



MATERIAL SAFETY DATA SHEET

Spent Sulfuric Acid

VALERO MARKETING & SUPPLY COMPANY
and Affiliates
P.O. Box 696000
San Antonio, TX 78269-6000

Emergency Phone Numbers

24 Hour Emergency: 866-565-5220
Chemtrec Emergency: 800-424-9300

General Assistance

General Assistance: 210-345-4593

BRAND NAMES: Valero, Diamond Shamrock, Shamrock, Ultramar, Beacon, Total

Section 1. Chemical Product and Company Identification

Common / Trade name : Spent Sulfuric Acid

Synonym : Spent Alkylation Acid

SYNONYMS/COMMON NAMES: 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 product and are not reflected in this document. Consult specification sheets for technical information. This product contains ingredients that are considered to be hazardous as defined by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

Material uses : 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.

MSDS # : 605

CAS # : Mixture

Section 2. Composition, information on ingredients

<u>Name</u>	<u>CAS number</u>	<u>Concentration (%)</u>
Sulfuric Acid	7664-93-9	88 - 92
Distillates (petroleum), alkylate	64741-73-7	6 - 8
Dmiethyl Sulfate	77-78-1	<0.2
Diethyl Sulfate	64-67-5	<0.2

Section 3. Hazards Identification

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. Sulfuric Acid is extremely corrosive to skin, eyes and mucous membranes. Concentrated sulfuric acid is very reactive when mixed with water. If blending water and acid, always add acid to water slowly, never pour water into concentrated acid.

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 and boiling in the range of 401° to 608°F.

Physical state : Liquid. (COLORLESS TO DARK BROWN OILY LIQUID [NOTE: PURE COMPOUND IS A SOLID BELOW 51 F. OFTEN USED IN AQUEOUS SOLUTION])

Emergency overview : Warning!

Continued on next page

CAUSES SKIN IRRITATION.
 CONTAINS MATERIAL WHICH CAUSES DAMAGE TO THE FOLLOWING ORGANS:
 LUNGS, MUCOUS MEMBRANES, RESPIRATORY TRACT, SKIN, EYE, LENS OR
 CORNEA, TEETH.
 SUSPECT CANCER HAZARD.
 CONTAINS MATERIAL WHICH MAY CAUSE CANCER.
 Avoid contact with skin and clothing. Wash thoroughly after handling. Risk of cancer depends on duration and level of exposure.

- Routes of entry** : Dermal contact. Eye contact. Inhalation. Ingestion.
- Potential acute health effects**
- Eyes** : Severely corrosive to the eyes. Inflammation of the eye is characterized by redness, watering and itching. May cause corneal opacity. Liquid, spray or mist may produce tissue damage, particularly to mucous membranes of eyes, mouth and respiratory tract.
- Skin** : Corrosive to skin on contact. Skin contact can produce inflammation and blistering. Skin inflammation is characterized by itching, scaling, reddening or, occasionally, blistering.
- Inhalation** : Corrosive to the respiratory system. Inhalation of the spray or mist may produce severe irritation of respiratory tract, characterized by coughing, choking or shortness of breath. Possible risk of irreversible effects. After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis.
- Ingestion** : Irritating to mouth, throat and stomach. May cause burns to mouth, throat and stomach. May be fatal if swallowed.
- Medical conditions aggravated by over-exposure** : Preexisting eye, skin, and respiratory disorders may be aggravated by exposure to this product.
- Over-exposure signs/symptoms** : Nasal and respiratory tract irritation, central nervous system effects including excitation, euphoria, contracted eye pupils, dizziness, drowsiness, blurred vision, fatigue, nausea, headache, loss of reflexes, tremors, convulsions, seizures, loss of consciousness, coma, respiratory arrest or sudden death could occur as a result of long term and/or high concentration exposure to vapors. May also cause irregular heart rhythm. After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis.

See toxicological information (section 11)

Section 4. First Aid Measures

- Eye contact** : In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention immediately.
- Skin contact** : In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention.
- Inhalation** : If inhaled, remove to fresh air. If breathing is difficult, give oxygen. If not breathing, give artificial respiration. Get medical attention.
- Ingestion** : Do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If potentially dangerous quantities of this material have been swallowed, call a physician immediately.
- Notes to physician** : In case of ingestion, treat symptomatically. Consideration should be given to the use of an intratracheal tube, to prevent aspiration. Individuals intoxicated by the product should be hospitalized immediately. Positive pressure ventilation may be necessary. After the initial episode, individuals should be followed for the delayed appearance of pulmonary edema and chemical pneumonitis. Individuals with chronic pulmonary disease will be more seriously impaired, and recovery from inhalation exposure may be complicated. In case of skin injection, prompt debridement of the wound is necessary to minimize necrosis and tissue loss.

