Sulfuric acid: Human health tier II assessment

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CAS Number: 7664-93-9

Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

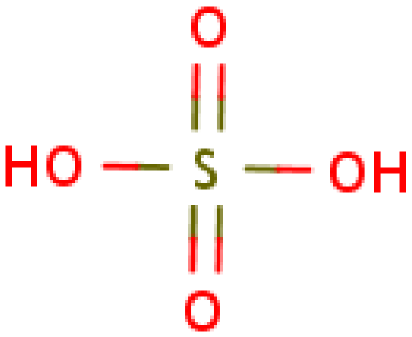
This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit:www.nicnas.gov.au

Disclaimer

Acronyms & Abbreviations

Chemical Identity

Synonyms	dihydrogen sulfate oil of vitriol
Structural Formula	
Molecular Formula	H2O4S
Molecular Weight (g/mol)	98.08
Appearance and Odour (where available)	Clear, colourless oily liquid.
SMILES	O=S(=O)(O)O

Import, Manufacture and Use

Australian

The following Australian industrial uses were reported under previous mandatory and/or voluntary calls for information.

Sulfuric acid has reported cosmetic, domestic or commercial uses as a pH regulating agent.

Sulfuric acid has reported domestic uses in:

- odour agents; and
- anticondensation agents.

The chemical has reported commercial use in:

- process regulators;
- photochemicals; and
- conductive agents.

The total volume introduced into Australia, reported under previous mandatory and/or voluntary calls for information, was in the range more than or equal to 1000000 tonnes.

The following non-industrial uses have been identified in Australia:

- dairy cleansers; and
- food processing aids.

International

The following international uses have been identified through: the European Union (EU) Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) dossiers; Galleria Chemica; the Substances and Preparations in Nordic countries (SPIN) database; the European Commission Cosmetic Ingredients and Substances (CosIng) database; the United States (US) Personal Care Products Council International Nomenclature of Cosmetic Ingredients (INCI) Dictionary; the US Household Products Database; the Environmental Working Group (EWG) Skin Deep database; and the US National Library of Medicine's Hazardous Substances Data Bank (HSDB).

Sulfuric acid has reported functions as pH adjusters in cosmetic products including hair products such as conditioners, dyes, colours and permanent waves.

The chemical has reported domestic uses in:

- glass etching solutions (arts and crafts);
- auto products such as rain repellants and wheel cleaners;
- silicone removers;
- silver polish;
- laundry products such as stain removers, bleaches and degreasers;
- dishwasher detergents;

- cleaning products;
- drain cleaners;
- rust removers;
- bleaching agents;
- adhesives and binding agents;
- colouring agents;
- corrosion inhibitors;
- fertilisers;
- fillers;
- odour agents;
- paints, lacquers and varnishes;
- surface treatment; and
- surface-active agents.

Sulfuric acid has commercial uses in:

- absorbents and adsorbents;
- anti−freezing agents;
- anti−set−off and anti−adhesive agents;
- fixing agents;
- construction materials;
- conductive agents;
- flux agents for casting;
- hydraulic fluids and additives;
- lubricants and additives;
- oxidising agents;
- photo chemicals;
- pH−regulation agents;
- process regulators;
- reprographic agents;
- solvents;
- tanning agents; and
- welding and soldering agents.

Sulfuric acid has site limited uses:

- in electroplating agents;
- as an intermediate; and
- in stabilisers.

Non-industrial uses include:

- pesticides;
- drinking water treatment chemicals;
- pharmaceuticals;
- pond and aquarium water clarifiers; and
- food additives.

Restrictions

Australian

This chemical is listed in the *Poisons Standard—the Standard for the Uniform Scheduling of Medicines and Poisons* (SUSMP) in Schedule 6 (SUSMP, 2015).

Schedule 6

'SULFURIC ACID (excluding its salts and derivatives) **except**:

(a) in fire extinguishers; or

(b) in preparations containing 0.5 per cent or less of sulfuric acid (H_2SO_4).'

