

# New observations on occupational exposure limits for sulfuric acid

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### **Introduction**

Sulfuric acid was first assessed to be carcinogenic in 1997 in a report of the World Health organization WHO (IARC). Based on this report, the Senate committee dealing with the control of harmful substances in the workplace submitted the first proposal justifying a lower occupational exposure limit [2]. This proposal contained a list of many individual studies. In the investigations which were part of the survey, golden hamsters, for example, were exposed to concentrated sulfuric acid mist produced by ultrasonic spraying at a concentration of more than 200 mg per m<sup>3</sup> of breathable air. Only irritation of the mucous membranes was diagnosed. Only one group of workers in a single company that works with concentrated sulfuric acid has been statistically screened for symptoms of disease. Strict scientific evidence to justify new standards cannot be derived from this case. Essentially, the studies were based only on experimentation with concentrated sulfuric acid or sulfuric acid enriched with SO<sub>3</sub>, so-called oleum.

The results can be summarized as follows:

- Up to concentrations of 2 mg H<sub>2</sub>SO<sub>4</sub>/m<sup>3</sup>, no effects could be recorded on measurements of pulmonary function.
- A classification in cancer category 4 can be derived (if at all) only for high concentrations.
- Studies involving animal experimentation give no evidence for effects that cause or promote cancer.
- There are no indications for a genotoxic effect.
- There are no indications for a mutagenic effect of sulfuric acid on germ cells.

Despite these comparatively harmless findings, some of the ambiguous results were interpreted as warnings. It is important that health and safety should have absolute priority and, from an ethical point of view, no costs should be spared. Furthermore, some preventative measures should be taken in cases of doubt. Nevertheless, an important aspect has not been taken into account when considering sulfuric acid. The WHO surveys only contain alarming indications, if any, concerning concentrated sulfuric acid, sulfur trioxide, SO<sub>3</sub>, and oleum (fuming sulfuric acid supersaturated with SO<sub>3</sub>). However, only dilute solutions are used in the metal surface treatment industries, electroplating and anodizing. In spite of this, in recent years, only *sulfuric acid* without any differentiation has been mentioned globally in the numerous argumentative discussions that have taken place in industrial associations or experts' committees, which have struggled to reach a reasonable estimation of the potential toxicological risk.

Concentrated sulfuric acid has destructive effects on human, animal and plant tissues. Many organic substances are carbonized in contact with concentrated sulfuric acid because the acid separates the water from them and readily binds it chemically (picture 1). If, however, after water absorption, the concentration falls below 85.4%, there is no longer present any molecules with the formula H<sub>2</sub>SO<sub>4</sub>, as we will demonstrate in the following text. In dilute solutions of sulfuric acid, organic substances dissolve without changing (picture no 2).

The occupational exposure limit is the maximum average time-weighted concentration of a substance in the air of a workplace over a given time period. It indicates the concentration of a substance for which acute or chronic harmful effects on health in general are not to be expected.

It can be already concluded from the previous examples and from the comparison between pictures 1 and 2 that there are fundamental differences between concentrated sulfuric acid and dilute solutions as far as acute harmful effects on health are concerned.

The occupational exposure limits are determined in the Technical Rules for Dangerous Substances (TRGS 900) with quasi force of law. From 1995 until 28 February 2006, the following values applied

for sulfuric acid and sulfur trioxide (measured as sulfuric acid); these values were differentiated according to industry,

- For instance, an etching bath of more than 12 meters length and 1.2 meters width, which cannot be covered because of the process:  $0,5 \text{ mg/m}^3$
- Production using sulfuric acid in the electroplating industry:  $0,2 \text{ mg/m}^3$
- Others:  $0,1 \text{ mg/m}^3$
- 



*Picture 1:  
Effect of 20% dilute sulfuric acid (left) and concentrated sulfuric acid (right) on a sugar cube after one minute; already after a few seconds, a yellowish coloration is visible for the concentrated sulfuric acid, which rapidly becomes brown and then goes to a black coloration.*



