59°-199°
- Gasoline: -45°
Specific and API Gravity

**Specific gravity** is the ratio of the density of a substance to the density (mass of the same unit volume) of a reference substance (Freshwater Water 1.0, Saltwater ~1.03)

**API Gravity** is the oil industry standard used to determine and classify the density of oil

- If API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks. In salt water 6.5-7

Oil with a specific gravity less than 1 or an API degree of >10 API

- Fresh water  (Specific gravity = 1 and API=10)

Oil with a specific gravity greater than 1 or an API degree of <10 API
Oil sands and bitumen (Class C) have a specific gravity in the range of 7 to 9 °API and viscosity above 10,000 cP.
Crude Oil Toxicity (EPA)

Remember: “oil” is a mixture of many different chemicals

- EPA Class A: Light, Volatile Oils: These oils are highly fluid and highly toxic to humans and include jet fuel and gasoline.

- EPA Class B: Non-Sticky Oils: These oils are waxy and less toxic to humans and include diesel fuel and light crude oil.

- EPA Class C: Heavy, Sticky Oils: These oils are brown or black and sticky or tarry and include most crude oils. Their toxicity is low, but if spilled, their impacts on waterfowl and wildlife can be severe.

- EPA Class D: Non-Fluid Oils: These oils are non-toxic and include heavy crude oils. They are difficult to clean up, and if spilled, their impacts on waterfowl and wildlife can be severe.
Crude Oil Toxicity Possibilities:

- **Possible components:** Benzene, Hydrogen sulfide, Ethylbenzene, Toluene, Xylene, Naphthalene, others

- **BTEX** is an acronym that stands for benzene, toluene, ethylbenzene, and xylenes. These compounds are some of the volatile organic compounds (VOCs) found in petroleum derivatives such as petrol (gasoline). Toluene, ethylbenzene, and xylenes have harmful effects on the central nervous system.

- **Hydrogen sulfide is extremely toxic.** A major factor in its toxicity is its ability to fatigue the sense of smell. \(H_2S\) loses the typical rotten eggs odor when the concentration rises, and exposed workers may not be aware of increased gas concentrations. Exposure to concentrations above 600 ppm can be rapidly fatal.
Alberta Tar Sands

- What are Tar Sands (Bitumen)?
  - A heavy black viscous oil
  - Tar sands cannot be pumped from the ground in its natural state; tar sand deposits are mined, usually using strip mining or open pit techniques, or the oil are extracted by underground heating with additional upgrading.

http://ostseis.anl.gov/guide/tarsands/
On May 7, 2014, the Secretary of Transportation issued an Emergency Restriction/Prohibition Order to all railroad carriers that transport in a single train 1,000,000 gallons (approximately 35 rail cars) or more of UN 1267, Petroleum crude oil, Class 3, produced from the Bakken shale formation in the Williston Basin (Bakken crude oil).
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Around 600 million bbls of crude oil was transferred by rail in 2014.
THE TAR SANDS PIPELINE BOOM

Industry has announced the intention to build more than 10,000 miles of pipelines at a cost of almost $40 billion over the next five years to send an additional 3.1 million barrels a day of crude oil from Canada's oil sands to global markets.

<table>
<thead>
<tr>
<th>Pipeline</th>
<th>Cost</th>
<th>Length</th>
<th>Capacity (maximum)</th>
<th>Projected Start Date</th>
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<td>completed</td>
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<td>512</td>
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<tr>
<td>Flanagan South</td>
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<td>600</td>
<td>585,000</td>
<td>2014</td>
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<tr>
<td>Trailbreaker</td>
<td>0.346</td>
<td>524</td>
<td>200,000</td>
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</tr>
<tr>
<td>Montréal Pipeline</td>
<td>0.1</td>
<td>236</td>
<td>400,000</td>
<td>on hold</td>
</tr>
<tr>
<td><strong>Totals</strong></td>
<td><strong>38.446 billion</strong></td>
<td><strong>10,708 miles</strong></td>
<td><strong>3,130,000 barrels per day</strong></td>
<td></td>
</tr>
</tbody>
</table>

*项目正在考虑中 **额外的新出口能力仅适用于出口

ILLUSTRATION BY Catherine Mann

April 2012
Keystone XL Pipeline
THE TAR SANDS PIPELINE BOOM

Industry has announced the intention to build more than 10,000 miles of pipelines at a cost of almost $40 billion over the next five years to send an additional 3.1 million barrels a day of crude oil from Canada's oil sands to global markets.