Schedule 6 chemicals are described as 'Substances with a moderate potential for causing harm, the extent of which can be reduced through the use of distinctive packaging with strong warnings and safety directions on the label'. Schedule 6 chemicals are labelled with 'Poison' (SUSMP, 2015).

The chemical is listed in Category III - Illicit Drug Reagents/Essential Chemicals of the Code of Practice for Supply Diversion into Illicit Drug Manufacture (PACIA, 2008).

International

No known restrictions have been identified.

Existing Work Health and Safety Controls

Hazard Classification

The chemical is classified as hazardous, with the following risk phrases for human health in the Hazardous Substances Information System (HSIS) (Safe Work Australia):

C; R35 (corrosivity)

Exposure Standards

Australian

The chemicals has an exposure standard of 1 mg/m^3 time weighted average (TWA) and 3 mg/m^3 short-term exposure limit (STEL).

International

The following exposure standards are identified (Galleria Chemica).

An exposure limit of 0.05–1 mg/m^3 TWA and 0.1–3 mg/m^3 STEL in different countries such as the USA (California, Hawaii, Minnesota, Vermont), Canada (Alberta, British Columbia, Yukon), South Africa, Malaysia, India and Denmark.

Health Hazard Information

Sulfuric acid is a strong mineral acid that dissociates readily in water to form sulfate ions (SO_4^{2-}) and hydrogen ions (H^+). The dissolution in water is strongly exothermic, so a vigorous reaction occurs when water is added to sulfuric acid. It is a powerful acidic oxidiser which can cause ignition or explosion when it comes into contact with many materials (OECD, 2001).

Sulfuric acid is corrosive and irritating and causes direct local effects on the skin, eyes and gastrointestinal tract after exposure to sufficient concentrations. Exposure to high concentrations rapidly destroys tissue, causing severe burns. If much of the skin is involved, exposure is accompanied by shock, collapse, and symptoms similar to those seen in severe burns. Repeated contact with dilute solutions can cause dermatitis, and repeated or prolonged inhalation of a mist of sulfuric acid can cause inflammation of the respiratory tract, leading to chronic bronchitis. Inhalation of concentrated vapour 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 (HSDB).

The effects of sulfuric acid are the result of the H^+ ion rather than an effect of the sulfate anion. The acid rapidly dissociates in water and the anion will enter the body electrolyte pool. This is supported by experiments which have studied the active component in inorganic acids on various endpoints, using different acids or salts (HCl, NH_4HSO_4, $(NH_4)_2SO_4$, Na_2SO_4). In these studies, the authors concluded that the observed effects seemed to be due to the H^+ ion while the anion appeared to have no effect (OECD, 2001). Sulfate is an endogenous constituent of the blood arising from the metabolism of sulfur-containing amino acids and ingestion of sulfate in food and water. It is required for the synthesis of many important sulfur-containing compounds (NAS, 2004). Sulfate is homeostatically regulated by the kidneys and excess is excreted in the urine (Fernandes et al, 2001). The body pool of this anion is large, and it is therefore unlikely that occupational exposures would significantly modify the normal body load (OECD, 2001).

Small droplets of sulfuric acid (aerosol/mist) can also be inhaled and cause local effects on the respiratory tract. The effects of inhaled sulfuric acid aerosols will depend on many factors including concentration, the length of exposure, the particle size of the aerosol (which determines the location in the respiratory tract where sulfuric acids aerosols will deposit), humidity, buffering capacity of the airways and the species studied (OECD, 2001).

Sulfuric acid has a low vapour pressure (<0.001 hPa at 20 °C). However, mists and aerosols can be formed in some industrial applications. This situation can occur because sulfur trioxide, the anhydride of sulfuric acid, generates very dense sulfuric acid mists with atmospheric humidity. However, this occurs only in the event of accidental leakage of sulfur trioxide, and is not a result of normal activity. Other sulfuric acid uses that are important sources of sulfuric acid mists in the workplace are car and industrial battery loading; metal sheet cleaning for surface treatment; electro-chemical production of zinc and copper (sulfuric acid is driven off as fine droplets by evolved hydrogen); and loading and discharging of sulfuric acid. The occupational exposure standard for sulfuric acid mitigates risks associated with mists and aerosols (OECD, 2001). While carcinogenicity is relevant in the case of acid mist conditions, the sulfate ion is not considered to be carcinogenic.

