

Oleum, Sulfur Trioxide, and Sulfuric Acid

These three very corrosive chemicals are closely related. Oleum is cloudy, oily, fuming liquid or sometimes a solid which releases sulfur trioxide in contact with air as in a spill. This sulfur trioxide reacts quickly with any air moisture producing a fine sulfuric acid mist. Inhalation at low concentrations for a short period irritates the nose, throat, and lungs. Prolonged exposure or higher concentrations causes a burning sensation, coughing, gagging, chest pain, fluid in lungs, and possible suffocation and death. The effects of inhalation may be delayed. The mist also severely irritates eyes and skin.

We will look at these chemicals, its uses, and examine several accidents involving oleum spills. Oleum spills are very dangerous because chemical contact can “suck” the water out of organic materials leaving a black char generating a lot of heat and possibly resulting in fire. If water is sprayed on the chemical, a sulfuric acid mist will likely be formed which is difficult to control and dangerous to inhale.

Physical Properties of Oleum, Sulfur Trioxide, and Sulfuric Acid

Oleum is excess sulfur trioxide dissolved in sulfuric acid. Another name for Oleum is “Sulfuric acid, fuming”. It is sometimes shipped by railcar under UN 1831. The chemical may also be transported tanker truck, pipeline or in smaller containers. The Emergency Response Guidebook under UN 1831 makes a distinction between “Sulfuric acid, fuming, with less than 30% free Sulfur trioxide” and “Sulfuric acid, with not less than 30% free Sulfur trioxide”. For example, a tank car containing 90 tons of oleum with 30% free sulfur trioxide contains 60 tons of sulfuric acid and 30 tons of free sulfur trioxide dissolved in the sulfuric acid. Sometimes this is called “30% oleum”. Oleum and sulfuric acid comes in different strengths, which have different melting and boiling points and different densities.

Table 1. Physical Properties of Different Oleum Strengths (pure sulfuric acid and pure sulfur trioxide listed for comparison)

% Free Sulfur trioxide	Melting point	Boiling point	Sp Grav. Liquid (water=1)	Vapor Pressure at 20°C/68°F
0 (pure sulfuric acid)	10°C/50°F	337°C / 639°F	1.84	<0.001 atm
20%	2°C / 35.6°F	138°C / 280°F	1.93	<0.001 atm
34%	20°C / 68°F	112°C / 233°F	1.92	0.007 atm
65%	5°C / 41°F	60°C / 140°F	1.99	0.104 atm
100% (pure sulfur trioxide, gamma form)	16.8°C / 62.2°F	45°C / 113°F	1.92	0.57 atm (25°C)
100% (pure sulfur trioxide, beta form)	32.5°C / 90.5°F	45°C / 113°F	1.92	0.45 atm (25°C)
100% (pure sulfur trioxide, alpha form)	62°C / 143.6°F	converts to gamma, bp 45°C	1.92	0.096 atm (25°C)

Pure sulfur trioxide (gamma form) may polymerize forming beta or alpha forms which have higher melting point temperatures and lower vapor pressures. The gamma form can convert spontaneously to the beta or alpha forms and back again. If an alpha form of sulfur trioxide (melting point 62°C) is heated to its melting point, it converts to the gamma form (boiling point 45°C) and suddenly boils; if heated in a closed container, the container may explode. Sulfur trioxide is a white solid at temperatures below its melting point. Stabilizers or inhibitors may be added to the gamma form to prevent polymerization.

The term “pure sulfuric acid” in table 1 is somewhat of a misnomer because if “100%” sulfuric acid is heated, more sulfur trioxide vaporizes than the water component. At its boiling point of 337°C (639°F) and one atmosphere pressure, the concentration of sulfuric acid might be about 93.3% (balance water), and this is what boils even though the starting concentration might be say a commercial grade of 98%. Chemists refer to this as the azeotropic concentration. However, sulfur trioxide is very soluble in cold or ambient temperature sulfuric acid, and manufacturers add sulfur trioxide producing 98% (97 to 98.5%) commercial grade and various concentrations of oleum.

The melting point of sulfuric acid is somewhat of a hard thing to define. Temperatures reported in the literature can vary from the values given in table 1, and represent the difficulty in defining the amount of sulfur trioxide present, or a temperature when sulfuric acid changes from a “viscous liquid” to a “solid”.

Table 2. Physical Properties of Different Sulfuric Acid Solution Strengths

% Sulfuric acid (balance water)	Melting point	Boiling point	Sp Grav. Liquid (water=1) at 20°C	Vapor Pressure at 20°C/68°F
10% (1 Normal laboratory acid)	-2°C/28.4°F	102°C / 215°F	1.07	0.022 atm
33.5% (battery acid)	-64°C / -83°F	110°C / 230°F	1.24	0.017 atm
60% (fertilizer acid)	-64°C / -83°F	140°C / 284°F	1.50	0.004 atm
73.6% (Glover acid)	-39°C / -38°F	178°C / 352°F	1.65	0.0006 atm
93.3% (azeotropic concentration)	-32°C / -26°F	337°C / 639°F	1.83	<0.001atm
98% (commercial)	-2°C / -28.4°F	337°C / 639°F	1.84	<0.001 atm

Boiling point, specific gravity, and vapor pressure information from Chemical Engineers Handbook, 4th edition, McGraw Hill. Melting points are not a precise number, and published information varies.

The 2008 Emergency Response Guidebook makes distinctions between the different grades of sulfuric acid, oleum or fuming sulfuric acid, and sulfur trioxide (table 3).

