1. Product and Company Identification

Material name: Spent Sulfuric Acid
Revision date: 06-10-2011
Version #: 01
CAS #: Mixture
MSDS Number: 605
Product use: This product is intended for use as a refinery feedstock, fuel or for use in engineered processes. Use in other applications may result in higher exposures and require additional controls, such as local exhaust ventilation and personal protective equipment.

Synonym(s): Spent alkylation acid
See section 16 for complete information.

Manufacturer/Supplier: Valero Marketing & Supply Company and Affiliates
P.O. Box 696000
San Antonio, TX 78269-6000
General Assistance 210-345-4593

Emergency: 24 Hour Emergency 866-565-5220
1-800-424-9300 (CHEMTREC USA)

2. Hazards Identification

Physical state: Solid.
Appearance: Colorless to dark brown, oily liquid.

Emergency overview: DANGER!
Causes skin, eye and respiratory tract burns. Harmful if inhaled. Possible cancer hazard - may cause cancer based on animal data.

OSHA regulatory status: This product is considered hazardous under 29 CFR 1910.1200 (Hazard Communication).

Potential health effects:

Routes of exposure: Inhalation. Eye contact. Skin contact. Ingestion.

Eyes: Causes eye burns.
Skin: Causes skin burns.
Inhalation: Causes respiratory tract burns. Harmful if inhaled.
Ingestion: May cause burns in mucous membranes, throat, esophagus and stomach.

Chronic effects: Possible cancer hazard - may cause cancer based on animal data.

Signs and symptoms: Contact with this material will cause burns to the skin, eyes and mucous membranes. Persons with pre-existing respiratory tract, skin and lung (such as asthma) disorders may be aggravated by exposure to this product.

Potential environmental effects: The product may affect the acidity (pH-factor) in water with risk of harmful effects to aquatic organisms.

3. Composition / Information on Ingredients

<table>
<thead>
<tr>
<th>Components</th>
<th>CAS #</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>7664-93-9</td>
<td>88 - 92</td>
</tr>
<tr>
<td>Distillates (petroleum), alkylate</td>
<td>64741-73-7</td>
<td>6 - 8</td>
</tr>
<tr>
<td>Diethyl sulfate</td>
<td>64-67-5</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>Dimethyl sulfate</td>
<td>77-78-1</td>
<td>&lt;0.2</td>
</tr>
</tbody>
</table>
Composition comments
This product is a blend of sulfuric acid and hydrocarbon produced in a sulfuric acid based petroleum alkylation unit. It may contain approximately 0.5% dialkyl sulfates including dimethyl and diethyl sulfate. The alkylation distillates in this product are a complex combination of hydrocarbons produced by distillation of the reaction products of isobutene with mono-olefinic hydrocarbons usually ranging in carbon numbers from C3 through C5. It consists of predominately branched-chain saturated hydrocarbons having carbon numbers in the range of C11 through C17.

4. First Aid Measures
First aid procedures
Eye contact
Immediately flush eyes with plenty of water for at least 15 minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Call a physician or poison control center immediately.

Skin contact
Wash off immediately with soap and plenty of water. Remove contaminated clothing and shoes. Call a physician or poison control center immediately. Wash clothing separately before reuse. Destroy or thoroughly clean contaminated shoes.

Inhalation
Move to fresh air. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Call a physician or poison control center immediately.

Ingestion
Rinse mouth thoroughly. Do not induce vomiting without advice from poison control center. Do not give mouth-to-mouth resuscitation. If vomiting occurs, keep head low so that stomach content does not get into the lungs. Call a physician or poison control center.

Notes to physician
In case of shortness of breath, give oxygen. Keep victim warm. Keep victim under observation. Symptoms may be delayed.

General advice
If exposed or concerned: get medical attention/advice. Ensure that medical personnel are aware of the material(s) involved, and take precautions to protect themselves. Show this safety data sheet to the doctor in attendance. Wash contaminated clothing before re-use.

5. Fire Fighting Measures
Flammable properties
No unusual fire or explosion hazards noted.

Extinguishing media
Suitable extinguishing media

Unsuitable extinguishing media
Do not use a solid water stream as it may scatter and spread fire.

Protection of firefighters
Protective equipment and precautions for firefighters
Wear full protective clothing, including helmet, self-contained positive pressure or pressure demand breathing apparatus, protective clothing and face mask.