No carcinogenic effect was observed in carcinogenicity studies conducted by inhalation with sulfuric acid aerosol using three different animal species. Small increases in tumour incidence were reported in rats and mice after chronic gastric intubation or intratracheal instillation of sulfuric acid solution, but no clear conclusion can be drawn from these studies. Several epidemiological studies have suggested a relationship between exposure to inorganic acid mists containing sulfuric acid and an increased incidence of laryngeal cancer. IARC has concluded that 'occupational exposure to strong inorganic mists containing sulfuric acid is carcinogenic for humans (Group 1).' Concerns have been raised that confounding factors could not be fully excluded. This classification applies to exposure to the mist (or aerosol) and not to sulfuric acid per se. It is likely that sulfuric acid aerosols in sufficiently high concentrations are deposited in preferred locations in the nasopharyngeal and/or laryngeal regions, where they cause repetitive injury, inflammation and repair. The resulting increased cell proliferation, in conjunction with other carcinogenic agents, may well be responsible for the observed, rather weak association between exposure and effect. Such preferential deposition and extremely localised induced effects (squamous metaplasia and persistent proliferation) have been demonstrated in rodents in a 28 day inhalation study in rats (OECD, 2001) (see **Repeated Dose Toxicity** section).

Because sulfate ions are naturally present in the body and effective homeostatic mechanisms work to maintain these levels, chronic systemic health effects such as repeated dose toxicity, carcinogenicity and reproductive toxicity are not expected following exposures at non-irritating concentrations. The available animal data for repeated dose toxicity, genotoxicity and reproductive toxicity are negative and support this conclusion (OECD, 2001). Sulfuric acid is permitted to be used as a food processing aid in Australia, indicating its low potential for chronic toxicity (FSANZ, 2015).

NICNAS identified disodium sulfate and dipotassium sulfate as being of low concern to human health (NICNAS, 2012).

Toxicokinetics

In a non-guideline study investigating the clearance via the blood of radiolabelled sulfuric acid aerosol in rats, dogs and guinea pigs, the half-time for 50 % clearance of sulfuric acid from the lungs of the animals into the blood following inhalation exposure was two to nine minutes (REACH).

Gastrointestinal absorption of sulfate can occur in the stomach, small intestine, and colon. When soluble sulfate salts (e.g. potassium sulfate or sodium sulfate) are consumed, more than 80 % of oral sulfate doses are absorbed, as shown by isotopic tracer studies. Sulfate that is not absorbed in the upper gastrointestinal tract passes to the large intestine and colon, where it is either excreted in the faeces, reabsorbed, or reduced by anaerobic bacteria to metabolites, such as hydrogen sulphide (IOM, 2004).

Acute Toxicity

Oral

Sulfuric acid is of low toxicity with a median lethal dose (LD50) of approximately 2140 mg/kg bw. In a non-guideline study conducted on unfasted Carworth-Wistar rats (5 animals of a single sex/dose group) the animals were gavaged with reagent grade (95–98 %) sulfuric acid in water at 0.25 g/mL at different doses (unreported) and observed for 14 days. Based on the pattern of mortalities, the 'most probable median lethal dose' is reported to be 2140 (1540–2990) mg/kg bw (REACH).

Dermal

No data are available.

Inhalation

A number of acute inhalation toxicity studies are available for rats, mice, rabbits and guinea pigs. The effects of sulfuric acid following inhalation are entirely due to local irritation of the respiratory tract, thus classification for acute inhalational toxicity is not recommended despite low median lethal concentrations (LC50s). There is no evidence for the systemic toxicity of sulfuric acid in any study as effects are limited to the site of contact. The main macroscopic and/or microscopic alterations observed in the respiratory tract after acute exposure to sulfuric acid aerosol are haemorrhage, oedema, atelectasis (partial collapse or incomplete inflation of the lung) and thickening of the alveolar wall in the lung of guinea pigs, haemorrhage and oedema of the lungs and/or ulceration of the turbinate, trachea and larynx in rats and mice. These lesions are related to the corrosive/irritant effect of sulfuric acid.