Keystone 1 Pipeline

Illustration by Catherine Mann
The Tar Sands Pipeline Boom

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THE TAR SANDS PIPELINE BOOM

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ILLUSTRATION BY Catherine Mann
April 2012
Bitumen, transported as Dil-bit, Syn-bit, Rail-bit, Access Western Blend (AWB), Pipeline Sales Oil (PSO), Bow River (BR); Cold Lake Blend (CLB); Christina Lake Dil-bit Blend (CDB), Christina Lake Blend (CSB); Western Canadian Blend (WCB); Western Canadian Select (WCS); Wabasca Heavy (WH)
MATERIAL SAFETY DATA SHEET

1. CHEMICAL PRODUCT & COMPANY IDENTIFICATION

PRODUCT: Bitumen

MANUFACTURER: Syncrude Canada Ltd.
P.O. Box 2009
Fort McMurray, AB
Canada T9K 8L1
Emergency Telephone No. (780) 790-5694

SYNONYMS: Coker Feed, LC-Finer Feed, Vacuum Distillation Unit Feed,
Plant 7 Bitumen Product
Syncrude Sample Tag #s: 071019, 072019, 221001, 371001

PRODUCT USE: Process stream extracted bitumen, coker feed.

PREPARED BY: Nathalie Bérubé
(780) 790-4544

DATE OF PREPARATION/REVISION: March 7, 2006

2. COMPOSITION, INFORMATION ON INGREDIENTS

CAS #: 6052-42-4

Tapped heavy oil extracted from oil sands. Black or brownish, tar-like texture. A complex combination of high molecular weight organic compounds with carbon numbers greater than C16, with high carbon-to-hydrogen ratios. It also contains small amounts of various metals such as nickel, iron, and vanadium.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW:
A black or dark brown, highly viscous liquid. Heated bitumen can cause severe skin burns and eye injury. Eye, skin, gastrointestinal, and respiratory tract irritation can occur. Poisonous hydrogen sulfide gas may accumulate in confined spaces.

ROUTE OF ENTRY: Skin contact, Eye contact, Inhalation, Ingestion

EFFECTS OF ACUTE EXPOSURE:
EYES: Hot bitumen and bitumen fumes may cause severe irritation and burns. Cold bitumen may cause slight irritation. Bitumen dust may cause irritation characterized by burning, redness, swelling, and watering.

5. PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE: Black or brownish, tar-like texture.
ODOUR: Solvent-like odour.
PHYSICAL STATE: Viscous liquid
pH: Not applicable
VAPOUR PRESSURE: Not available
VAPOUR DENSITY (air = 1): Not available
FREEZING POINT: Not applicable
BOILING RANGE (deg C): IBP 290°C, 40-45% boiling at 504°C
SPECIFIC GRAVITY: 1.02 @ 20°C

EVAPORATION RATE (in Butyl Acetate = 1): Essentially non-volatile at ambient temperatures

CONE OF WATER/OIL DISTRIBUTION: Not miscible with water
ODOUR: Thin stream; not available

10. STABILITY AND REACTIVITY

STABILITY: Stable

CONDITIONS TO AVOID: Not applicable

MATERIALS TO AVOID: Strong oxidizing materials. This product may dissolve or soften some plastics.

HAZARDOUS COMBUSTION PRODUCTS: Carbon monoxide, Carbon dioxide, oxides of nitrogen and sulphur, soot, uncombusted hydrocarbons.

11. TOXICOLOGICAL INFORMATION

LD50: 5 to 15 g/kg (oral), >5 g/kg (oral) - mice, rats
3-4 g/kg (rat-intragastric), >3.16 g/kg (dermal) - rabbits

LC50: No data found.