Fire fighting equipment/instructions
Wear full protective clothing, including helmet, self-contained positive pressure or pressure demand breathing apparatus, protective clothing and face mask. Fight fire from maximum distance or use unmanned hose holders or monitor nozzles. Move containers from fire area if you can do it without risk. In the event of fire, cool tanks with water spray.

Specific methods
In the event of fire and/or explosion do not breathe fumes.

Hazardous combustion products
Carbon oxides. Sulfur oxides.

6. Accidental Release Measures
Personal precautions
Keep unnecessary personnel away. Local authorities should be advised if significant spills cannot be contained. Keep upwind. Keep out of low areas. Ventilate closed spaces before entering. Do not touch damaged containers or spilled material unless wearing appropriate protective clothing. See Section 8 of the MSDS for Personal Protective Equipment.

Environmental precautions
Avoid dispersal of spilled material and runoff and contact with soil, waterways, drains and sewers. Stay upwind and away from spill. Wear appropriate protective equipment including respiratory protection as conditions warrant. Do not enter or stay in area unless monitoring indicates that it is safe to do so. Isolate hazard area and restrict entry to emergency crew. Review Fire Fighting Measures section before proceeding with clean up. Stop leak if it can be done without risk. Use water spray to disperse vapors. If spill of any amount is made into or upon navigable waters, the contiguous zone, or adjoining shorelines, contact the National Response Center at 800-424-8802. For highway or railway spills, contact Chemtrec at 800-424-9300.

Methods for containment
Dike the spilled material, where this is possible. Prevent entry into waterways, sewers, basements or confined areas.
Methods for cleaning up

Small spills: Absorb spill with vermiculite or other inert material, then place in a container for chemical waste. Clean surface thoroughly to remove residual contamination. This material and its container must be disposed of as hazardous waste.

Large Spills: Prevent product from entering drains. Do not allow material to contaminate ground water system. Should not be released into the environment.

Other information

Clean up in accordance with all applicable regulations.

7. Handling and Storage

Handling

Wear personal protective equipment. Do not breathe mist or vapor. Do not get in eyes, on skin, on clothing. Do not taste or swallow. Avoid prolonged exposure. Use only with adequate ventilation. Wash thoroughly after handling. When using, do not eat, drink or smoke. Avoid release to the environment.

Storage

Keep container tightly closed in a cool, well-ventilated place. Keep away from food, drink and animal feedingstuffs. Keep out of the reach of children.

8. Exposure Controls / Personal Protection

Occupational exposure limits

ACGIH

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Value</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Sulfuric Acid</td>
<td>TWA</td>
<td>0.5 mg/m3</td>
<td>(total dust)</td>
</tr>
</tbody>
</table>

US. ACGIH Threshold Limit Values

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>TWA</td>
<td>0.1 ppm</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>TWA</td>
<td>0.2 mg/m3</td>
<td>Thoracic fraction.</td>
</tr>
</tbody>
</table>

US. OSHA Table Z-1 Limits for Air Contaminants (29 CFR 1910.1000)

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>PEL</td>
<td>5 mg/m3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 ppm</td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>PEL</td>
<td>1 mg/m3</td>
</tr>
</tbody>
</table>

Canada. Alberta OELs (Occupational Health & Safety Code, Schedule 1, Table 2)

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>TWA</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 mg/m3</td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>STEL</td>
<td>3 mg/m3</td>
</tr>
<tr>
<td></td>
<td>TWA</td>
<td>1 mg/m3</td>
</tr>
</tbody>
</table>

Canada. British Columbia OELs. (Occupational Exposure Limits for Chemical Substances, Occupational Health and Safety Regulation 296/97, as amended)

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>Ceiling</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>TWA</td>
<td>0.2 mg/m3</td>
</tr>
</tbody>
</table>

Canada. Ontario OELs. (Ministry of Labor - Control of Exposure to Biological or Chemical Agents)

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>TWA</td>
<td>0.5 mg/m3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 ppm</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>TWA</td>
<td>0.2 mg/m3</td>
<td>Thoracic fraction.</td>
</tr>
</tbody>
</table>

Canada. Quebec OELS. (Ministry of Labor - Regulation Respecting the Quality of the Work Environment)

<table>
<thead>
<tr>
<th>Components</th>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfate (77-78-1)</td>
<td>TWA</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.52 mg/m3</td>
</tr>
<tr>
<td>Sulfuric acid (7664-93-9)</td>
<td>STEL</td>
<td>3 mg/m3</td>
</tr>
<tr>
<td></td>
<td>TWA</td>
<td>1 mg/m3</td>
</tr>
</tbody>
</table>
Components | Type | Value
--- | --- | ---
Dimethyl sulfate (77-78-1) | TWA | 0.1 ppm
 | | 0.52 mg/m3