Groups of Fischer 344 rats (5/sex/dose) were exposed (whole body) to aerosols of sulfuric acid in a study protocol broadly compliant with OECD TG 403 except that exposure was for 1, 2, 4, or 8 hours and the surviving animals were observed for 21 rather than 14 days. The LC50 was found to be 0.375 mg/L following 4 hours' exposure to sulfuric acid (REACH).

Corrosion / Irritation

Corrosivity

Sulfuric acid is classified as hazardous with the risk phrase 'Causes severe burns' (C; R35) in the HSIS (Safe Work Australia). The available data support this finding for concentrated sulfuric acid.

This is consistent with the pKa (a term used to describe the strength of an acid—lower values indicate stronger acids) for sulfuric acid, <0 at 25°C.

Skin irritation studies performed using diluted sulfuric acid (10 %) in rabbits, guinea-pigs and humans found that dilute sulfuric acid is not irritating (OECD, 2001). Conflicting results are observed in eye irritation studies depending on the protocol used (OECD/EU or US). However, the buffering and dilution effects of tears could explain the different conclusions since sulfuric acid was instilled into the conjunctival sac of the eye in some of the studies while acid was administered directly to the central corneal surface in other studies (OECD, 2001).

Acute inhalation exposure to sulfuric acid aerosols causes a range of effects in the respiratory system including decrease in particle clearance rates at lower concentrations (<1.0 mg/m^3) to changes in lung function (>1.0 mg/m^3). Asthmatics and those with hyper-reactive airways appear more sensitive to the broncho-constrictive effects of the aerosol. Repeated exposure to higher concentrations of aerosol (>3.0 mg/m^3) has been reported to cause damage to the incisors (OECD, 2001).

Sensitisation

Skin Sensitisation

No data are available.

Observation in humans

Sulfuric acid has been in industrial use for many decades, and skin burns due to concentrated sulfuric acid are well documented. However, skin sensitisation secondary to skin irritation or burns has never been described, despite the fact that severe chemical irritation and burns are known to create favourable conditions for the induction of contact allergy. Repeated contact with more diluted sulfuric acid is known to cause skin dessication, ulceration and chronic purulent inflammation around the nails. These symptoms are quite different from those seen in acute or chronic allergic dermatitis. Skin contact with weak solutions of sulfuric acid (about 10 %) has been quite common in the viscose rayon industry for nearly a century. Despite widespread human contact with dilute solutions, sulfuric acid allergy has never been noted (OECD, 2001).

Repeated Dose Toxicity

Inhalation

Repeated dose inhalation toxicity tests with sulfuric acid mists revealed treatment-related findings limited to histopathology and cell proliferation of the larynx, consistent with a local irritant effect of the substance (OECD, 2001).

Groups of female Wistar rats were exposed to aerosols of sulfuric acid (mists) at target concentrations of 0, 0.2, 1.0 or 5.0 mg/m^3 for six hours a day, five days a week for five or 28 days. Additional groups exposed to 0 or 5.0 mg/m^3 (nominal concentration) for 28 days were investigated following recovery periods of four or eight weeks. Effects of exposure were limited to the larynx. Squamous metaplasia and significant cell proliferation was seen following exposure to 1.38 and 5.52 mg/m^3 for five and 28 days; findings had decreased in severity following the recovery periods. Findings following exposure to 0.3 mg/m^3 for 28 days were limited to minimal metaplasia (with no proliferation); no effects were apparent following exposure to 0.3 mg/m^3 for five days. The lowest observed adverse concentration (LOAEC) for this study is therefore considered to be 0.3 mg/m^3 (REACH).

Risk Characterisation

Critical Health Effects

Sulfuric acid is corrosive or irritating to the skin, eyes, gastrointestinal and respiratory tracts at concentrations greater than 10 %.