Table 3. Listings in the Emergency Response Guidebook

Name (U.S.)	Name (Canadian/British)	UN#	Guide #
Sulfuric acid, with not more than 51% acid	Sulphuric acid, with not more than 51% acid	2796	157
Sulfuric acid, with more than 51% acid	Sulphuric acid, with more than 51% acid	1830	137
Sulfuric acid, spent	Sulphuric acid, spent	1832	137
Sulfur trioxide	Sulphur trioxide	1829	137
Sulfuric acid, fuming, with less than 30% free sulfur trioxide	Sulphuric acid, fuming, with less than 30% free sulphur trioxide	1831	137
Sulfuric acid, fuming, with not less than 30% free sulfur trioxide	Sulphuric acid, fuming, with not less than 30% free sulphur trioxide	1831	137

The word “oleum” might be used instead of “sulfuric acid, fuming”.

An important distinction between these listings for emergency responders is that a water stream should never be directly added to more concentrated grades (>51%) of sulfuric acid, sulfur trioxide, or sulfuric acid, fuming (oleum). The heat generated by addition of a water stream can cause the chemical to spatter producing a fine sulfuric acid aerosol or mist which is dangerous to inhale. Sulfuric acid, with not more than 51% sulfuric acid, is already somewhat diluted with water; the heat generated by addition of water to a spill will be less, and dangerous sulfuric acid mist formation is minimal. Water should not be directly added to any container regardless of strength. If necessary to dilute a container of sulfuric acid with water, the sulfuric acid should be slowly added to a large volume of water. If someone has contacted sulfuric acid (or oleum or sulfur trioxide), immediately flush the skin or eyes with running water for 20 minutes regardless of strength. Even 10% sulfuric acid can cause organic materials such as paper to “char” if left in contact long enough.

Notice the differences in wording of the Emergency Response Guidebook guide numbers 137 and 157:

<p>GUIDE 137 SUBSTANCES - WATER-REACTIVE - CORROSIVE</p> <p>POTENTIAL HAZARDS</p> <p>HEALTH</p> <ul style="list-style-type: none"> · CORROSIVE and/or TOXIC; inhalation, ingestion or contact (skin, eyes) with vapors, dusts or substance may cause severe injury, burns or death. · Fire will produce irritating, corrosive and/or toxic gases. · Reaction with water may generate much heat that will increase the concentration of fumes in the air. · Contact with molten substance may cause severe burns to skin and eyes. · Runoff from fire control or dilution water may cause pollution. <p>FIRE OR EXPLOSION</p>

- EXCEPT FOR ACETIC ANHYDRIDE (UN1715), THAT IS FLAMMABLE, some of these materials may burn, but none ignite readily.
- May ignite combustibles (wood, paper, oil, clothing, etc.).
- Substance will react with water (some violently), releasing corrosive and/or toxic gases and runoff.
- Flammable/toxic gases may accumulate in confined areas (basement, tanks, hopper/tank cars, etc.).
- Contact with metals may evolve flammable hydrogen gas.
- Containers may explode when heated or if contaminated with water.
- Substance may be transported in a molten form.
- **CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.**
- As an immediate precautionary measure, isolate spill or leak area in all directions for at least 50 meters (150 feet) for liquids and at least 25 meters (75 feet) for solids.
- Keep unauthorized personnel away.
- Stay upwind.
- Keep out of low areas.
- Ventilate enclosed areas.

PROTECTIVE CLOTHING

- Wear positive pressure self-contained breathing apparatus (SCBA).
- Wear chemical protective clothing that is specifically recommended by the manufacturer. It may provide little or no thermal protection.
- Structural firefighters' protective clothing provides limited protection in fire situations ONLY; it is not effective in spill situations where direct contact with the substance is possible.

EVACUATION

Spill

- See Table 1 - Initial Isolation and Protective Action Distances for highlighted materials. For non-highlighted materials, increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".

Fire

- If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

FIRE

- **When material is not involved in fire, do not use water on material itself.**

Small Fire

- Dry chemical or CO₂.
- Move containers from fire area if you can do it without risk.

Large Fire

- Flood fire area with large quantities of water, while knocking down vapors with water fog. If insufficient water supply: knock down vapors only.

Fire involving Tanks or Car/Trailer Loads

- Cool containers with flooding quantities of water until well after fire is out.
- Do not get water inside containers.
- Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- ALWAYS stay away from tanks engulfed in fire.

SPILL OR LEAK

- Fully encapsulating, vapor protective clothing should be worn for spills and leaks with no fire.
- Do not touch damaged containers or spilled material unless wearing appropriate protective clothing.
- Stop leak if you can do it without risk.
- Use water spray to reduce vapors; do not put water directly on leak, spill area or inside container.
- Keep combustibles (wood, paper, oil, etc.) away from spilled material.

Small Spill

- Cover with DRY earth, DRY sand or other non-combustible material followed with plastic sheet to minimize spreading or contact with rain.
- Use clean non-sparking tools to collect material and place it into loosely covered plastic containers for later disposal.
- Prevent entry into waterways, sewers, basements or confined areas.

FIRST AID

- Move victim to fresh air.
- Call 911 or emergency medical service.
- Give artificial respiration if victim is not breathing.
- **Do not use mouth-to-mouth method if victim ingested or inhaled the substance; give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.**
- Administer oxygen if breathing is difficult.
- Remove and isolate contaminated clothing and shoes.
- In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes.
- For minor skin contact, avoid spreading material on unaffected skin.
- Removal of solidified molten material from skin requires medical assistance.
- Keep victim warm and quiet.
- Effects of exposure (inhalation, ingestion or skin contact) to substance may be delayed.
- Ensure that medical personnel are aware of the material(s) involved and take precautions to protect themselves.

GUIDE 157 SUBSTANCES - TOXIC and/or CORROSIVE (Non-Combustible / Water-Sensitive)

POTENTIAL HAZARDS

HEALTH

- **TOXIC**; inhalation, ingestion or contact (skin, eyes) with vapors, dusts or substance may cause severe injury, burns or death.
- Reaction with water or moist air will release toxic, corrosive or flammable gases.
- Reaction with water may generate much heat that will increase the concentration of fumes in the air.
- Fire will produce irritating, corrosive and/or toxic gases.
- Runoff from fire control or dilution water may be corrosive and/or toxic and cause pollution.