Section 5. Fire Fighting Measures

- Flammability of the product** : May be combustible at high temperature.
- Auto-ignition temperature** : 232.2 to 456.1°C (450 to 853°F)
- Flash point** : Open cup: >93.36°C (200°F) (Tag Open Cup - Modified ASTM D 3143).
- Flammable limits** : Lower: 1% Upper: 8%
- Products of combustion** : These products are carbon oxides (CO, CO₂), nitrogen and sulfur oxides (NO_x, SO_x), particulate matter, VOC's.
- Fire-fighting media and instructions** : Use an extinguishing agent suitable for the surrounding fire. Foam, dry chemical or carbon dioxide type extinguishing agents may all be suitable for product, depending on size or potential size of fire and circumstances related to the situation. Plan fire protection and response strategy through consultation with local fire protection authorities or appropriate specialists.
Fires involving small amounts of combustibles may be smothered with suitable dry chemical. Use water on combustibles burning in vicinity of this material but use care as water applied directly to this acid results in evolution of heat and causes spattering.
No specific hazard.
- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.
- Special remarks on fire hazards** : Hydrocarbon liquid is volatile and gives off invisible vapors. Either the liquid or vapor may settle in low areas or travel some distance along the ground surface to ignition sources where they may ignite or explode.
Keep product away from ignition sources such a heat, sparks, lights, static electricity, and open flames.
Sulfuric acid is not flammable but highly reactive and capable of igniting finely divided combustible materials on contact. It reacts violently with water and organic materials with evolution of heat. Extremely hazardous in contact with many materials, particularly carbides, chlorates, fulminates, nitrates, picrates, powdered metals and other combustible materials. Attacks many metals releasing hydrogen.

Section 6. Accidental Release Measures

- Personal precautions** : Immediately contact emergency personnel. Keep unnecessary personnel away. Use suitable protective equipment (section 8).
- Environmental precautions** : If facility or operation has an "oil or hazardous substance contingency plan", activate its procedures. 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. Extremely flammable. Review Fire and Explosion Hazard Data before proceeding with clean up. Keep all sources of ignition (flames, smoking, flares, etc.) and hot surfaces away from release. Contain spill in smallest possible area. Recover as much product as possible (e.g., by vacuuming). Stop leak if it can be done without risk. Use water spray to disperse vapors. Spilled material may be absorbed by an appropriate absorbent, and then handled in accordance with environmental regulations. Prevent spilled material from entering sewers, storm drains, other unauthorized treatment or drainage systems and natural waterways. Contact fire authorities and appropriate federal, state and local agencies. 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.

Section 7. Handling and Storage

- Handling** : Avoid contact with skin and clothing. Keep container closed. Use only with adequate ventilation. Avoid breathing vapor or mist. Wash thoroughly after handling. To avoid fire or explosion, dissipate static electricity during transfer by grounding and bonding containers and equipment before transferring material. Use good personal hygiene practices. After handling this product, wash hands before eating, drinking, or using toilet facilities.
- Storage** : Keep container tightly closed. Keep container in a cool, well-ventilated area.

Section 8. Exposure controls, personal protection

- Engineering controls** : Provide a readily-accessible eyewash facility and quick-drench safety shower. Keep container tightly closed and in a well-ventilated place. Local exhaust ventilation should be provided.

Personal protection

- Eyes** : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts.
- Skin** : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Respiratory** : 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.
- Hands** : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
- Personal protective equipment (Pictograms)** : Consult your Supervisor or S.O.P. for special handling directions.



- Personal protection in case of a large spill** : Splash goggles. Full suit. Boots. Gloves. Suggested protective clothing might not be adequate. Consult a specialist before handling this product. Wear MSHA/NIOSH-approved self-contained breathing apparatus or equivalent and full protective gear.

Component

Sulfuric Acid

Exposure limits

ACGIH TLV (United States, 1/2004). Notes: Thoracic fraction. See Appendix C, paragraph B. Thoracic Particulate Mass TLVs (TPM-TLVs) for those materials that are hazardous when deposited anywhere within the lung airways and the gas-exchange region.

ACGIH 2004 Adoption Refers to Appendix A -- Carcinogens.

Sulfuric acid contained in strong inorganic acid mists

TWA: 0.2 mg/m³ 8 hour/hours. Form: All forms

NIOSH REL (United States, 12/2001).

TWA: 1 mg/m³ 10 hour/hours. Form: All forms

OSHA PEL (United States, 8/1997).