ACUTE:
An acute oral, dermal, ocular and inhalation toxicity study was performed using bitumen (bitumen diluted with naphtha) from the Alberta oil sands. No animals (rats and mice) died following a single oral dose of 5 g/kg. No animals (rabbits) died following a single dermal dose of 3.16 g/kg. The rabbits did experience moderate skin irritation (Drabkins score of 3/5) and desquamation. Rabbits experienced slight eye irritation (Drabkins score of 1/10) with conjunctival redness. No mortalities (rabs) occurred following a 6-hour inhalation exposure to 1.146 g/m³, however, lung discoloration and decreased lung weight was observed. (Reference 1)
2. REGULATED COMPONENTS

The following components are defined in accordance with subparagraph 13(a) (I) to (IV) or paragraph 14(a) of the hazardous product act.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>CAS#</th>
</tr>
</thead>
<tbody>
<tr>
<td>BITUMEN</td>
<td>40-70</td>
</tr>
<tr>
<td>LIGHT NAPHTHA</td>
<td>35-40</td>
</tr>
<tr>
<td>NATURAL GAS CONDENSATE</td>
<td>15-40</td>
</tr>
</tbody>
</table>

IMPERIAL OIL

MATERIAL SAFETY DATA SHEET

Date Prepared: September 27, 1982
Revision: September 27, 1982
Edition: ESC

1. PRODUCT IDENTIFICATION

(a) PRODUCT NAME: BITUMEN
(b) DENSITY: 15.5 kg/L
(c) SPECIFIC HEAT: 1.88 kJ/kg
(d) VAPOR PRESSURE: 0.1 bar
(e) OCTANE NUMBER: 40
(f) FLAMMABILITY: 0.9 L/min
(g) UPPER FLAMMABLE LIMIT: 3.5%

2. REGULATED COMPONENTS

The following components are defined in accordance with subparagraph 13(a) (I) to (IV) or paragraph 14(a) of the hazardous product act.

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<td>35-40</td>
</tr>
<tr>
<td>NATURAL GAS CONDENSATE</td>
<td>15-40</td>
</tr>
</tbody>
</table>

SECTION 1 - MATERIAL IDENTIFICATION

Material Name: HEAVY CRUDE OIL/DILUENT MIX
Synonyms: Bow River, Cold Lake Blend, Christina Lake Blend, Cold Lake Diluent
NºPA: Fire: 2, Reactivity: 0
Use: Process streams, fuel and lubricant production
MDM Classification: Class 2, Div. 2.1, Sub-Section 3.4
TDC: B, Div. 2, Class D, Div. 2, Sub-Div. A and B
TDC Shipping Name: Sulfuric Acid
TDC Grade: 3
TDC Packing Group: C
Manufacturer/Supplier: CANADIAN ENERGY INC.
Address: 500 Centre Street E, PO Box 1000
Calgary, AB T2P 5G5
Emergency Telephone: 1-877-453-3085

SECTION 2 - HAZARDOUS INGREDIENTS OF MATERIAL

| Hazardous | Approximate | C.A.S. | LD50/LC50 | Exposure
<table>
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<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxicity</td>
<td>5-30</td>
<td>8052-42-4</td>
<td>5 mg/L (OSHA PEL)</td>
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<tr>
<td>HBR</td>
<td>5-20</td>
<td>8052-42-4</td>
<td>5 mg/L (OSHA PEL)</td>
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<tr>
<td>NBR</td>
<td>5-20</td>
<td>8052-42-4</td>
<td>5 mg/L (OSHA PEL)</td>
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<tr>
<td>TBR</td>
<td>5-20</td>
<td>8052-42-4</td>
<td>5 mg/L (OSHA PEL)</td>
<td></td>
</tr>
<tr>
<td>Teflon</td>
<td>5-20</td>
<td>8052-42-4</td>
<td>5 mg/L (OSHA PEL)</td>
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</table>

SECTION 3 - PHYSICAL DATA FOR MATERIAL

Physical State: Liquid
Vapor Pressure: 760 mm Hg
Evaporation Rate: 0.4 kg/m³
Coefficient of Water/Oil Distribution: 0.1
Odor & Appearance: Brown/bright liquid, hydrocarbon

SECTION 4 - FIRE AND EXPLOSION

Flammability: Yes
Extinguishment: Foam, CO₂ dry chemical
Special Precautions: Use water spray to cool fire-exposed containers, and to disperse vapor if spill has not ignited. Cut off fuel and allow flames to burn out.