FIRE OR EXPLOSION

- Non-combustible, substance itself does not burn but may decompose upon heating to produce corrosive and/or toxic fumes.
- Vapors may accumulate in confined areas (basement, tanks, hopper/tank cars etc.).
- Substance will react with water (some violently), releasing corrosive and/or toxic gases and runoff.
- Contact with metals may evolve flammable hydrogen gas.
- Containers may explode when heated or if contaminated with water.
- **CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.**
- As an immediate precautionary measure, isolate spill or leak area in all directions for at least 50 meters (150 feet) for liquids and at least 25 meters (75 feet) for solids.
- Keep unauthorized personnel away.
- Stay upwind.
- Keep out of low areas.
- Ventilate enclosed areas.

PROTECTIVE CLOTHING

- Wear positive pressure self-contained breathing apparatus (SCBA).
- Wear chemical protective clothing that is specifically recommended by the manufacturer. It may provide little or no thermal protection.
- Structural firefighters' protective clothing provides limited protection in fire situations **ONLY**; it is not effective in spill situations where direct contact with the substance is possible.

EVACUATION

Spill

- See Table 1 - Initial Isolation and Protective Action Distances for highlighted materials. For non-highlighted materials, increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".

Fire

- If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

EMERGENCY RESPONSE

FIRE

- Note: Most foams will react with the material and release corrosive/toxic gases.

Small Fire

- CO₂ (except for Cyanides), dry chemical, dry sand, alcohol-resistant foam.

Large Fire

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

Fire involving Tanks or Car/Trailer Loads

- Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
- Do not get water inside containers.
- Cool containers with flooding quantities of water until well after fire is out.
- Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- ALWAYS stay away from tanks engulfed in fire.

SPILL OR LEAK

- ELIMINATE all ignition sources (no smoking, flares, sparks or flames in immediate area).
- All equipment used when handling the product must be grounded.
- Do not touch damaged containers or spilled material unless wearing appropriate protective clothing.
- Stop leak if you can do it without risk.
- A vapor suppressing foam may be used to reduce vapors.
- DO NOT GET WATER INSIDE CONTAINERS.
- Use water spray to reduce vapors or divert vapor cloud drift. Avoid allowing water runoff to contact spilled material.
- Prevent entry into waterways, sewers, basements or confined areas.

Small Spill

- Cover with DRY earth, DRY sand or other non-combustible material followed with plastic sheet to minimize spreading or contact with rain.
- Use clean non-sparking tools to collect material and place it into loosely covered plastic containers for later disposal.

FIRST AID

- Move victim to fresh air.
- Call 911 or emergency medical service.
- Give artificial respiration if victim is not breathing.
- **Do not use mouth-to-mouth method if victim ingested or inhaled the substance;**

give artificial respiration with the aid of a pocket mask equipped with a one-way valve or other proper respiratory medical device.

- Administer oxygen if breathing is difficult.
- Remove and isolate contaminated clothing and shoes.
- In case of contact with substance, immediately flush skin or eyes with running water for at least 20 minutes.
- For minor skin contact, avoid spreading material on unaffected skin.
- Keep victim warm and quiet.
- Effects of exposure (inhalation, ingestion or skin contact) to substance may be delayed.
- Ensure that medical personnel are aware of the material(s) involved and take precautions to protect themselves.

Manufacture and Use

Originally, oleum, sulfur trioxide, and sulfuric acid were synthesized from sulfur or from sulfur-containing ores. This is still being done, but with today's emphasis on clean air and water and pollution reduction, it is more economical to recycle spent sulfuric acid or remove naturally occurring sulfur from fossil fuels. Instead of discharging hydrogen sulfide or sulfur dioxide to the atmosphere or discharging sulfide or sulfate compounds in a wastewater, the sulfur could be recovered and sold as sulfur or as sulfuric acid or oleum or gypsum.

Metal smelting plants, the iron and steel industry, refineries, and other industries may incorporate Spent Acid Regeneration Plants. These plants combust spent acid with natural gas or refinery gas producing gaseous sulfur dioxide which is oxidized to sulfur trioxide. Sulfur trioxide is then absorbed in concentrated sulfuric acid to make more sulfuric acid or oleum. Operation of a Spent Acid Regeneration Plant is less costly than purchasing new chemicals and discharging spent acid as waste. Refineries might also burn hydrogen sulfide forming sulfur dioxide which is then oxidized to sulfur trioxide, which in turn is absorbed in concentrated sulfur trioxide forming oleum.

Direct addition of sulfur trioxide to water results in uncontrollable heat release and formation of a fine sulfuric aerosol. Commercially (contact process), the sulfur dioxide and air enter a converter vessel containing a catalyst such as vanadium pentoxide resulting in generation of heat and sulfur trioxide. Excess heat must be removed for the reaction to be completed requiring inter stage cooling and contact with more catalyst. The mixture is then fed to an absorption tower under controlled cooling conditions where sulfur trioxide is hydrated to sulfuric acid. There is still some unconverted sulfur dioxide left in the gas stream which is contacted with more catalyst at a controlled temperature producing sulfur trioxide which is absorbed in absorption towers. A sketch of the process is in a book by James G. Speight, "Chemical Process and Design Handbook", McGraw Hill, 2002. Another source is

http://www2.emersonprocess.com/siteadmincenter/PM%20Rosemount%20Analytical%20Documents/Liq_AppData_2800-22.pdf.

Oleum is probably the most common form for transporting large amounts of sulfuric acid compounds from the producer (usually an oil refinery) to industrial users. Oleum is usually transported in the U.S. by special rail tank cars fitted with steam conduits within the tank car. The United Kingdom uses road tankers. The oleum form of transport is safer than shipping concentrated sulfuric acid, partly because oleum is a solid at certain concentrations whereas sulfuric acid is a liquid, and partly because oleum is less bulky. The industrial user then carefully heats the tank car using the steam conduits to melt the oleum which is removed as a liquid. From oleum, the user can obtain sulfur trioxide by heating or dilute to obtain sulfuric acid.

