

## Safety review

## Hazards of sulphuric acid

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## Summary

Sulphuric acid (or sulfuric acid) (H<sub>2</sub>SO<sub>4</sub>) (CAS: 7664939) is a dense oily colourless liquid. The acid was historically referred to as Oil of Vitriol, from the Latin *vitreus*, meaning glassy since the concentrated acid has a glassy appearance. The concentrated acid is very hygroscopic (i.e. absorbs water from the atmosphere) and is a powerful dehydrating and drying agent.

Both the concentrated acid and diluted solutions can cause serious burns and are highly corrosive to a wide range of materials, including steel, aluminum, zinc, etc.

This paper describes the key chemical properties of the acid, along with its principle hazards and an outline of the safety precautions that should be adopted to ensure that the compound is used safely. Also included is a discussion on some of the accidents that have occurred and the lessons that can be learned.

**Keywords:** Sulphuric acid

## Introduction

The concentrated acid and its aqueous solutions find considerable use in a wide range of applications. In fact as early as 1843, Liebig<sup>1</sup> wrote: "we may fairly judge of the commercial prosperity of a country from the amount of sulphuric acid it consumes". Some of the wide-scale applications for sulphuric acid include: the manufacture of fertilisers (e.g. ammonium sulphate), rayon, detergents, pickling (metal cleaning) and as an electrolyte in car batteries.

Sulphuric acid is now almost exclusively manufactured using the Contact Process<sup>2</sup>. The Contact Process plant has undergone significant change from its original design to raise efficiencies with respect to its energy and environmental demands. The majority of the acid is manufactured using the inter-pass absorption or double contact double absorption (DCDA) process. Sulphuric acid is also manufactured to a lesser extent via the wet sulphuric acid process (WSA process).

The Contact Process uses three distinct chemical reactions. Initially, the first stage involves the combustion of sulphur or roasting of metal sulphides (zinc blende, iron pyrites, and galena) to generate sulphur dioxide (SO<sub>2</sub>). The SO<sub>2</sub> is then mixed with excess air and thoroughly purified to prevent "poisoning" (impairment) of the vanadium catalyst (incorporating either VO<sup>3+</sup> or V<sub>2</sub>O<sub>5</sub>) to form sulphur trioxide (SO<sub>3</sub>). To ensure optimum efficiencies and a good yield of SO<sub>3</sub>, conditions are typically operated at around 450°C and at pressures ranging from 1-2 atmospheres. The SO<sub>3</sub> is then

cooled and undergoes absorption to generate the sulphuric acid. Here, the SO<sub>3</sub> is dissolved in concentrated sulphuric acid to form oleum or fuming sulphuric acid (H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>) which carefully undergoes stoichiometric dilution with H<sub>2</sub>O to yield the concentrated acid. Direct absorption of the SO<sub>3</sub> in water is somewhat unsatisfactory because the exothermic reaction (heat evolved) is so great that it vaporises the H<sub>2</sub>SO<sub>4</sub>, which condenses to form a fog of tiny corrosive droplets that are slow to settle out. This production process is summarised below:

## Stage 1

**either:**  $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$  (sulphur)

**or:**  $2ZnS_{(s)} + 3O_{2(g)} \rightarrow 2ZnO_{(s)} + 2SO_{2(g)}$  (zinc blende)

$2PbS_{(s)} + 3O_{2(g)} \rightarrow 2PbO_{(s)} + 2SO_{2(g)}$  (galena)

$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$  (iron pyrites)

**Stage 2**  $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

**Stage 3**  $SO_{3(g)} + H_2SO_{4(l)} \rightarrow 2H_2SO_{4(l)}$

## The hazards of sulphuric acid

Pure concentrated sulphuric acid is a colourless oily dense liquid (density of 1.84 gcm<sup>-3</sup>), which has a great affinity for water, with which it reacts exothermically (generating considerable heat), often very violently. When diluting the acid, it should always be cautiously added to water and *never* the reverse. If water is added directly to the acid it reacts violently with considerable heat evolution and spurting. During dilution continuous stirring and cooling is necessary to ensure the less dense water completely mixes with the acid and heat dissipation respectively.