Public Risk Characterisation

Sulfuric acid is used in cosmetic products at low concentrations, such as in hair products, where the pH of the product is close to neutral. It is also found in domestic products where low pHs are important for product functionality such as various types of cleaning products. However, concentrated sulfuric acid is not expected to be available to the public.

The main route of public exposure is expected to be contact with eyes and skin. Labelling for formulations containing sulfuric acid is controlled by the Poisons Standard (SUSMP, 2015). Provided that the appropriate precautions are taken to avoid skin and eye contact or inhaling chemical aerosols when using products with higher concentrations of the chemicals at low pH, the risk from the use of domestic and cosmetic products is not considered to be unreasonable.

Occupational Risk Characterisation

During product formulation, dermal, ocular and inhalation exposure might occur, particularly where manual or open processes are used. These could include transfer and blending activities, quality control analysis, and cleaning and maintaining equipment. Worker exposure to the chemical at lower concentrations could also occur while using formulated products containing the chemical. The level and route of exposure will vary depending on the method of application and work practices employed.

NICNAS Recommendation

Current risk management measures are considered adequate to protect public and workers’ health and safety, provided that all requirements are met under workplace health and safety, and poisons legislation as adopted by the relevant state or territory. No further assessment is required.

Regulatory Control

Public Health

Products containing this chemical should be labelled in accordance with state and territory legislation (SUSMP, 2015).

Work Health and Safety

The chemical is recommended for classification and labelling under the current approved criteria and adopted GHS as below. This assessment does not consider classification of physical and environmental hazards.

Hazard	Approved Criteria (HSIS)[a]	GHS Classification (HCIS)[b]
Irritation / Corrosivity	Causes severe burns (C; R35)*	Causes severe skin burns and eye damage - Cat. 1A (H314)

[a] Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2004)].

[b] Globally Harmonized System of Classification and Labelling of Chemicals (GHS) United Nations, 2009. Third Edition.

[*] Existing Hazard Classification. No change recommended to this classification

Advice for consumers

Products containing the chemical should be used according to the instructions on the label.

Advice for industry

Control measures

Control measures to minimise the risk from oral, dermal, ocular or inhalation exposure to the chemical should be implemented in accordance with the hierarchy of controls. Approaches to minimise risk include substitution, isolation and engineering controls. Measures required to eliminate, or minimise risk arising from storing, handling and using a hazardous chemical depend on the physical form and the manner in which the chemical is used. Examples of control measures that could minimise the risk include, but are not limited to:

- using closed systems or isolating operations;
- using local exhaust ventilation to prevent the chemical from entering the breathing zone of any worker;
- air monitoring to ensure control measures in place are working effectively and continue to do so;
- minimising manual processes and work tasks through automating processes;
- work procedures that minimise splashes and spills;
- regularly cleaning equipment and work areas; and
- using protective equipment that is designed, constructed, and operated to ensure that the worker does not come into contact with the chemical.

Guidance on managing risks from hazardous chemicals are provided in the *Managing risks of hazardous chemicals in the workplace—Code of practice* available on the Safe Work Australia website.

Personal protective equipment should not solely be relied upon to control risk and should only be used when all other reasonably practicable control measures do not eliminate or sufficiently minimise risk. Guidance in selecting personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

Obligations under workplace health and safety legislation

Information in this report should be taken into account to help meet obligations under workplace health and safety legislation as adopted by the relevant state or territory. This includes, but is not limited to:

- ensuring that hazardous chemicals are correctly classified and labelled;
- ensuring that (material) safety data sheets ((M)SDS) containing accurate information about the hazards (relating to both health hazards and physicochemical (physical) hazards) of the chemical are prepared; and
- managing risks arising from storing, handling and using a hazardous chemical.

Your work health and safety regulator should be contacted for information on the work health and safety laws in your jurisdiction.

Information on how to prepare an (M)SDS and how to label containers of hazardous chemicals are provided in relevant codes of practice such as the *Preparation of safety data sheets for hazardous chemicals—Code of practice* and *Labelling of workplace hazardous chemicals—Code of practice*, respectively. These codes of practice are available from the Safe Work Australia website.

A review of the physical hazards of the chemical has not been undertaken as part of this assessment.

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