Industrial uses are many, and may include:

- Roughly 60% of sulfuric acid production worldwide is used in the manufacture of phosphoric acid and phosphate-based fertilizers.
- Sulfuric acid is used in the iron and steel industry to remove rust and scale from rolled sheets and billets.
- Sulfuric acid is used to make aluminum sulfate from aluminum oxide (bauxite), which in turn has uses in water purification and paper manufacture.
- Refineries use sulfuric acid in the manufacture of isooctane from isobutene and isobutylene to boost the octane rating of gasoline.
- Steam power plants use sulfuric acid to regenerate their demineralizers in production of boiler water feed.
- Vehicle batteries contain about 33 or 34% sulfuric acid.
- Oleum is used as a dehydrating agent in the manufacture of many kinds of explosives such as TNT.
- The manufacture of many chemicals use sulfuric acid or oleum or sulfur trioxide in its manufacture.
- Ore processing is another use of sulfuric acid.

Total worldwide production of sulfuric acid including oleum is about 185 million U.S. tons annually (in 2002). U.S. production is almost 50 million tons annually

Manufacture of Illegal Drugs and Explosives

International commerce of sulfuric acid is controlled by the “United Nations Convention Against Illicit Traffic in Narcotic Drugs and Psychotropic Substances, 1988”. A copy of this document can be obtained at the website, http://www.unodc.org/pdf/convention_1988_en.pdf. Sulfuric acid and its salts or derivatives fall in their table II listings which include chemicals widely used in industry but can also be used in manufacture of illegal drugs. What this document means is that transactions of sulfuric acid (sales and exports or imports in the United States) are subject to regulation and monitoring by the U.S. agencies involved in drug enforcement. The possession and use of the chemicals in table II is not illegal; for example, sulfuric acid is used in vehicle batteries. Several of the other chemicals listed in table II are also readily available from

home improvement and hardware stores and are used for legitimate purposes (thinning varnishes, cleaning, stripping old finishing and refinishing, scale removal, etc.).

Oleum is used as a dehydrating chemical in the manufacture of explosives such as TNT. This chemical (oleum) is not readily available to individuals and is dangerous to handle and could be acquired by theft. It is conceivable that responders could encounter oleum in raiding a clandestine laboratory. Instructions for manufacture of small quantities of oleum and sulfur trioxide can be found on the Internet using starting materials that an individual might acquire, for example http://www.sciencemadness.org/member_publications/SO3_and_oleum.pdf.

Accidental Oleum Release near Pittsburgh PA in 2008, 2500 Residents Evacuated or Shelter in Place.



illustrations from Chemical Safety Board final report



This accident was investigated by the Chemical Safety Board. Their final report issued 5 October 2009 is available at <http://www.csb.gov/UserFiles/file/INDSPEC%20Final.pdf>.

The oleum release occurred shortly after 3 PM on Saturday 11 October 2008 at the INDSPEC Chemical Corporation resorcinol facility in Petrolia, Pennsylvania. The release occurred during transfer operations, when operators were transferring oleum from a railcar into a pressure vessel (there are three horizontal pressure vessels, tank 612 shown at left); the oleum was then

pumped to process tanks (there are two, process tank 1502 which overflowed is pictured at the right). The tanks are inside the oleum storage building. Oleum is transferred continuously from process tanks to the resorcinol production area when the production area is in operation. Oleum is used in the manufacture of resorcinol, which in turn is used as an automobile tire adhesive and as a chemical intermediate in the manufacture of other organic chemicals. The INDSPEC plant in Petrolia produces 50 million pounds of resorcinol annually and is the only U.S. commercial producer of resorcinol.

Information as to what happened was later obtained from security videos (one inside the oleum building and one just outside the building to the south) and from interviews from plant operators.

- At 2:13 PM, an alarm beacon indicated a high level of oleum in process tank 1502, but at that time the operator on duty had exited the oleum storage building and control room, and left the facility by 2:15 PM. No one was in the area.
- At 2:18 PM, process tank 1502 reached the high-level setpoint, activating another alarm.
- At 3:12 PM, sulfuric acid mist began escaping in the area of tank.
- At around 4:15 PM, employees saw a white mist escaping the oleum storage area doors and notified the shift supervisor who thought there was an oleum leak in the transfer line(which proved later not to be the case), and ordered the transfer line to be blown clean with pressurized air. However, security videos (4:21 PM) showed an increase in intensity of the mist. At 4:29 PM, white sulfuric acid mist was visible outside the building.
- The shift supervisor acting as incident commander orders a facility evacuation (30 employees). At 4:55 PM the facility security guard notifies the INDSPEC hazardous materials response team. Concurrent with facility evacuation, local police and the volunteer fire department are notified, who begin evacuating residents or issue orders to shelter in place. An EPA team was dispatched from Wheeling WV.
- At 4:58 PM, the shift supervisor instructed the INDSPEC responders to spray the oleum building with water to knock down the sulfuric acid mist; this action was ineffective and may have even increased the mist. The INDSPEC responders tried to enter the building wearing Level A personal protective equipment, and were able to determine that a transfer tank was running and overflowing one of the process tanks. Liquid oleum also spilled on the Level A-suited responders before they were able to retreat.
- The INDSPEC responders were unable to shut off the transfer pump because they could not reach the local electrical room safely because it was flooded with water used to spray the building. Eventually, at about 7 PM, electricians were able to disconnect the electrical supply remotely. It was later determined that vessel 612 used to supply the process tank had emptied by about 5:50 PM.
- About 2500 community people were evacuated or sheltered in place within a three mile radius of the plant. Authorities went from door-to-door. The sulfuric acid mist cloud moved westward and tended to be close to the ground. By 2 AM the next day, EPA monitoring showed no trace of sulfuric acid vapors from the release, and residents

were allowed to return. There were no deaths or injuries, except for a minor injury to one of the responders from sulfuric acid inhalation.