The acid is a powerful dehydrating agent, removing water or the elements of water (hydrogen and oxygen) from a wide range of substances, e.g. sugar, paper, wood, etc. The concentrated acid has a freezing point of 10.4°C and boiling point of 338°C, whereby it begins to decompose into sulphur trioxide (highly corrosive and toxic) and steam. The acid forms a maximum constant boiling point (azeotropic) mixture with water, containing 98.7% acid at 1 atmosphere.

Sulphuric acid reacts with a wide range of substances including: wood, paper, nitrates, carbides, halides (e.g. chlorides), alkalis, perchlorates, metallic powders, etc. Although it is not combustible, it should be noted that the acid reacts with many metals, including iron, aluminum, zinc, etc., to generate highly flammable hydrogen gas, which is a potential explosion hazard when mixed with air. The acid reacts with a considerable range of organic compounds and specialist advice should be sought from authoritative publications on the range of incompatibilities, such as Bretherick's Handbook of Reactive Chemical Hazards<sup>3</sup> and Sax's Properties of Industrial

Materials<sup>4</sup>.

The pure acid and its solutions are extremely corrosive to human tissues, particularly the eyes and skin (dermatitis and chemical burns). In addition, sulphuric acid vapours and sulphur trioxide (SO<sub>3</sub>) are also very irritating and damaging to the eyes (conjunctivitis), respiratory system (pulmonary edema, bronchitis; emphysema); mouth (stomatitis) and teeth (dental erosion). Sulphuric acid mist is also believed to be a carcinogen.

The UK Health and Safety Executive (HSE)<sup>5</sup> has set a long-term exposure limit (8-hr TWA reference period) Workplace Exposure Limit (WEL) for sulphuric acid mist at 0.05mg.m<sup>-3</sup>. Sulphuric acid is classified and labelled in accordance with the new EU CLP Regulations<sup>6</sup> as "Danger" and has the following Globally Harmonised System (GHS) corrosive pictogram:



### Precautions to be taken when handling sulphuric acid

In accordance with many country's legal requirements and best practices for occupational health and safety, the first consideration that must be examined prior to using sulphuric acid is "can the material be ideally eliminated or alternatively, be substituted for a substance that presents less risk?" In addition, from a Process Safety standpoint, the application of Inherent Safety<sup>7</sup> principles (i.e. Minimise, Substitute, Moderate and Simplify) should be evaluated and applied particularly in the concept and early process design stages. Situations where the acid has been substituted with safer substitutes include the metal surface cleaning processes; here the acid has been substituted with less hazardous chemicals or eliminated by using technology (e.g. ultrasonics, mechanical polishing, etc.) all of which have been applied with considerable success.

As discussed above, the concentrated acid has a great affinity with water, and considerable heat is generated on diluting the acid with temperatures typically exceeding 130°C

on mixing. Therefore, the only safe way to dilute concentrated sulphuric acid is to add the acid to water with constant stirring to dissipate the heat generated on mixing, and *never* the reverse. If stirring is negated, then the denser acid forms a layer at the bottom of the container.

Carbon steel is the most common and economical material used for conveying strong solutions of sulphuric acid<sup>8</sup>. However, carbon steel has limitations in terms of its application, particularly with regards to the unstable, easily displaced protective (passive) layer formed inside the carbon steel pipe from contact with the acid. Other construction materials for transferring the acid include: Duplex Stainless Steel, Monel, Incoloy (Alloy 20), borosilicate glass (e.g. Pyrex), etc. Where hot, concentrated acid needs to be transferred the use of silicon stainless steels should be used. Impurities in the acid such as chlorides, etc., causes considerable corrosion to stainless steel pipe. In these cases, the addition of molybdenum to the stainless steel can considerably improve its corrosion resistance<sup>9</sup>. Where the acid is stored, conveyed and used, regular inspection and maintenance of plant and equipment must be undertaken to minimise the potential for loss of containment.