TWA: 1 mg/m³ 8 hour/hours. Form: All forms

Dmiethyl Sulfate

ACGIH TLV (United States, 1/2004). Skin Notes: Substance identified by other sources as a suspected or confirmed human carcinogen. 1996 Adoption Refers to Appendix A -- Carcinogens.

TWA: 0.1 ppm 8 hour/hours. Form: All forms

NIOSH REL (United States, 12/2001). Skin Notes: See Appendix A -

NIOSH Potential Occupational Carcinogen

TWA: 0.1 ppm 10 hour/hours. Form: All forms

OSHA PEL (United States, 8/1997). Skin

TWA: 1 ppm 8 hour/hours. Form: All forms

Consult local authorities for acceptable exposure limits.

Section 9. Physical and Chemical Properties

Physical state	: Liquid. (COLORLESS TO DARK BROWN OILY LIQUID [NOTE: PURE COMPOUND IS A SOLID BELOW 51 F. OFTEN USED IN AQUEOUS SOLUTION])
Odor	: Hydrocarbon.
Molecular formula	: H ₂ O ₄ S
Boiling point	: 290°C (554°F)
Melting/freezing point	: 10.56°C (51°F)
Specific gravity	: 1.84 (Water = 1)
Solubility	: Soluble in cold water.

Section 10. Stability and reactivity data

Stability and reactivity	: The product is stable.
Incompatibility with various substances	: Extremely reactive or incompatible with oxidizing agents, reducing agents, organic materials, acids, water.

Section 11. Toxicological Information**Toxicity data**

The main toxicological effects of this material are attributable to sulfuric acid.

Sulfuric Acid (Acute) Among laboratory animals, guinea pigs are more sensitive to sulfuric acid than rats, mice, or rabbits. Death in guinea pigs results from severe laryngeal spasm and bronchial constriction. The LC₅₀ values for an 8-hour exposure to sulfuric acid range from about 20 to 60 mg/m³, depending on the age of the animals and the particle size of the sulfuric acid mist. Young animals (1 month) are more sensitive than adults (18 months). At lethal concentrations, 2.7 µm particles are more toxic than 0.8 µm particles. A concentration of 8 mg/m³ (1 µm particle size) produced no mortality, but lung pathology developed following 8-hour exposures; extending the exposure time to 72 hours did not produce deaths; however, it did increase the severity of the pulmonary injury.

(Human Studies) In numerous case reports and reviews of the literature document the clinical toxicology of ingested sulfuric acid, with particular attention to esophageal and gastric necrosis.

Inhalation studies have been conducted on normal, unacclimated human subjects, who were exposed to sulfuric acid mist concentrations ranging from 0.35 to 5 mg/m³ and the duration of exposure ranged from 5 to 15 minutes. Concentrations below 1 mg/m³ could not be detected by odor, taste or irritation. For two subjects, the threshold was 1 mg/m³, a concentration of 3 mg/m³ was noticed by all, and 5 mg/m³ was considered very objectionable to some but less so to others. A deep breath at the last concentration usually produced coughing. Pneumotachograph tracings, showing changes in pulmonary function of 15 subjects exposed to measured sulfuric acid mist concentrations, were also present.

Dimethyl Sulfate Cases of dimethyl sulfate poisonings in industrial workers were reported in the Italian, German, and French literature. Signs and symptoms uniformly found after each exposure began with headache and giddiness with burning of the eyes, reaching maximal intensity in from 2 to 10 hours after the first eye effects. The condition becomes progressively worse with painful, reddened eyes; photophobia; irritation of nose and throat; hoarseness and loss of voice; cough; oppression in the chest; difficult breathing and swallowing; and vomiting, diarrhea, and scalding urination. Painful and difficult urination persists for 3 to 4 days, and congestion of mucous membranes and edema of the larynx may persist for 2 weeks. In some cases examined 6 years later, there was some impairment of liver function and reduction in the visual fields for various colors. When death occurs, the signs indicate circulatory failure. The eye effects are probably attributable to the metabolism of dimethyl sulfate to methanol and sulfuric acid. Dimethyl sulfate is readily absorbed through the intact skin, causing blistering, ulceration, necrosis, and systemic intoxication.