- An estimated 3,300 lbs of oleum overflowed from the tank. [The operator was fired].

The Chemical Safety Board report included a brief section on why the oleum transfer pump did not have an automatic shutoff tied to the high-level switch on the process tank. An alarm went off when the oleum level increased, but the transfer pump did not automatically shut off. A former operator told the Chemical Safety Board that prior to 1980, when the facility was owned by Koppers Company, the facility was plagued by frequent electrical shutdowns and spare parts were difficult to obtain, and a temporary power supply bypass was installed. A former supervisor at that time verbally told operators to use the temporary emergency power supply with a separate switch receptacle which operated the pumps that transfer oleum from the pressure vessels to the process tanks. The temporary power supply did not have automatic high level shutoff features, and this was not corrected when Beazer acquired Koppers in 1988, nor when INDSPEC later took over operations. Nothing was written up on the bypass. That "temporary" bypass of a safety feature lasted roughly 30 years, and operators forgot that the system lacked controls to shut off the pump in response to a high level alarm.

The chemical workers' unions and the United Steelworkers Union criticized the Chemical Safety Board final report for what they called as being too weak and vague in its recommendations. Also the unions complained that they were shut out of the investigations. The unions wanted specific and hard-hitting recommendations. This was reported in Chemical and Engineering News for October 12, 2009 [see <http://pubs.acs.org/cen/news/87/i41/8741notw7.html>]. INDSPEC faces more than \$150,000 in state environmental and federal OSHA fines.

Oleum Rail Road Tank Car Spill, 26 July 1993, Richmond CA, 24,000 people sought medical attention.



Photo of release from http://www.sulphuric-acid.com/TechManual/Plant_Safety/safety_accidents.htm

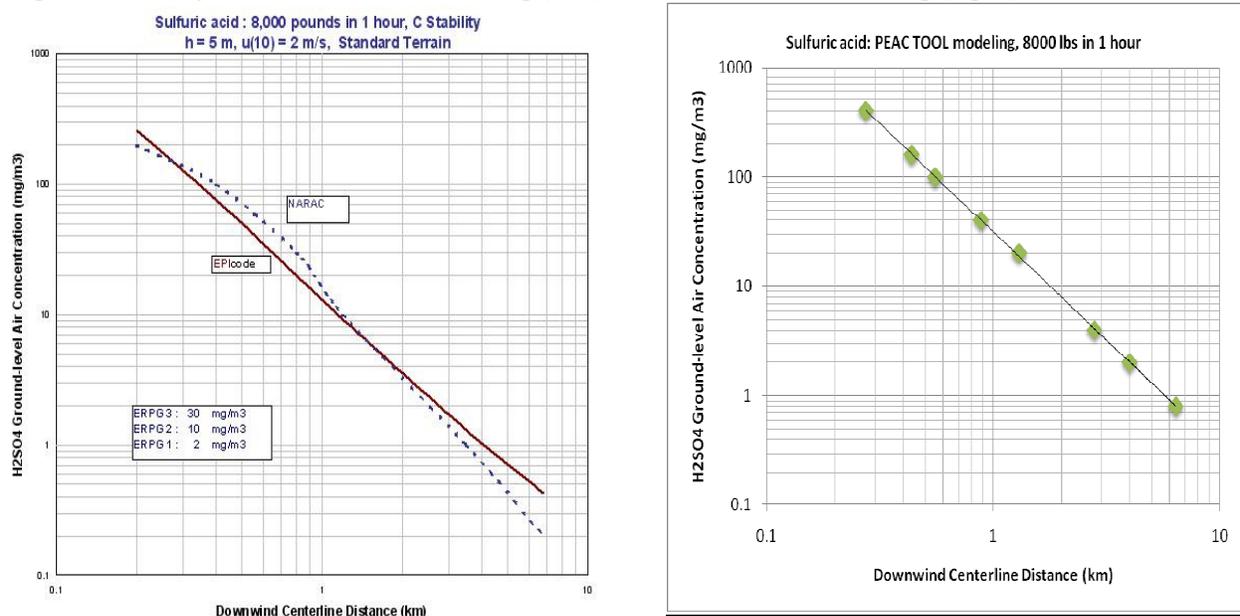
During the morning of 26 July 1993 workers at General Chemical Company in Richmond, California began heating a 100-ton capacity railroad tank car containing 13,000 gallons of 35 grade (35% excess sulfur dioxide) oleum. The workers followed standard procedures for heating the tank car by running steam through heating coils on the tank car in order to reduce the oleum viscosity prior to transfer to storage tanks on site, but apparently the tank overheated. At about 7:15 AM, a safety valve unexpectedly ruptured even though the tank car's pressure gauge read 55 psi but the valve was designed to release at 100 psi. The result was a steady stream of vapor that began to escape through the three-inch diameter valve on the rail car. The release was sulfur trioxide which quickly reacted with air moisture and condensed as a fine sulfuric acid mist. The hot vapors initially began to rise, but winds carried the plume cloud to the north and east over neighborhoods and industrial areas of Richmond, San Pablo, El Sobrante, and Pinole before dissipating over San Pablo Bay. The cloud was described in the news media as 1000 feet high and up to eight miles wide. Highways, rail lines, and public transportation were blocked requiring people to shelter in place. At about 11 AM, the rail car was successfully capped preventing additional release. No one was killed, but initially 3,200 people sought medical attention at emergency rooms of hospitals complaining of breathing difficulties, nausea, irritated skin and burning eyes, and burning throat. Most were treated and released but 22 people were hospitalized. The number of people seeking medical attention eventually rose to about 24,000 after a week.