Engineering risk control measures should be the top priority for preventing contact with the acid and the deployment of PPE must be deemed the last resort. Nevertheless, where the acid is handled and risk control warrants PPE, the mandatory wearing of eye/face protection, gloves and protective clothing should be fully considered. A full-face shield and gauntlets should be the preferred option over wearing goggles/glasses and gloves, since the former provides greater protection to the wearer. Gloves should be impervious and be of butyl, Viton, Neoprene or PVC composition. Where the diluted acid is handled (typically, 32% battery acid) then rubber gloves can also be worn. Users are advised to consult the manufacturer's Safety Data Sheet (SDS) for specific safety advice. The new REACH<sup>10</sup> Regulations require manufacturers to provide specific safety information including steps needed to reduce exposure, e.g engineering controls and PPE necessary to protect health, and emergency action, etc.

Emergency eye wash stations should be strategically located within the workplace where there is possibility of splashing. Due consideration should also be given to the provision of emergency showers where workers could suffer complete body coverage. All emergency facilities must be regularly inspected and maintained to ensure that fresh stocks of saline eye wash, etc., are ready at hand and that the showers work in the event of an emergency.

In addition, facilities for dealing with spillages should be sited in areas where the acid is stored or used. The NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response code<sup>11</sup> provides concise and authoritative advice on the emergency management of sulphuric acid, particularly with regards to dealing with spillages, etc.

### Uses of sulphuric acid

Sulphuric acid is one of the widely most used inorganic chemicals. Listed below are some of sulphuric acid's applications:

### Fertiliser

Sulphuric acid's main use is in the production of two fertilisers (calcium hydrogen phosphate and ammonium sulphate). Calcium hydrogen phosphate (or "superphosphate") is produced by the reaction of the acid with calcium phosphate. Conversely, ammonium sulphate is generated by the neutralisation of sulphuric acid with ammonia.

### Battery acid

The diluted acid (29-32%) is used as an electrolyte in lead-acid accumulators (e.g. vehicle batteries, etc.)

### Metal finishing

Considerable quantities of the acid find use in the pretreatment of ferrous metals to remove rust, prior to galvanising, tinning, etc.

### Petroleum alkylation

The concentrated acid is used in the petroleum industry to assist the reaction of low molecular weight olefins (propene, butene, etc.) with isoparaffins generating the higher molecular weight paraffins, which are more commercially valuable.

Other uses of the acid include the manufacture of dyes, titanium dioxide, synthetic detergents, hydrochloric acid, nitric acid, etc.

## Incidents involving sulphuric acid

### Three workers sprayed with acid

The facility used 96% sulphuric acid that was conveyed around the facility in 50 year old pipework. Adjacent to the pipework, three contractors were working on an unrelated task in the road of the chemical plant. Nearby the pipework split showering the workers with an acid jet spray reaching 20 metres into the air as it was forced through the small perforation. The jet spray hit the contractors without any warning and they all sustained chemical burns. Fortunately, prompt showering prevented more serious injuries. The investigation team found that the company did have plans to inspect the pipework but the inspection dates had been missed and priority had been given to other pipework carrying other hazardous substances, which were considered a greater risk to people both on and off site. The company was criticised for not having a rigorous on-going integrity management system for the thorough and timely inspection of its ageing pipework.