SECTION 5 - REACTIVITY DATA

Chemical Stability: Stable
Incompatibility: Yes
Reactivity: Yes
Hazardous Decomposition Products: Carbon monoxide, carbon dioxide, sulfur oxides
Toxicity to humans, including carcinogenicity, reproductive and developmental toxicity, neurotoxicity, and acute toxicity.
3. TYPICAL PHYSICAL AND CHEMICAL PROPERTIES

**PHYSICAL STATE:** Liquid

**SPECIFIC GRAVITY:** 0.9 to 1.2

**ODOR/APEARANCE:** "Tarry" odour and associated smell of "rotten eggs" due to hydrogen sulphide presence; black liquid

**VAPOR PRESSURE:** 12 to 21 kPa at 24 deg C

**VAPOR DENSITY:** Not Available

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<table>
<thead>
<tr>
<th>IMPERIAL OIL</th>
<th>MATERIAL SAFETY DATA SHEET</th>
</tr>
</thead>
<tbody>
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<table>
<thead>
<tr>
<th>MATERIAL NAME</th>
<th>HEAVY CRUDE OIL-DILUENT MIX</th>
</tr>
</thead>
</table>

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**SECTION 1 – MATERIAL IDENTIFICATION**

**Material Name:** HEAVY CRUDE OIL-DILUENT MIX

**Synonyms:** Charro Lake Diluent Blend (CLD), Charro Lake Blend (CLB), Wabasso Heavy (W25)

**Use:** Process streams, fluids and lubricants production

**WHMIS Classification:** Class B, Div. 2, Class D, Div. 2, Sub-Dev. A, and B

**NFA:** 2.2

**TDG Class:** 3

**TDG Packaging Group:** II (boiling point 35 deg C or above, and flash point less than 23 deg C)

**Manufacturer/Supplier:** CENOVUS ENERGY INC.

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**SECTION 2 – HAZARDOUS INGREDIENTS OF MATERIAL**

| Ingredient | Concentration (%) | C.A.S. | LD50/LC50 | Exposure
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.03 - 0.3</td>
<td>71-43-2</td>
<td>LD50, LC50</td>
<td>PEL, TLV</td>
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<tr>
<td>Hydrogen Sulphide</td>
<td>&lt;0.1</td>
<td>7783-08-04</td>
<td>PEL, TLV</td>
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**SECTION 3 – PHYSICAL DATA FOR MATERIAL**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (%)</th>
<th>C.A.S.</th>
<th>LD50/LC50</th>
<th>Exposure</th>
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<td>Benzen</td>
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<td>LD50, LC50</td>
<td>PEL, TLV</td>
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<tr>
<td>Hydrogen Sulphide</td>
<td>&lt;0.1</td>
<td>7783-08-04</td>
<td>PEL, TLV</td>
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</tr>
</tbody>
</table>

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**SECTION 4 – FIRE AND EXPLOSION**

**Flash Point (deg C):** -35 (FMC)

**Upper Explosive Limit (ppm):** 0.8

**Auto-Ignition Temp. (deg C):** 250

**Hazardous Combustion Products:** Carbon monoxide, carbon dioxide, sulphur oxides

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**SECTION 5 – REACTIVITY DATA**

**Chemical Stability:** Stable

**Compatibility:** Yes

**Incompatibility:** Not Applicable

**Reactivity:** Yes

**Hazardous Decomposition Products:** Carbon monoxide, carbon dioxide, sulphur oxides
Health Safety Aspects most Associated with the Diluents

Diluents Possibly found in Tar Sands Oil

- Alcohols
- Ethers
- Metals
- Methane
- Pentane
- Butanes
- Other Hydrocarbons
- Possibly H₂S
Enbridge Pipeline Kalamazoo River Spill

- July 2010 843,000 gallons of Dilbit spilled into Talmadge Creek and the Kalamazoo River impacting about 35 miles of the river

Dilbit specific gravity of .75 up to .92/93 Between two days and two weeks the oil began to sink.