A settlement agreement was between General Chemical Corporation and Contra Costa County Superior Court (July 1995) in which General Chemical Corporation agreed to pay \$180 million in damages, of which \$92.8 million would be set aside to pay damages to 59,000 people who filed lawsuit claims in a class-action suit, \$40 million for legal expenses, and the balance for more severely injured persons and punitive damages. Only subjective evidence of injury and proximity to the plant were required for people to join the suit. General Chemical also agreed to spend \$800,000 for building a health clinic in Richmond, and \$1.5 million for a community benefit fund to support the children and families in Richmond (<http://www.richmondchildren.org/history.asp>). General Chemical also paid \$1.18 million in fines to government agencies. In court documents, the company said that it had a negative net worth of \$223 million.

After the release, state and local agencies requested that the Atmospheric Release Advisory Capability (ARAC) at Lawrence Livermore National Laboratory (LLNL) model the plume cloud using real-time wind fields. The results of the modeling (1994) are presented in a paper, UCRL-JC-118082, submitted to the 5th Topical Meeting on Emergency Preparedness and Response, Savannah GA, and are available at <http://www.osti.gov/bridge/servlets/purl/10114145-46ntwK/webviewable/>. Initially, the ARAC team was given the "worst case", the entire oleum tank contents released over 1.5 hours. Later the source release rate was revised to a number based on release of half the tank contents over 3.76 hours (the time between 7:15 AM and 11 AM, or 3.276 kg/s). Another estimate placed the release rate as being even less. ARAC also modeled a 1 kg/s (8000 lbs/hr) release as shown in figure 1.

A comparison of some of the ARAC modeling results with PEAC tool predictions is presented in figure 1. Both comparisons used 8000 lbs of sulfuric acid mist released in 1 hour (equivalent to 1 kg/s average release rate). The PEAC tool presents information in parts per million (ppm) sulfuric acid; to compare with ARAC modeling, the “ppm” numbers were multiplied by 4.08 to get mg/m^3 . The ARAC modeling plot (two different models were graphed by ARAC) was taken from the website <http://www.epicode.com/epiwebcase.html>.

Figure 1. Comparison of ARAC Modeling (left) with PEAC tool Modeling (right)



The green points on the PEAC tool graph represent different runs using the PEAC tool; the entire sequence of points can be generated in about a minute. The ARAC Modeling assumed that the effective settling velocity of the sulfuric acid mist was 1 centimeter per second for the Richmond release, whereas the PEAC tool assumed no settling velocity. Therefore the concentrations corresponding to any downwind distance are somewhat higher for the PEAC tool compared with ARAC modeling, but the numbers are still fairly close. The responder would not ordinarily know what settling velocity to use for the sulfuric acid mist, and the assumption of a zero settling velocity in the PEAC tool would give a more conservative answer.

The modeling done by ARAC also illustrates the difficulty in estimating how much chemical was released to the surroundings. Knowing the amount of chemical released is an essential part of modeling. Nowhere could this writer (John Nordin) find information on the weight of the tank car before and after the release, which would provide a good number of how much total chemical was released. The oleum/trisulfur dioxide released would be converted to sulfuric acid mist, which can be calculated. Additionally, the circumstances of the spill suggest that the release rate was not uniform over the time period as what was assumed by ARAC. What is known is that a safety release valve failed. The circumstances suggested that the pressure inside the tank was probably not reading correctly. Temperature measurements inside the rail road tank car would answer the question. The tank contents when overheated to above the

boiling point (233°F) would flash, and from this temperature the fraction flashed could be calculated and modeled as a short-term or instantaneous release. Also, we could not find out any information as to whether any oleum was spilled on the ground. Presumably after the safety release valve failed, operators would have shut off the steam supply or heat source; if not, the rail car would continue to release chemical at a fairly high rate. If the steam heat was turned off, little additional oleum -sulfur trioxide would vaporize from the rail car as the vapor pressure under ambient conditions is low (about 0.01 atm). The ARAC report does not address this, and the PEAC tool modeling can only mimic the conditions assumed by the ARAC group.

Oleum Spill, 2002 Train derailment, Tennessee, 3300 people Evacuated, No Deaths



On 15 September 2002 at approximately 11:20 AM, a Norfolk Southern freight train derailed near Farragut, Tennessee. Three locomotives and 25 cars derailed including a tank car containing 10,600 gallons of fuming sulfuric acid (oleum) which was ruptured in the wreck. The spilled oleum reacted with ground moisture and air moisture releasing heat resulting in a fine sulfuric acid aerosol/mist. The heated sulfuric acid mist tended to rise into the air as shown in the photo to the left.

Emergency management agency personnel from Knox County responded and implemented a mandatory evacuation of residents living within a 1.3 mile radius of the derailment site, and a voluntary 3-mile evacuation distance from the site. The evacuation order was lifted for some areas on 16 September at 9 PM, and by 7 AM on 17 September, all residents were allowed to return. There were no deaths or serious injuries, but 15 residents and two police officers went to a local hospital and were later released. Additional details and more photos are in the National Transportation Safety Board report RAB-03-05, see

<http://www.nts.gov/publictn/2003/RAB0305.htm>.

Photo source:

http://www.callspsi.com/images/200_OleumDerailment3.jpg

Knoxville News – Sentinel. Photo also use by Suburban Emergency Management Project, <http://www.semp.us/publications> and others.

While most of the oleum in the railroad tank car was spilled and pooled on the ground, an unknown quantity was also released into the air as fine sulfuric acid mist. Later court

testimony (<http://www.websupp.org/data/EDTN/3:03-cv-00442-53-EDTN.pdf>) indicated that the amount of sulfuric acid mist released to the air was unknown, and air quality monitoring did not begin until about 6 hours after the accident, with sulfuric acid being detected in six out of more than 450 air samples.