*Picture 2  
Effect of 20% dilute sulfuric acid (left) and concentrated sulfuric acid (right) on a sugar cube after 30 minutes; already after a few minutes, the sugar cube in the concentrated sulfuric acid is completely carbonized unlike the sugar cube in the dilute sulfuric acid which only dissolves.*

This differentiation contradicts the definition of occupational exposure limits and is meaningless because a substance cannot be more harmful at workplace A than at workplace B (and vice versa). For comparison, the values for other mineral acids are mentioned:

- Hydrochloric acid (muriatic acid):  $3 \text{ mg/m}^3$
- Nitric acid:  $5.2 \text{ mg/m}^3$
- Phosphoric acid:  $2 \text{ mg/m}^3$

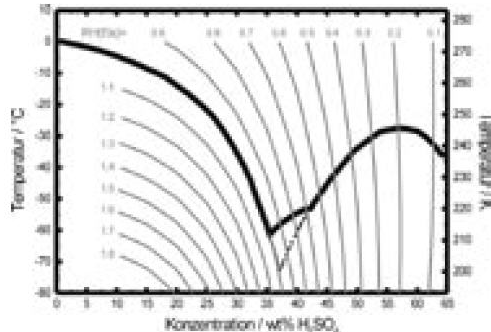
In the present official standard TRGS900 for the year 2006, sulfuric acid is not mentioned. It is however to be found in a working list of the committee for dangerous substances (AGS). This committee expressly draws attention to the fact that the values given in the list should serve as guidance for the work of Subcommittee III and are not meant as occupational exposure limits according to the Decree on Dangerous Substances or TRGS 900 respectively. In this working list one can find hydrocyanic acid (or prussic acid) with a value of  $11 \text{ mg/m}^3$  and additionally a possible safety factor of 4.

### ***Effects of an occupational exposure limit:***

For the surface treatment of metals and plastics, dilute solutions of sulfuric acid are essential and indispensable. Especially anodizing plants, i.e. plants for the surface treatment of aluminium, have no alternative to sulfuric acid. The electroplating industry uses many different acid electrolytes containing sulfates. In addition, it uses acid etching solutions and pickling solutions which are necessary simply for derusting steel parts, as well as acid cleaning solutions.

The equilibrium vapour pressure over dilute solutions of sulfuric acid [3] corresponds to that of water or rather ice and no acid escapes from such solutions into the air (the opposite to hydrochloric acid) (Chart 3)

If it happens that acidity can be detected by measurements in the air above the electrolyte tanks which contain dilute solutions of sulfuric acid, these can only be fine mists comprising very small droplets with particle dimensions of the order of 1  $\mu\text{m}$ . Such aerosols always occur when hydrogen is evolved. In addition, aerosols and fume can arise in spraying applications; spray pre-treatment installations are increasingly used in the pre-treatment before powder coating.



*Chart 3  
The equilibrium vapour pressure of H<sub>2</sub>SO<sub>4</sub> solutions corresponding to relative humidity RH(ice) [3]. The points (wt%, T) in the phase diagram at RH(Ice) = 1 lie exactly on the melting curve of ice.*

Air agitation does not trigger the production of aerosols in the treatment electrolyte. It only helps disperse the aerosols. In fact, it is the small hydrogen bubbles which reach the surface that produce the fine aerosol mist with individual particles in  $\mu\text{m}$  dimensions.

With acid etching, the development of hydrogen occurs on the surface of the piece of metal being treated; with electrolytic process, the development occurs at the cathodes.

In principle, it would be possible to reduce the action of aerosols in the workplace by air extraction. However, in the case of large tanks as needed for the etching of steel and especially in aluminium surface treatment plants (for instance, typical anodizing tanks are 7 metres long and over one metre wide), the flow conditions are very unfavourable. The aerosol particles which are more inert than gases cannot really be removed effectively using normal air extraction installations to enable compliance with an occupational exposure limit of 0.1  $\text{mg}/\text{m}^3$ . Anodizing lines without any air extraction reliably comply with the current criterion for the maximum concentration of 1  $\text{mg}/\text{m}^3$  (German: MAK) as shown by a high number of measurements in recent years. In general, air extraction installations are not common in anodizing lines and also not required. Air extraction also removes heat, that is the warm air in the workplace, and any additional energy requirement is ecologically critical. And should one of the extracted substances be harmful, then the air cannot go untreated into the environment because the German Federal law about emissions applies in such cases (BLm SchG.)