Ingredient name	Test	Result	Route	Species
Sulfuric Acid	LD50	2140 mg/kg	Oral	Rat
Dimethyl Sulfate	LD50	205 mg/kg	Oral	Rat
	LD50	140 mg/kg	Oral	Mouse
	LDLo	45 mg/kg	Oral	Rabbit
Diethyl Sulfate	LD50	880 mg/kg	Oral	Rat
	LD50	647 mg/kg	Oral	Mouse

IDLH : 15 mg/m³

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Chronic effects on humans : **CARCINOGENIC EFFECTS:** Classified A2 (Suspected for humans.) by ACGIH [Sulfuric Acid]. Classified A3 (Proven for animals.) by ACGIH [Dimethyl Sulfate]. Classified 2A (Probable for human.) by IARC, 2 (Reasonably anticipated to be human carcinogens.) by NTP [Dimethyl Sulfate]. Classified 2A (Probable for human.) by IARC, 2 (Reasonably anticipated to be human carcinogens.) by NTP [Diethyl Sulfate].

Contains material which causes damage to the following organs: lungs, mucous membranes, upper respiratory tract, skin, eye, lens or cornea, teeth.

Other toxic effects on humans : Very dangerous in case of skin contact (corrosive, irritant, sensitizer, permeator), eye contact (irritant), ingestion or inhalation.

Specific effects

Carcinogenic effects : Contains material which may cause cancer. Risk of cancer depends on duration and level of exposure.

Target organs : Contains material which causes damage to the following organs: lungs, mucous membranes, upper respiratory tract, skin, eye, lens or cornea, teeth.

Section 12. Ecological Information

Ecotoxicity data

<u>Ingredient name</u>	<u>Species</u>	<u>Period</u>	<u>Result</u>
Dmiethyl Sulfate	Lepomis macrochirus (LC50)	96 hour/hours	7.5 mg/l

Products of degradation : These products are sulfur oxides (SO₂, SO₃ etc.).


Toxicity of the products of biodegradation : N/A

Section 13. Disposal Considerations


Waste disposal : Do not puncture or incinerate container. Disposal of this product, solutions and any by-products should at all times comply with the requirements of environmental protection and waste disposal legislation and any regional local authority requirements.

Consult your local or regional authorities.

Section 14. Transport Information

<u>Regulatory information</u>	<u>UN number</u>	<u>Proper shipping name</u>	<u>Class</u>	<u>Packing group</u>	<u>Label</u>	<u>Additional information</u>
DOT Classification	UN1832	SULFURIC ACID, SPENT	8	II		<p>Reportable quantity 1000 lbs. (453.6 kg)</p> <p>Limited quantity Yes.</p> <p>Packaging instruction Passenger aircraft Quantity limitation: Forbidden.</p> <p>Cargo</p>

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						aircraft Quantity limitation: 30 L Special provisions A3, A7, B2, B83, B84, IB2, N34, T8, TP2, TP12
TDG Classification	UN1830	SULFURIC ACID WITH MORE THAN 51 PER CENT ACID; OR SULPHURIC ACID WITH MORE THAN 51 PER CENT ACID	8	II		Not available.

Section 15. Regulatory Information

United States

U.S. Federal regulations : TSCA 8(a) PAIR: Dimethyl Sulfate
TSCA 8(b) inventory: Sulfuric Acid; Distillates (petroleum), alkylate; Dimethyl Sulfate; Diethyl Sulfate
SARA 302/304/311/312 extremely hazardous substances: Sulfuric Acid
SARA 302/304 emergency planning and notification: Sulfuric Acid
SARA 302/304/311/312 hazardous chemicals: Sulfuric Acid
SARA 311/312 MSDS distribution - chemical inventory - hazard identification: Sulfuric Acid: reactive, Immediate (acute) health hazard, Delayed (chronic) health hazard
Clean Water Act (CWA) 307: No products were found.
Clean Water Act (CWA) 311: Sulfuric Acid
Clean Air Act (CAA) 112 accidental release prevention: No products were found.
Clean Air Act (CAA) 112 regulated flammable substances: No products were found.
Clean Air Act (CAA) 112 regulated toxic substances: No products were found.

SARA 313

	<u>Product name</u>	<u>CAS number</u>	<u>Concentration</u>
Form R - Reporting requirements	: Sulfuric Acid	7664-93-9	88 - 92
	: Dmiethyl Sulfate	77-78-1	<0.2
	: Diethyl Sulfate	64-67-5	<0.2
Supplier notification	: Sulfuric Acid	7664-93-9	88 - 92
	: Dmiethyl Sulfate	77-78-1	<0.2
	: Diethyl Sulfate	64-67-5	<0.2

SARA 313 notifications must not be detached from the MSDS and any copying and redistribution of the MSDS shall include copying and redistribution of the notice attached to copies of the MSDS subsequently redistributed.