The environmental response contractor HEPACO was quickly contacted (11:30 AM) after the release (<http://www.hepaco.com/>) to mitigate the effects of the spill, and work with the local fire department. Mitigation included mixing several truckloads of soil and lime brought into the area and using this material to construct containment dikes and neutralizing the spilled liquid oleum, and decontamination of rail cars. At 2 AM on September 16, two large water streams were applied to the area around the tanker, the wash water being contained in dikes. The contained and neutralized water was released as storm water after neutralization.

An evaluation of residential evacuation for the incident was published in S.M. Smith, T. Kress, M.J. Tremethick, S. Lennon, A. Lawson, H. Clark, and J. Harnish, "Research implications: an evaluation practices following a train derailment/oleum spill Incident", International Journal of Emergency Management 2007. Vol 4, no. 4, pp. 600-609.

Other Sulfuric Acid, Sulfur, and Oleum Spills

See list and summaries at http://www.sulphuric-acid.com/TechManual/Plant_Safety/safety_accidents.htm.

Sulfuric acid is a widely-used chemical, and there are many spills. Examples are at this website.

Role of the PEAC Tool

Chemical spills can be very complex. Chemicals can behave very differently, and responders would not ordinarily have a degree in chemistry. The PEAC tool is organized to give responders information quickly for the situation at hand. The responder can look up information on oleum, for example, and access basic information on this chemical.

PEAC-WMD

File Edit Tools Incident Help Test

Lookup By: Names

Lookup: Enter Agent Name...

Chemical Information

Chemical Information

Oleum
 CAS 8014-95-7
 UN 1831
[GUIDE 137 - SUBSTANCES - WATER-REACTIVE - CORROSIVE](#)

Colorless dark brown-black fuming oily liquid; odorless corrosive poison

WARNING: This reacts with water to produce acid and heat. The results given here DO NOT provide for reaction with water.

NFPA Information



Health (Blue): 3 Extreme Danger
 Fire (Red): 0 Will not burn
 Instability (Yellow): 2 Violent Chemical Change
 Special (White): No Water

Chemical Agent (PEACID: 2392) (ChemIndex: 2235) (Primary Name: Oleum) **Agent at a Glance**

SULFURIC ACID (FUMING)
 CAS 8014-95-7
 UN 1831
[GUIDE 137 - SUBSTANCES - WATER-REACTIVE - CORROSIVE](#)



Protocols can be accessed, for example, for advanced and basic life support:

<ul style="list-style-type: none"> SULFURIC ACID (AQUEOUS) SULFURIC ACID (FUMING) SULFURIC ACID (FUMING) SULFURIC ACID (FUMING) SULFURIC ACID (FUMING) SULFURIC ACID (FUMING) SULFURIC ACID ALUMINUM SALT (AL₂(SO₄)₃) SULFURIC ACID ALUMINUM SALT (AL₂(SO₄)₃) SULFURIC ACID ALUMINUM(3+) SALT (3:2) SULFURIC ACID ALUMINUM(3+) SALT (3:2) Sulfuric acid ammonium ceric dihydrate Sulfuric acid and Hydrofluoric acid mixtures SULFURIC ACID CHLOROXYDRIN Sulfuric acid diethyl ester SULFURIC ACID DODECYL ESTER SODIUM SALT SULFURIC ACID FUMING Sulfuric acid fuming, with less than 30% free sulfur trioxide Sulfuric acid fuming, with not less than 30% free sulfur trioxide Sulfuric acid indium(3+) salt (3:2) SULFURIC ACID IRON SALT (1:1) SULFURIC ACID MANGANESE SALT (1:1) MONOHYDRATE Sulfuric acid monododecyl ester magnesium salt 	<p>PROTOCOL 1</p> <p>TOXICITY LEVEL 4 PROTECTION LEVEL A</p> <p>DESCRIPTION (Acids) A broad group of chemicals, acids may be solid, liquid, or gaseous in form. Liquids and gases usually have a characteristically pungent odor. Liquids may be fuming. Some of the inorganic acids, such as hydrochloric acid (HCl), nitric acid (HNO₃), and sulfuric acid (H₂SO₄), are high-production chemicals and are considered a basic raw material for many industries. Several classes of organic substances are classified as acids, particularly the carboxylic acids, the amino acids, and the nucleic acids.</p> <p>HEALTH HAZARD Acids are toxic to the skin, eyes, and mucous membranes. Direct contact may result in severe, corrosive burns. Inhalation of concentrated vapor may be fatal within minutes.</p> <p>PROTECTION These products require full protection and should be EPA Level A. The rescuer should wear chemical resistant encapsulated clothing and self-contained breathing apparatus. Patient care personnel should wear chemical resistant impervious clothing, gloves, shoe covers with self-contained breathing apparatus when caring for field decontaminated victims. As further decontamination occurs, step down to an appropriate respirator. See manufacturer's materials safety data sheets for appropriate materials.</p> <p>SYMPTOMS</p> <ul style="list-style-type: none"> -Red, inflamed skin, eyes, and mucous membranes. -Severe burns and pain. -Destruction of the cornea, blindness. -Abdominal pain, nausea, vomiting (vomitus may have a coffee ground appearance). -Shortness of breath, chest pain, pulmonary edema. -Dizziness, shock, convulsions, coma. -Weak and rapid pulse, circulatory collapse. <p>BASIC LIFE SUPPORT</p> <ul style="list-style-type: none"> -Remove victim from contaminated atmosphere. -Decontaminate as indicated below. -Thoroughly flush exposed eyes with water until arrival at the hospital or until the pH returns to normal.
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Protective Clothing for different manufactures:

The screenshot shows the PEAC-WMD software interface. The main window displays 'All Chemical Protective Clothing' for the selected agent, Sulfuric Acid (Fuming). The interface includes a search bar, a list of chemical agents, and detailed protective clothing recommendations.