Why???
Enbridge Pipeline Kalamazoo River Spill

- July 2010 843,000 gallons of Dilbit into Talmadge Creek and the Kalamazoo River impacting about 35 miles of the river

Dilbit specific gravity of .75 -.92/.93 Between two days and two weeks the oil began to sink.

Why???

Loss of light ends and sedimentation
Representative diluted bitumen products, Access Western Blend (AWB) Gravity implications

Rates of evaporation for AWB was found in one study occurred at a mass loss of 15.9% of its mass, within 6 hours at 15°C. Within 24 hours, the relative mass losses were 18.4%.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fresh (0%)</th>
<th>W1 (8.5%)</th>
<th>W2 (16.9%)</th>
<th>W3 (25.3%)</th>
<th>W4 (25.5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur Content (g/L)</td>
<td>3.0</td>
<td>4.1</td>
<td>4.5</td>
<td>4.9</td>
<td>4.8</td>
</tr>
<tr>
<td>Water Content (g/L)</td>
<td>1.5</td>
<td>0.9</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>&lt; -5</td>
<td>&lt; -5</td>
<td>29</td>
<td>159</td>
<td>173</td>
</tr>
<tr>
<td>Four Point (°C)</td>
<td>&lt; -25</td>
<td>&lt; -25</td>
<td>-6</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>Density (g/mL) at 0°C</td>
<td>0.9399</td>
<td>0.9646</td>
<td>0.9949</td>
<td>1.0214</td>
<td>1.0211</td>
</tr>
<tr>
<td>Density (g/mL) at 15°C</td>
<td>0.9253</td>
<td>0.9531</td>
<td>0.9846</td>
<td>1.0127</td>
<td>1.0140</td>
</tr>
<tr>
<td>Density (g/mL) at 20°C</td>
<td>0.9148</td>
<td>0.9547</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic Viscosity (mPa.s) at 0°C</td>
<td>1.30E+03</td>
<td>9.82E+03</td>
<td>2.04E+05</td>
<td>9.35E+07</td>
<td>&gt;1.00E+08</td>
</tr>
<tr>
<td>Dynamic Viscosity (mPa.s) at 15°C</td>
<td>347</td>
<td>1.72E+03</td>
<td>2.97E+04</td>
<td>2.52E+05</td>
<td>7.91E+06</td>
</tr>
<tr>
<td>Dynamic Viscosity (mPa.s) at 40°C</td>
<td>59.8</td>
<td>348</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emulsion Stability Class</td>
<td>Entrained</td>
<td>Entrained</td>
<td>Entrained</td>
<td>Entrained</td>
<td>N/A</td>
</tr>
<tr>
<td>Complex Modulus (Pa)</td>
<td>44.6</td>
<td>89.7</td>
<td>467</td>
<td>1.26E+04</td>
<td>N/A</td>
</tr>
<tr>
<td>Water Content (%w/w)</td>
<td>40</td>
<td>35</td>
<td>33</td>
<td>6</td>
<td>N/A</td>
</tr>
<tr>
<td>Surface Tension (Air/Oil, mN/m)</td>
<td>31.2</td>
<td>31.9</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Surface Tension (Air/Water, mN/m)</td>
<td>30.2</td>
<td>31.1</td>
<td>31.2</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Interfacial Tension (Oil/Water, mN/m)</td>
<td>24.8</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Interfacial Tension (Oil/Water, mN/m)</td>
<td>24.2</td>
<td>28.0</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Interfacial Tension (Oil/Brine, mN/m)</td>
<td>23.0</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Interfacial Tension (Oil/Brine, mN/m)</td>
<td>23.8</td>
<td>26.0</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>

NM – Not Measurable, too viscous;
DNF – Did not Form, too viscous;
N/A – Not applicable;
*Measured at 8.8% evaporated via sparging.
Shale Oils
In 2014 a total of 185,036,779.91 barrels of shale crude exported from the Corpus Christi area.
Shale Oils, AKA Tight oil, AKA LTO (Light Tight Oil), or Condensates is petroleum that consists of light crude oil contained in petroleum-bearing formations of low permeability, often shale or tight sandstone.