**Engineering controls**
Provide adequate general and local exhaust ventilation. Use process enclosures, local exhaust ventilation, or other engineering controls to control airborne levels below recommended exposure limits. It is recommended that all dust control equipment such as local exhaust ventilation and material transport systems involved in handling of this product contain explosion relief vents or an explosion suppression system or an oxygen deficient environment. Ensure that dust-handling systems (such as exhaust ducts, dust collectors, vessels, and processing equipment) are designed in a manner to prevent the escape of dust into the work area (i.e., there is no leakage from the equipment). Use only appropriately classified electrical equipment and powered industrial trucks.

**Personal protective equipment**

**Eye / face protection**
Safety glasses.

**Skin protection**
Wear chemical-resistant, impervious gloves. Full body suit and boots are recommended when handling large volumes or in emergency situations. Flame retardant protective clothing is recommended.

**Respiratory protection**
Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator. If workplace exposure limits for product or components are exceeded, NIOSH approved equipment should be worn. Proper respirator selection should be determined by adequately trained personnel, based on the contaminants, the degree of potential exposure and published respiratory protection factors. This equipment should be available for nonroutine and emergency use.

**General hygiene considerations**
Consult supervisor for special handling instructions. Keep away from food and drink. Wash hands before breaks and immediately after handling the product. Provide eyewash station and safety shower. Handle in accordance with good industrial hygiene and safety practice.

### 9. Physical & Chemical Properties

**Appearance**
Colorless to dark brown, oily liquid.

**Color**
Colorless to dark brown.

**Odor**
Hydrocarbon.

**Odor threshold**
Not available.

**Physical state**
Solid.

**Form**
Oily liquid.

**pH**
Acidic

**Melting point**
51 °F (10.56 °C)

**Freezing point**
Not available.

**Boiling point**
554 °F (290 °C)

**Flash point**
Not available.

**Evaporation rate**
Not available.

**Flammability limits in air, upper, % by volume**
Not available.

**Flammability limits in air, lower, % by volume**
Not available.

**Vapor pressure**
Not available.

**Vapor density**
Not available.

**Specific gravity**
1.84

**Solubility (water)**
Soluble.

**Partition coefficient (n-octanol/water)**
No data available.

**Auto-ignition temperature**
Not available.

**Decomposition temperature**
Not available.
10. Chemical Stability & Reactivity Information

Chemical stability
Stable under normal temperature conditions and recommended use.

Conditions to avoid
None known.

Incompatible materials

Hazardous decomposition products
Sulfur oxides.

Possibility of hazardous reactions
Hazardous polymerization does not occur.

11. Toxicological Information

Toxicological data

Components | Test Results |
---------- | ------------|
Sulfuric acid (7664-93-9) | Acute Oral LD50 Rat: 2140 mg/kg |

Acute effects
Causes skin, eye and respiratory tract burns. Harmful if inhaled.

Local effects

US ACGIH Threshold Limit Values: Skin designation
Dimethyl sulfate (CAS 77-78-1) Can be absorbed through the skin.

Chronic effects
Repeated contact with dilute sulfuric acid solutions can cause dermatitis, and repeated or prolonged inhalation of a mist of sulfuric acid can cause inflammation of the upper respiratory tract, leading to chronic bronchitis. Inhalation of concentrated vapor or mists from hot acid or oleum can cause rapid loss of consciousness with serious damage to lung tissue. Severe exposure may cause a chemical pneumonitis; erosion of the teeth due to exposure to strong acid fumes has been recognized in industry.

Carcinogenicity
Possible cancer hazard - may cause cancer based on animal data.

ACGIH Carcinogens
Dimethyl sulfate (CAS 77-78-1) A3 Confirmed animal carcinogen with unknown relevance to humans.

IARC Monographs. Overall Evaluation of Carcinogenicity
Diethyl sulfate (CAS 64-67-5) 2A Probably carcinogenic to humans.
Dimethyl sulfate (CAS 77-78-1) 2A Probably carcinogenic to humans.

US NTP Report on Carcinogens: Anticipated carcinogen
Diethyl sulfate (CAS 64-67-5) Anticipated carcinogen.
Dimethyl sulfate (CAS 77-78-1) Anticipated carcinogen.