### A storage tank ruptures in a galvanising plant

A galvanising company used sulphuric acid as a metal cleaning agent in their production process. An externally located horizontal 3,777 gallon storage tank containing 93% sulphuric acid ruptured releasing its contents. The tank's acid was used to replenish the sulphuric acid dip tanks and it was never designed or manufactured as a pressure vessel. The company's employees responded to the loss of containment incident by constructing a dike, from gravel, lime and sand. Whilst the company's forklift truck drivers removed the nearby galvanised poles that were being corroded by the acid, the acid reacted exothermically with the lime in the dike releasing copious white fumes containing sulphuric acid

mist. These irritant white clouds enveloped the responding employees. Management immediately called the local Fire Department HAZMAT team who responded to the scene. Upon arrival at the facility, the HAZMAT team instructed the employees to stop work and responded to the incident. Many site employees suffered burns and respiratory distress. Eighteen employees were decontaminated and referred to hospital for medical assessment and care, of which 14 employees were detained in hospital overnight.

A subsequent investigation found that the external tank had ruptured during the transfer of the 93% acid to the dip tanks located inside the plant. Compressed air was used to pressurise the tank to aid transfer of the 93% acid to the dip tanks. The plant's compressed air line travelled through an in-line air dryer which had not been maintained according to the manufacturer's recommendations. The compressed air to the external acid storage tank was normally reduced from 120psig to 30psig by a regulator. However, the engineering design criteria specified that regulator should have a set point of 10–15 psig. The regulator was subsequently found to be set at 90psig and had been recently replaced and did not meet the original regulator design criteria. The team concluded that over-pressurisation within the tank led to the loss of containment.

### An employee is cut and suffers chemical burns after a fall into sulphuric acid

An employee was unpacking 2.5 litre (Winchester) bottles containing reagent grade 98% sulphuric acid, and transferring the bottles onto a delivery transport cart. The employee lost his grip on one of the bottles and dropped it. He slipped and fell into the acid and broken glass, sustaining deep lacerations to his right wrist and 2<sup>nd</sup> and 3<sup>rd</sup> degree chemical burns to 20 percent of his body.

### Worker handling sulphuric acid falls and receives burns

A tanker driver for an industrial chemical supply company was delivering corrosive liquids to a customer. Whilst preparing to transfer the sulphuric acid from his delivery tanker, he fell from the ladder and inadvertently opened the transfer valve. As a result of the accident, he received extensive chemical burns to his leg, face, and arms.

## Conclusion

Sulphuric acid has wide scale uses in the manufacture of a great range of industrial chemicals and commercial products. When handled with due care and respect, the acid can be used safely. Full consideration should be given to any incompatibility and rigorous design and safety mechanisms (i.e. choice of correct construction materials, inspection, maintenance, etc.) must be in place to minimise any loss of containment. These systems must be complemented with appropriate emergency arrangements and facilities to timely and effectively deal with any first-aid case, spillages, etc.

## Further reading

For further accounts of accidents with sulphuric acid see: [http://www.sulphuric-acid.com/techmanual/Plant\\_Safety/](http://www.sulphuric-acid.com/techmanual/Plant_Safety/)

safety\_accidents.htm

## References

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## Incident

# Lessons not learned...

An accidental explosion at an electronics plant in North Andover, USA, resulted in the death of a man.

The plant worker died on 09 October 2013 in Boston, US. He was caught in the epicentre of a fiery explosion in a laboratory at the Dow Chemical plant the previous day and suffered extensive burn injuries.

According an investigation by the Massachusetts Fire Marshall and North Andover Fire Department, the explosion was caused by the exposure of trimethylindium, a pyrophoric chemical, to the air.

It is understood that this was due to a malfunction of the container, or human error.

The fire at the plant following the explosion was quickly contained by the plant's sprinkler system and the fire department. The worker, the only person in the laboratory at

the time of the explosion, was airlifted to hospital for treatment of his injuries.

The federal Occupational Safety and Health Administration (OSHA) launched an independent investigation and the U.S. Chemical Safety board has also requested information on the incident<sup>1</sup>.

LPB recently reported a similar incident in the UK in which an operator received extensive injuries in a fire involving the same pyrophoric chemical<sup>2</sup>.

## References

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