Represented as:
High concentration of light end petroleum hydrocarbons (C-1-C5, methane, ethane, propane and butanes)

Results in:
- Increased vapor pressure
- Increase in volatility
- Lowering of the flashpoint
- Lowering of the boiling point

Also, the lighter ends MAY have higher H₂S
Flammability of Shale oils

National Fire Protection Association (NFPE) = 3-4
ie: sensitive to static discharge

Explosive Limits variable  LEL 0.4 to 15.0 UEL

Flashpoint  -40° to 212°F or -74°-122° AFPM

Flammability

The greatest volume of one code determines the marking. The only exception is if a more severe code has a volume of 3 gallons or greater, then that code is used instead of a lower code of greater volume. If the laboratory total volume of flammables or combustibles is less than one pint for all, then the rating for the laboratory for this area shall be zero.

Flammability (Red) Detailed Description of Flammable Rating

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Danger: Flammable gas or extremely flammable liquid</td>
</tr>
<tr>
<td>3</td>
<td>Warning: Flammable liquid flash point below 100°F</td>
</tr>
<tr>
<td>2</td>
<td>Caution: Combustible liquid flash point of 100°F to 200°F</td>
</tr>
<tr>
<td>1</td>
<td>Flammable if heated</td>
</tr>
<tr>
<td>0</td>
<td>Not combustible</td>
</tr>
</tbody>
</table>

USCG Strike team presentation, 2015
Thick shale deposits do not allow for migration of gasses. Scott Tinker, BEG
Lac-Magantic, Quebec. 63 Railcars, Confirmed 47 deaths
Material Safety Data Sheet

Product Name: CRUDE OIL SWEET

Physical State: Liquid

Odor Threshold (PPM): Not Available

Vapor Pressure (mm Hg): 0.001

Evaporation Rate (Mfr vs. ASTM): Not Available

Boiling Point (°C): Not Available

F Flash Point: 60°C (140°F)

Flash Point: 0°C (32°F)

Autoignition Temperature: 220°C (430°F)

Flammable Limits: 1 to 15

Lethal Concentration: 500 ppm

GENERAL HAZARD: DECOMPOSITION TEMPERATURE: Not Established

Extinguishing Media:

- Water: Not available
- Foam: Not available
- Dry Chemical: Not available
- halon:
- Carbon dioxide:
- Dry powder:
- Alcohol:
- Non-conducting water:

Other Considerations: Not available

Fire Fighting Procedures: Protective actions to take during fire fighting:

- Firefighters: When handling the material:
  - Wear a complete breathing apparatus
  - Use water mist
  - Use fire-resistant gloves

- General:

- Spills:
  - Use water or foam
  - Neutralize with a dry chemical

Health Hazard:

- Inhaling:
  - Not available

Reactivity:

- Reacts with:
  - Not available

Toxicity Data:

- CAS #: Not available
- RTECS #: Not available

Handling:

- Storage:
  - Not available
- Disposal:
  - Not available

Toxicological Data:

- No data available

Additional Information:

- Not available

Date of Last Revision: 11/2/2011
Reids Vapor Pressure (RVP) Eagle Ford has a RVP of 14-15, RVP gasoline Max 9.0 psi summer and below 14.7 PSI for winter Gasoline
Most Crudes are Group 3 Oils
- Moderately volatile
- Moderate to high viscosity
- Specific Gravity 0.82 – 0.85
- Variable toxicity in water column
- May coat or smother organisms
- Non-homogenous mixture

Scenario:
1,000 bbl spill in open water
Wind 15 knots, Water temp 75° F
Fate across 5 day period
Group 1 & 2 Refined Products
- Highly volatile
- Low viscosity
- Specific Gravity <0.8 – 0.85
- Highly toxic in water column
- Do not coat or smother organisms
- Homogenous mixture