Another possibility to reduce the formation of aerosols is to have foam coverage on the working electrolytes. In this case, the increased use of chemical products is to be valued negatively for the ecological balance. An enrichment of such foam coverage by hydrogen also has to be assessed critically in terms of fire protection. In the case of air extraction, an alarm and a safety device have to be considered because, if the ventilation breaks down, there may be an accumulation of explosive mixtures in the narrow pipes of the air extraction system. That can virtually never happen in open space.

In Japan a technology involving direct extraction from the cathode area has been implemented in the anodizing plants for decades. In this case the cathode area is protected by a textile fabric optimized from the point of view of mesh size and made of a stable plastic fibre. The mesh size is selected so that the hydrogen bubbles are retained and so it does not offer too much resistance to the current flowing through it. The aim of such direct air extraction from the cathode area is not and was not to comply with occupational exposure limits in Japan, but rather to protect sensitive electronic measurement and control devices from humid aerosols. For this reason it has long remained a special case in the Japanese region, because only there were microprocessor technology and automation used at a very

early development stage (as far as video cameras on transport cranes which are obviously poorly protected locations).

The German Institute for Work Protection (Berufsgenossenschaftliches Institut für Arbeitsschutz – BGIA) gives recommendations for compliance with occupational exposure limits. The Institute also collects all official analysis data from measurements by the trade organizations in Germany.

At an international level, thousands of anodizing plants are equipped with installations using dilute sulfuric acid electrolytes with concentrations corresponding to 18 weight%  $\text{H}_2\text{SO}_4$ . The capacity of the rectifiers amounts to more than 10 000 amperes and, in consequence, the development of hydrogen at the cathodes is important. Air extraction is seldom used. For decades, there has been no known case of acute or chronic harmful effects on the health of the workers in these plants caused, for instance, by aerosols.

All the preceding explanations are based on the assumption that sulfuric acid is properly measured in the air when considering the maximum concentrations in the workplace (German MAK) or the occupational limits.

The measurement method is as follows

- A quantifiable amount of air is passed through a filter which collects the small drops of aerosol.
- Then, with ion chromatography, the quantity of sulfate in the substance that adheres to the filter is measured.

Using this method, there is no evidence that any molecules of sulfuric acid were in the air. Only the sulfate anion is recorded, which is absolutely harmless from the ecological-toxicological point of view.

### ***The actual concentration of sulfuric acid***

As shown in the examples given in pictures 1 and 2, the concentrated sulfuric acid has a different effect from a dilute solution on a sugar cube, namely carbonizing and destruction. Every laboratory worker knows about the high heat evolution when concentrated sulfuric acid is diluted with water; dilution is only possible if the concentrated acid is poured into cold water with great caution. In so doing, the water heats up to its boiling point. On the other hand, dropping water into concentrated acid leads to violent, nearly explosive splashing of the liquid. This obviously means a violent exothermal chemical reaction that is a change to the substance which, in this case, is the sulfuric acid molecule  $\text{H}_2\text{SO}_4$ .

The system  $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$  is best investigated from a scientific point of view [4,5]. The discreet compounds, the so-called phases, which appear during the chemical reaction between sulfuric acid and water are well known and even the crystal structures have been clarified and, as a consequence, the molecular geometry [6].

Chart 4 shows the phase diagram of the system  $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ . In this phase diagram, there are two points which are especially important. At 84.5%  $\text{H}_2\text{SO}_4$ , there is a congruently melting phase which indicates a new stable compound. This new compound has practically the same melting point as sulfuric acid itself. The analysis of the crystal structure gives the clear result that we no longer have a  $\text{H}_2\text{SO}_4$  molecule but have an oxonium hydrogen sulfate.