State regulations : Pennsylvania RTK: Sulfuric Acid: (environmental hazard, generic environmental hazard); Dimethyl Sulfate: (special hazard, environmental hazard, generic environmental hazard); Diethyl Sulfate: (special hazard, environmental hazard, generic environmental hazard)
Massachusetts RTK: Sulfuric Acid; Dimethyl Sulfate; Diethyl Sulfate
New Jersey: Sulfuric Acid; Dimethyl Sulfate; Diethyl Sulfate

WARNING: This product contains chemical/chemicals known to the state of California to cause cancer, birth defects or other reproductive harm.: Dimethyl Sulfate; Diethyl Sulfate
WARNING: This product contains chemical/chemicals known to the state of California to cause cancer.: Dimethyl Sulfate; Diethyl Sulfate

Canada

- WHMIS (Canada)** : Class D-1A: Material causing immediate and serious toxic effects (Very toxic).
 Class D-2A: Material causing other toxic effects (Very toxic).
 Class E: Corrosive liquid.
 CEPA DSL: Sulfuric Acid; Distillates (petroleum), alkylate; Dimethyl Sulfate; Diethyl Sulfate

Section 16. Other Information

- Label requirements** : CAUSES SKIN IRRITATION.
 CONTAINS MATERIAL WHICH CAUSES DAMAGE TO THE FOLLOWING ORGANS:
 LUNGS, MUCOUS MEMBRANES, RESPIRATORY TRACT, SKIN, EYE, LENS OR CORNEA, TEETH.
 SUSPECT CANCER HAZARD.
 CONTAINS MATERIAL WHICH MAY CAUSE CANCER.

Hazardous Material Information System (U.S.A.)

Health	3
Fire hazard	1
Physical Hazard	2
Personal protection	

National Fire Protection Association (U.S.A.)

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Disclaimer

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Definitions of Material Safety Data Sheet Terminology**GOVERNMENT AGENCIES AND PRIVATE ASSOCIATIONS**

ACGIH - American Conference of Governmental Industrial Hygienists, (private association)

DOT - United States Department of Transportation

EPA - United States Environmental Protection Agency

IARC - International Agency for Research on Cancer, (private association)

NFPA - National Fire Protection Association, (private association)

MSHA - Mine Safety and Health Administration, U.S. Department of Labor

NIOSH - National Institute of Occupational Safety and Health, U.S. Department of Health and Human Services

NTP - National Toxicology Program, (private association)

OSHA - Occupational Safety and Health Administration, U.S. Department of Labor

Continued on next page

WHMIS- Workplace Hazardous Material Information System

CSA- Canadian Standards Association

HAZARD AND EXPOSURE INFORMATION

Acute Hazard - An adverse health effect which occurs rapidly as a result of short term exposure.

CAS # - American Chemical Society's Chemical Abstract service registry number which identifies the product and/or ingredients.

Ceiling - The concentration that should not be exceeded during any part of the working exposure

Chronic Hazard - An adverse health effect which generally occurs as a result of long term exposure or short term exposure with delayed health effects and is of long duration

Fire Hazard - A material that poses a physical hazard by being flammable, combustible, pyrophoric or an oxidizer as defined by 29 CFR 1910.1200

Hazard Class - DOT hazard classification

Hazardous Ingredients - Names of ingredients which have been identified as health hazards

IDLH- Immediately Dangerous to Life and Health, the airborne concentration below which a person can escape without respiratory protection and exposure up to 30 minutes, and not suffer debilitating or irreversible health effects. Established by NIOSH.

mg/m³ - Milligrams of contaminant per cubic meter of air, a mass to volume ratio

N/A - Not available or no relevant information found

NA - Not applicable

PEL - OSHA permissible exposure limit; an action level of one half this value may be applicable

ppm - Part per million (one volume of vapor or gas in one million volumes of air)

Pressure Hazard - A material that poses a physical hazard due to the potential of a sudden release of pressure such as explosive or a compressed gas as defined by 29 CFR 1910.1200

Reactive Hazard - A material that poses a physical hazard due to the potential to become unstable reactive, water reactive or that is an organic peroxide as defined by 29 CFR 1910.1200.

STEL - The ACGIH Short-Term Exposure Limit, a 15-minute Time-Weighted Average exposure which should not be exceeded at any time during a workday, even if the 8-hour TWA is less than the TLV.

TLV - ACGIH Threshold Limit Value, represented herein as an 8-hour TWA concentration.

8-hour TWA - The time weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

LD₅₀ - Single dose of a substance that, when administered by a defined route in an animal assay, is expected to cause the death of 50% of the defined animal population.

LC₅₀ - The concentration of a substance in air that, when administered by means of inhalation over a specified length of time in an animal assay, is expected to cause the death of 50% of a defined animal population.