Scenario:
1,000 bbl spill in open water
Wind 15 knots, Water temp 75° F
Fate across 5 day period
Very Light Crudes (Fracked Shale):
Combined characteristics of Group 1, 2 & 3
- Highly volatile
- Low viscosity
- Specific Gravity BK 0.82* EF0.77*
- Likely toxic in water column
- Unlikely to coat or smother organisms

Scenario:
1,000 bbl spill in open water
Wind 15 knots, Water temp 75° F
Fate across 5 day period

*Crude Oil Analysis, LSU 2014
Diluted Bitumen products initially behave much like Group 4
- Slightly volatile
- Highly viscous
- Specific Gravity 0.85 – 0.95
- Low toxicity in water column
- Will coat or smother organisms
- Homogenous mixture

Scenario:
1,000 bbl spill in open water
Wind 15 knots, Water temp 75° F
Fate across 5 day period
NRT Spill Considerations / Recommendations

Air Monitoring for Fire:

- \( \text{O}_2 \)
- \( \text{CO} \)
- Explosive Limits - LEL-UEL
- \( \text{H}_2\text{S} \)
- Benzene
- VOCs
- SOX and NOX
- Particulates

• Recommendation for 4 or 5 gas monitoring systems
• Photo ionization detectors (PID)/Flame ionization detectors (FID) for VOCs
• Chem. Specific monitors
Anticipated Effects Very Light Crude Oils
The Incident Commander must determine the response:

- Shoreline oiling: Anticipated to be light, appears responsive to high volume, low temperature wash
- Wildlife oiling: Due to low viscosity, unlikely to smother or coat. May be subject to ingestion during preening
- Water column toxicity: Potentially high, due to concentrations of aromatic compounds.
- Vegetation toxicity: Potentially high, due to concentrations of aromatic compounds.

- Offensive tactics (Safety number one priority)
- Defensive tactics (Well ahead of approaching spill)
- Nonintervention
Response Strategies
Very Light Crude Oils

• Cautions: Highly volatility, high explosive potential. Air monitoring required, control potential ignition sources

• Methods:
  • Boom it?: With caution, avoid confined spaces
  • Skim it?: Maybe, some recoverable oil may remain on water
  • Burn it?: Not recommended, could easily get out of control
  • Disperse it?: No need, naturally highly dispersible
Anticipated Effects Diluted Bitumen Products
The Incident Commander must determine the response:

- **Shoreline oiling:** Anticipated to be heavy. Oil is adhesive, and may require aggressive techniques for removal such as high temperature, high pressure wash or surface cleaning agents.

- **Wildlife oiling:** May be extensive due to smothering and coating effects.

- **Water column toxicity:** Likely low to moderate. Minimal dispersion of blended product in available date, but potentially high concentration of BTEX compounds in diluent.

- **Vegetation toxicity:** Variable. Not acutely toxic but likely to cause heavy coating.
Response Strategies
Diluted Bitumen Products

- Cautions: In contained spaces, highly volatile components may generate explosive potential, just like other crudes. However, current data does not suggest volatilization of diluent components at a faster rate because of the artificial mixing.

- Methods
  - Boom it?: Yes
  - Skim it?: Yes
  - Burn it?: May work when fresh, efficacy limited after weathering.
  - Disperse it?: Low dispersability even when fresh
Take Home and Caveats

- SDS Sheets may not depict true nature of product being carried.
- Little real world experience exists with spills of these types of oils
- Experimental data on behaviors of these oil is minimal
- We are learning as we go!
References

- Crude Oil Analysis from SPL Houston Laboratories, Certificate of Analysis #1030-14040719-001A, May 5, 2014, provided to Scott Miles, Louisiana State University
- EPA OSC website: www.epaosc.org/bridgerpipeline
- EPA website: http://www.epa.gov/enbridgesp
- Gulf Strike Team bulletin: Responder Awareness – North American Crude Oil Shipments
- NOAA ADIOS 2 Model, updated 1/28/15
- NOAA NOAA; Bakken Crude Oil Spill Barge E2MS 303 .ppt 2-2014
- NOAA, Unconventional Oils: A Responder’s Perspective, .ppt 2-2-15
Discussion