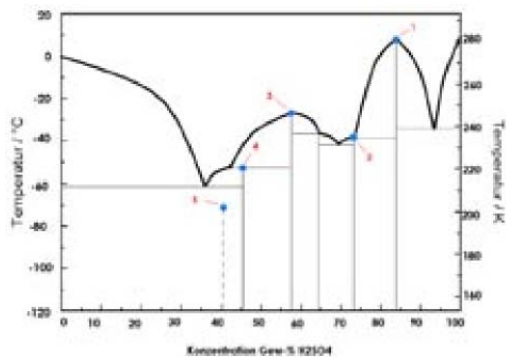


Chart 4:  
Phase diagram of the system  $H_2SO_4 - H_2O$ . The numbers show the intermediate phases listed in table 1.

Table 1: Phases or compounds in the system  $H_2SO_4 - H_2O$  [6] as evidenced by chemical structure.

$H_2SO_4 \cdot nH_2O$	Degree of hydration	Cation	Anion
84,5 wt%	1	$H_3O^+$	$HSO_4^-$
73,1 wt%	2	$H_3O^+$	$SO_4^{2-}$
57,6 wt%	6	$H_5O_2^+$	$SO_4^{2-}$
45,4 wt%	6,5	$H_5O_2^+/H_7O_3^+$	$SO_4^{2-}$
40,5 wt%	8	$H_5O_2^+$	$SO_4^{2-}$

The next prominent feature is to be found at 57.6%  $H_2SO_4$ . Also here we find a congruently melting phase and therefore a stable compound which can be clearly characterized by analysis of its crystal structure as an oxonium sulfate hydrate.

At 73,1 %, 64,5 %, 45,5 % and 40,5 %, one can safely prove and without any doubt the existence of four additional compounds and therefore separate molecules. These are also quite consistently oxonium sulfates or their hydrates. These melt, however, incongruently, which mean that they disintegrate into the previously mentioned stable compounds of oxonium hydrogen sulfate and oxonium sulfate hydrate or of oxonium sulfate hydrate and water.

Below the concentration which corresponds to 84.5%  $H_2SO_4$ , the molecule of sulfuric acid no longer occurs.

For the aqueous solution at 25°C, this was already proven in 1959 [7] by the Raman spectroscopy method and additionally by an independent series of measurements in 1971 [8].

As results of these measurements, chart 5 shows the relative concentrations of the species sulfate  $SO_4^{2-}$ , hydrogen sulfate  $HSO_4^-$  and  $H_2SO_4$ . The undissociated  $H_2SO_4$  molecule which corresponds chemically to concentrated sulfuric acid only appears above the concentration of 84.5%. At lower concentrations of sulfuric acid, only the anions sulfate and hydrogen sulfate occur, the latter as salts of oxonium ions and their hydrates.

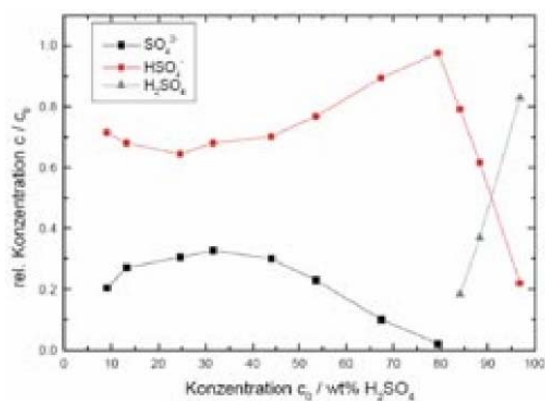


Chart 5:  
The variation of the relative concentrations  $c/c_0$  of the species  $SO_4^{2-}$ ,  $HSO_4^-$  and  $H_2SO_4$  in aqueous solutions of sulfuric acid. In complete accordance with the phase diagram of the systems  $H_2SO_4 - H_2O$ , the  $H_2SO_4$  molecule does not occur below a concentration of 84.5 weight %.