12. Ecological Information

Ecotoxicological data

Components | Test Results |
---------- | ------------|
Sulfuric acid (7664-93-9) | LC50 Western mosquitofish (Gambusia affinis): 42 mg/l 96 hours |

Ecotoxicity
The product may affect the acidity (pH-factor) in water with risk of harmful effects to aquatic organisms.

Persistence and degradability
No data available.

Bioaccumulation / Accumulation
No data available.

Partition coefficient (n-octanol/water)
No data available.

Mobility in environmental media
No data available.

13. Disposal Considerations

Disposal instructions
Dispose in accordance with all applicable regulations. Incinerate the material under controlled conditions in an approved incinerator. Do not allow this material to drain into sewers/water supplies. Do not contaminate ponds, waterways or ditches with chemical or used container.
14. Transport Information

DOT

Basic shipping requirements:
- UN number: UN1832
- Proper shipping name: Sulfuric acid, spent
- Hazard class: 8
- Packing group: II
- Labels required: 8

Additional information:
- Special provisions: A3, A7, B2, B83, B84, IB2, N34, T8, TP2, TP12
- Packaging exceptions: None
- Packaging non bulk: 202
- Packaging bulk: 242
- ERG number: 137

IATA

Basic shipping requirements:
- UN number: 1832
- Proper shipping name: Sulphuric acid, spent
- Hazard class: 8
- Packing group: II

Additional information:
- ERG code: 8L

IMDG

Basic shipping requirements:
- UN number: 1832
- Proper shipping name: SULPHURIC ACID, SPENT
- Hazard class: 8
- EmS No.: F-A, S-B

TDG

Basic shipping requirements:
- Proper shipping name: SULFURIC ACID, SPENT
- Hazard class: 8
- UN number: UN1832
- Packing group: II

Additional information:
- Special provisions: 19

15. Regulatory Information

US federal regulations

This product is a "Hazardous Chemical" as defined by the OSHA Hazard Communication Standard 29 CFR 1910.1200 (OSHA) and 8 CCR § 5194 (Cal/OSHA).

All components are on the U.S. EPA TSCA Inventory List.

TSCA Section 12(b) Export Notification(40 CFR 707, Subpt. D)

Not regulated.

US EPCRA (SARA Title III) Section 302 - Extremely Hazardous Spill: Reportable quantity
- Dimethyl sulfate (CAS 77-78-1) 100 LBS
- Sulfuric acid (CAS 7664-93-9) 1000 LBS

US EPCRA (SARA Title III) Section 302 - Extremely Hazardous Substance: Threshold Planning Quantity
- Dimethyl sulfate (CAS 77-78-1) 500 LBS
- Sulfuric acid (CAS 7664-93-9) 1000 LBS

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: De minimis concentration
- Diethyl sulfate (CAS 64-67-5) 0.1 %
- Dimethyl sulfate (CAS 77-78-1) 0.1 %
- Sulfuric acid (CAS 7664-93-9) 1.0 %

US EPCRA (SARA Title III) Section 313 - Toxic Chemical: Listed substance
- Diethyl sulfate (CAS 64-67-5) Listed
- Dimethyl sulfate (CAS 77-78-1) Listed
Sulfuric acid (CAS 7664-93-9) Listed.

CERCLA (Superfund) reportable quantity (lbs) (40 CFR 302.4)
- Sulfuric acid: 1000
- Diethyl sulfate: 10
- Dimethyl sulfate: 100

Superfund Amendments and Reauthorization Act of 1986 (SARA)
- Immediate Hazard: Yes
- Delayed Hazard: Yes
- Fire Hazard: No
- Pressure Hazard: No
- Reactivity Hazard: No