All Chemical Protective Clothing

Oleum
CAS 8014-95-7
UN 1831
[GUIDE 137 - SUBSTANCES - WATER-REACTIVE - CORROSIVE](#)

BOOT
Mfr: Bata HazMax
Material: NITRILE+PUR+PVC -(Rubber + polyurethane rubber + polyvinyl chloride)
Breakthrough: > 480 min

BOOT
Mfr: Lakeland Style TK740 (Tychem TK)
Material: Unknown
Breakthrough: > 480 min

BOOT
Mfr: Lakeland Style 72740 (Tychem SL)
Material: Unknown
Breakthrough: 450 min

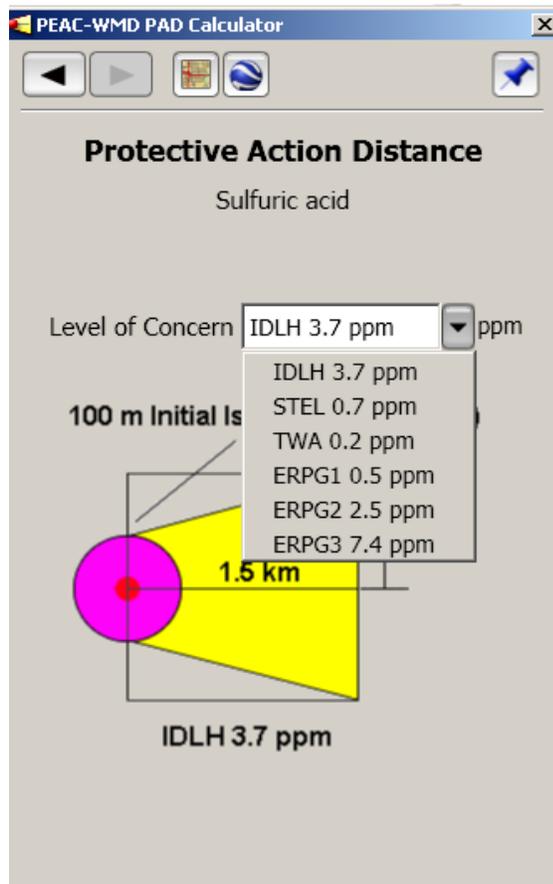
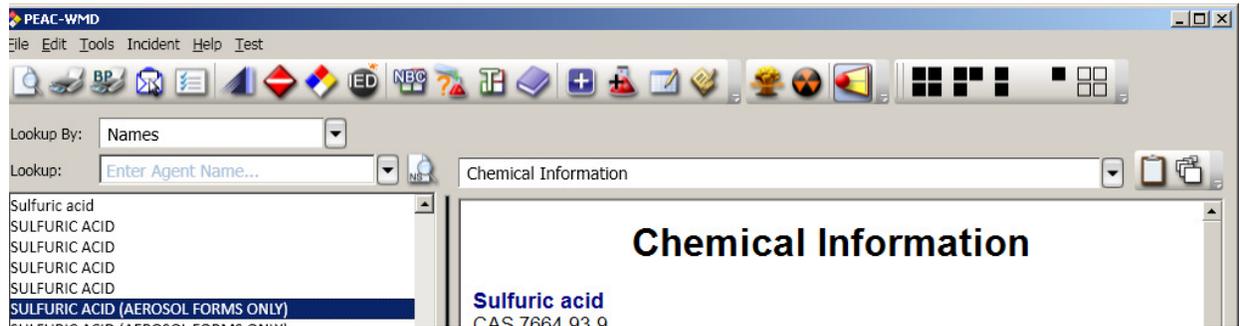
COVERALLS
Mfr: Lakeland Style TK100 (Tychem TK)

Chemical Agent (PEACID: 2392) (ChemIndex: 2235) (Primary Name: Oleum) **Agent at a Glance**

SULFURIC ACID (FUMING)
CAS 8014-95-7
UN 1831
[GUIDE 137 - SUBSTANCES - WATER-REACTIVE - CORROSIVE](#)

The interface also features a hazard diamond with a 3 in the blue section, a 0 in the red section, and a 2 in the yellow section, indicating a highly corrosive and toxic agent.

The PEAC tool user can model Protective Action Distances for different levels of concern. To initiate calculations the user clicks on the  icon.



Acute Exposure Guideline Levels

Acute Exposure Guideline Levels (Status: Intern)

Ten Minute AEGL-1: 0.2 mg/m³
 Thirty Minute AEGL-1: 0.2 mg/m³
 One Hour AEGL-1: 0.2 mg/m³
 Four Hour AEGL-1: 0.2 mg/m³
 Eight Hour AEGL-1: 0.2 mg/m³

Ten Minute AEGL-2: 8.7 mg/m³
 Thirty Minute AEGL-2: 8.7 mg/m³
 One Hour AEGL-2: 8.7 mg/m³
 Four Hour AEGL-2: 8.7 mg/m³
 Eight Hour AEGL-2: 8.7 mg/m³

Ten Minute AEGL-3: 270 mg/m³
 Thirty Minute AEGL-3: 200 mg/m³
 One Hour AEGL-3: 160 mg/m³
 Four Hour AEGL-3: 110 mg/m³
 Eight Hour AEGL-3: 93 mg/m³

Definitions

AEGL-1: The airborne concentration of a substance at or above which it is predicted that the general population, including "susceptible" individuals, could experience notable discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including "susceptible" individuals could experience irreversible or other serious, long-lasting health effects or impaired ability to escape.

AEGL-3: The airborne concentration of a substance at or above which it is predicted that the general population including "susceptible" individuals could experience life-threatening health effects or death.

"Susceptible" individuals may include persons in the 40 to 65 age bracket, smokers, or people who use alcohol; but not hyper-susceptible or hypersensitive individuals.

The AEGL-1 and AEGL-2 levels are also evaluated to ensure that the chemicals do not pose a greater than 0.0001 increased risk for cancer.

Source
 United States Environment Protection Agency

The PEAC tool can model Protective Action Distances for different release situations and meteorological conditions to look at the "worst case" for evacuation or shelter in place. The PEAC product can be connected to a printer to give a report, all this when answers are needed quickly.