Aerosol particles, especially those that come from the sulfuric compounds in the atmosphere, are important to the general comprehension of natural science. This has been investigated by *H. Vortisch* at the University of Berlin [9] in a thesis that deserves the qualification “exemplary”; reference is specifically made here to chapter 6: *The qualities of aqueous solutions of sulfuric acid* and also to the literature quoted. Concentrations of sulfuric acid from 0.02 up to 0.03 mg/m<sup>3</sup> with peaks around 0.1 mg/m<sup>3</sup> have been measured in the environment in Europe and in the USA. In the case of the famous atmospheric condition called smog, the values measured were up to 10 times higher (highest individual value of 0.68 mg/m<sup>3</sup> in London in 1962).[2]. Also in the light of this natural background, fixing the occupational limit at too low a level seems exaggerated.

As a further consequence, labelling requirements should also be revised for the formulations/recipes of chemical products. When using sulfuric acid in formulations, the acid changes on dilution. In formulations with below 84.5 wt%, it is no longer present and labelling as the corresponding acid hydrogen sulfate makes more sense, is more pragmatic and more in accordance with practice.

In the reference document of the European Commission on the best available techniques for the surface treatment of metals and plastics [10], there is a table on sulfuric acid that takes a clear position. In the section *Solutions which do not require air extraction*, the following information is given for etching solutions containing sulfuric acid. Sulfuric acid generally does not develop any acid mist at temperatures below 60°, which would otherwise require air extraction for health and safety reasons.

### **Summary**

Anodizing is not done in sulfuric acid. Sulfuric acid anodizing is only a colloquial expression. Over the concentration range below 84.5% H<sub>2</sub>SO<sub>4</sub> there are no H<sub>2</sub>SO<sub>4</sub> molecules in aqueous solutions but instead oxonium cations, hydrogen sulfate anions and sulfate anions as well as their hydrates. The same applies to all electroplating processes, to acid etching solutions and to acid cleaners, in which aqueous solutions of dilute sulfuric acid are used.

Hydrogen sulfates and other sulfates are harmless from the ecological / toxicological point of view. Noxious effects are only associated with acidity depending on concentration. This should and must apply then to all mineral acids in the same way.

The directive 2006/15/EG of the European Commission dated 7 February 2006 defines the European targets in terms of occupational limits to be determined at community level as a means to protect workers against the danger of chemical substances in the workplace. Occupational limits in the meaning of this EU directive are values which are based on health, are not binding, are derived from the latest scientific data and take into consideration the best available techniques. These are exposure limits below which no harmful effects are to be expected from a substance.

In Germany, there is presently an attempt to lower the previous maximum workplace concentration from 1 mg/m<sup>3</sup> down to 0.2mg/m<sup>3</sup> as the occupational limit. For many surface treatment plants, this value is not obtainable, especially for those plants which have specially large electrolyte tanks that cannot be retro-fitted with air extraction. This is however not required due to the fact that all information on the harmful effects of concentrated sulfuric acid do not apply because the H<sub>2</sub>SO<sub>4</sub> molecule does not occur in dilute solutions.

All measurements obtained up to now in aluminium surface treatment plants as well as in the electroplating industry with values more than 0.1 mg H<sub>2</sub>SO<sub>4</sub>/m<sup>3</sup> are wrong. They rely on erroneous analytical methods. Not sulfuric acid, but instead the comparatively harmless sulfate was measured.

Here it is absolutely necessary to proceed to a new evaluation according to the specification of the European directive. For the surface treatment industry, for the electroplating industry and for anodizing plants, an occupational limit for sulfuric acid or for sulfur trioxide is not relevant. In future, a new evaluation should be made for hydrogen sulfate that should take the harmful potential of other mineral acids as a basis.

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#### The author

Dr. rer. nat. Dieter Brodalla studied chemistry and medicine at the University of Düsseldorf and received his chemistry diploma with distinction; he was awarded a doctorate at the Institute for Inorganic Chemistry and Structural Chemistry with the rating "summa cum laude". He has specialized in aluminium surface treatment since 1984, first as Manager of the Specialty Department and Department for Product Development/Application Technology for Aluminium Surface Treatment at Henkel KGaA and since 1990 as Director of ALCON GmbH, Düsseldorf. He has worked for many years as a volunteer in many specialized committees such as DIN and ISO standardization as well as in technical committees of national and international associations. He has represented the field of aluminium surface treatment in numerous publications and presentations at international congresses.

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