Section 302 extremely hazardous substance (40 CFR 355, Appendix A)
- Yes

Section 311/312 (40 CFR 370)
- Yes

Drug Enforcement Administration (DEA) (21 CFR 1308.11-15)
- Not controlled

WHMIS status
- Controlled

WHMIS classification
- D1A - Immediate/Serious-VERY TOXIC
- E - Corrosive

WHMIS labeling

Inventory status

<table>
<thead>
<tr>
<th>Country(s) or region</th>
<th>Inventory name</th>
<th>On inventory (yes/no)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>Australian Inventory of Chemical Substances (AICS)</td>
<td>Yes</td>
</tr>
<tr>
<td>Canada</td>
<td>Domestic Substances List (DSL)</td>
<td>Yes</td>
</tr>
<tr>
<td>Canada</td>
<td>Non-Domestic Substances List (NDSL)</td>
<td>No</td>
</tr>
<tr>
<td>China</td>
<td>Inventory of Existing Chemical Substances in China (IECSC)</td>
<td>Yes</td>
</tr>
<tr>
<td>Europe</td>
<td>European Inventory of Existing Commercial Chemical Substances (EINECS)</td>
<td>Yes</td>
</tr>
<tr>
<td>Europe</td>
<td>European List of Notified Chemical Substances (ELINCS)</td>
<td>No</td>
</tr>
<tr>
<td>Japan</td>
<td>Inventory of Existing and New Chemical Substances (ENCS)</td>
<td>No</td>
</tr>
<tr>
<td>Korea</td>
<td>Existing Chemicals List (ECL)</td>
<td>Yes</td>
</tr>
<tr>
<td>New Zealand</td>
<td>New Zealand Inventory</td>
<td>Yes</td>
</tr>
<tr>
<td>Philippines</td>
<td>Philippine Inventory of Chemicals and Chemical Substances (PICCS)</td>
<td>Yes</td>
</tr>
<tr>
<td>United States &amp; Puerto Rico</td>
<td>Toxic Substances Control Act (TSCA) Inventory</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* A "Yes" indicates that all components of this product comply with the inventory requirements administered by the governing country(s)

State regulations

US - California Hazardous Substances (Director's): Listed substance
- Diethyl sulfate (CAS 64-67-5) Listed.
- Dimethyl sulfate (CAS 77-78-1) Listed.
- Sulfuric acid (CAS 7664-93-9) Listed.

US - California Proposition 65 - Carcinogens & Reproductive Toxicity (CRT): Listed substance
- Dimethyl sulfate (CAS 77-78-1) Listed: January 1, 1988 Carcinogenic.
US - Massachusetts RTK - Substance: Listed substance
Diethyl sulfate (CAS 64-67-5) Listed.
Dimethyl sulfate (CAS 77-78-1) Listed.
Sulfuric acid (CAS 7664-93-9) Listed.

US - New Jersey Community RTK (EHS Survey): Reportable threshold
Diethyl sulfate (CAS 64-67-5) 500 LBS
Dimethyl sulfate (CAS 77-78-1) 500 LBS
Sulfuric acid (CAS 7664-93-9) 500 LBS

US - New Jersey RTK - Substances: Listed substance
Diethyl sulfate (CAS 64-67-5) Listed.
Dimethyl sulfate (CAS 77-78-1) Listed.
Sulfuric acid (CAS 7664-93-9) Listed.

US - Pennsylvania RTK - Hazardous Substances: Listed substance
Diethyl sulfate (CAS 64-67-5) Listed.
Dimethyl sulfate (CAS 77-78-1) Listed.
Sulfuric acid (CAS 7664-93-9) Listed.

US - Pennsylvania RTK - Hazardous Substances: Special hazard
Diethyl sulfate (CAS 64-67-5) Special hazard.
Dimethyl sulfate (CAS 77-78-1) Special hazard.

16. Other Information

Other information
Note: This Material Safety Data Sheet applies to the listed products and synonym descriptions for Hazard Communication purposes only. Technical Specifications vary greatly depending on the products and are not reflected in this document. Consult specification sheets for technical information.

HMIS® ratings
Health: 3*
Flammability: 1
Physical hazard: 0

NFPA ratings
Health: 3
Flammability: 1
Instability: 0

Disclaimer
This Material Safety Data Sheet (MSDS) was prepared in accordance with 29 CFR 1910.1200 by Valero Marketing & Supply Co., ("VALERO"). VALERO does not assume any liability arising out of product use by others. The information, recommendations, and suggestions presented in this MSDS are based upon test results and data believed to be reliable. The end user of the product has the responsibility for evaluating the adequacy of the data under the conditions of use, determining the safety, toxicity and suitability of the product under these conditions, and obtaining additional or clarifying information where uncertainty exists. No guarantee expressed or implied is made as to the effects of such use, the results to be obtained, or the safety and toxicity of the product in any specific application. Furthermore, the information herein is not represented as absolutely complete, since it is not practicable to provide all the scientific and study information in the format of this document, plus additional information may be necessary under exceptional conditions of use, or because of applicable laws or government regulations.

Issue date
06-10-2011