Kirk-Othmer Encyclopedia of Chemical Technology.

SULFAMIC ACID AND SULFAMATES

Sulfamic acid [5329-14-6] (amidosulfuric acid), HSO_3NH_2, molecular weight 97.09, is a monobasic, inorganic, dry acid and the monoamide of sulfuric acid. Sulfamic acid is produced and sold in the form of water-soluble crystals. This acid was known and prepared in laboratories for nearly a hundred years before it became a commercially available product. The first preparation of this acid occurred around 1836 (1). Later work resulted in identification and preparation of sulfamic acid in its pure form (2). In 1936, a practical process which became the basis for commercial preparation was developed (3, 4). This process, involving the reaction of urea with sulfur trioxide and sulfuric acid, continues to be the main method for production of sulfamic acid.

Sulfamic acid has a unique combination of properties that makes it particularly well suited for scale removal and chemical cleaning operations, the main commercial applications. Sulfamic acid is also used in sulfation reactions, pH adjustment, preparation of synthetic sweeteners (qv), and a variety of chemical processing applications. Salts of sulfamic acid are used in electroplating (qv) and electroforming operations as well as for manufacturing flame retardants (qv) and weed and brush killers (see HErbicides).

1. Properties

1.1. Sulfamic Acid

1.1.1. Physical

Sulfamic acid is a dry acid having orthorhombic crystals. The pure crystals are nonvolatile, nonhygroscopic, colorless, and odorless. The acid is highly stable up to its melting point and may be kept for years without change in properties. Selected physical properties of sulfamic acid are listed in Table 1. Other properties are available in the literature (5–8).

1.1.2. Chemical Properties

Selected chemical properties of sulfamic acid are listed in Table 2; other properties are listed in Reference 9.

Whereas sulfamic acid is a relatively strong acid, corrosion rates are low in comparison to other acids (Table 3). The low corrosion rate can be further reduced by addition of corrosion inhibitors (see Corrosion and corrosion control).

1.1.2.1. Inorganic Reactions. Thermal decomposition of liquid sulfamic acid begins at 209°C. At 260°C, sulfur dioxide, sulfur trioxide, nitrogen, water, and traces of other products, chiefly nitrogen compounds, result.

Aqueous sulfamic acid solutions are quite stable at room temperature. At higher temperatures, however, acidic solutions and the ammonium salt hydrolyze to sulfates. Rates increase rapidly with temperature elevation, lower pH, and increased concentrations. These hydrolysis reactions are exothermic. Concentrated solutions heated in closed containers or in vessels having adequate venting can generate sufficient internal pressure to cause container rupture. An ammonium sulfamate, 60 wt % aqueous solution exhibits runaway

Table 1. Physical Properties of Sulfamic Acid

Property	Value
mol wt	97.09
mp, °C	205
decomposition temperature, °C	209
density at 25°C, g/cm^3	2.126
refractive indexes, 25 ± 3°C	
α	1.533
β	1.563
γ	1.568
solubility, wt %	
aqueous	
at 0°C	12.08
20°C	17.57
40°C	22.77
60°C	27.06
80°C	32.01
nonaqueous, at 25°C	
formamide	16.67
methanol	4.12
ethanol (2% benzene)	1.67
acetone	0.40
ether	0.01
71.8% sulfuric acid	0.00

Table 2. Chemical Properties of Sulfamic Acid

Property	Value
dissociation constant, at 25°C	0.101
heat of formation, kJ/mol[a]	−685.9
heat of solution, kJ/mol[a]	19.10
pH of aqueous solutions, at 25°C	
1.00 *N*	0.41
0.75 *N*	0.50
0.50 *N*	0.63
0.25 *N*	0.87
0.10 *N*	1.18
0.05 *N*	1.41
0.01 *N*	2.02

[a] To convert J to cal, divide by 4.184.

Table 3. 100-Day Metal Corrosion Rates in Aqueous Acid[a], mm

	Sulfamic acid		Hydrochloric acid	
Metal	20°C	40°C	20°C	40°C
iron	0.76	2.42	3.5	7.4
304 stainless steel	0.0001	0.0001	0.11	0.40
316 stainless steel	0.0000	0.0000	0.02	0.25
copper	0.013	0.036	0.53	1.63
aluminum	0.04	0.22	3.04	3.24
brass	0.014	0.032	0.098	0.037
gunmetal	0.002	0.022	0.29	1.40

[a] 5-wt % solution.

Table 4. Hydrolysis of Aqueous Sulfamic Acid at 80°C

	Quantity of HSO_3NH_2 lost to hydrolysis, wt %		
Time, h	1% solution	10% solution	30% solution
1	4.5	7.8	7.9
2	9.1	15.1	15.1
3.1	13.3	22.7[a]	22.0
5	16.9	28.3	27.5
6	20.6	34.3	32.8
7	24.2	39.5	37.5
8	27.3	43.7	

[a] Value given is at $\mathrm{pH} = 4.2$.

hydrolysis when heated to 200°C at pH 5 or to 130°C at pH 2. The danger is minimized in a well-vented container, however, because the 60 wt % solution boils at 107°C (8, 10). Hydrolysis reactions are:

$$HSO_3NH_2 + H_2O \longrightarrow NH_4HSO_4$$

$$NH_4SO_3NH_2 + H_2O \longrightarrow (NH_4)_2\,SO_4$$

Alkali metal sulfamates are stable in neutral or alkaline solutions even at boiling temperatures. Rates of hydrolysis for sulfamic acid in aqueous solutions have been measured at different conditions (Table 4) (8, 10).

Sulfamic acid readily forms various metal sulfamates by reaction with the metal or the respective carbonates, oxides, or hydroxides. The ammonium salt is formed by neutralizing the acid with ammonium hydroxide:

$$Zn + 2\ HSO_3NH_2 \longrightarrow Zn\,(SO_3NH_2)_2 + H_2$$

$$CaCO_3 + 2\ HSO_3NH_2 \longrightarrow Ca\,(SO_3NH_2)_2 + H_2O + CO_2$$

$$FeO + 2\ HSO_3NH_2 \longrightarrow Fe\,(SO_3NH_2)_2 + H_2O$$

$$Ni\,(OH)_2 + 2\ HSO_3NH_2 \longrightarrow Ni\,(SO_3NH_2)_2 + 2\ H_2O$$

$$NH_4OH + HSO_3NH_2 \longrightarrow NH_4SO_3NH_2 + H_2O$$

Nitrous acid reacts very rapidly and quantitatively with sulfamic acid:

$$HSO_3NH_2 + HNO_2 \longrightarrow H_2SO_4 + H_2O + N_2$$

This reaction can be used for the quantitative analysis of nitrites (3, 11). The reaction of sulfamic acid and concentrated nitric acid gives nitrous oxide (12, 13):

$$HSO_3NH_2 + HNO_3 \longrightarrow H_2SO_4 + H_2O + N_2O$$

Chlorine, bromine, and chlorates oxidize sulfamic acid to sulfuric acid and nitrogen (1, 14):

$$2\ HSO_3NH_2 + KClO_3 \longrightarrow 2\ H_2SO_4 + N_2 + KCl + H_2O$$

Chromic acid, permanganic acid, and ferric chloride do not oxidize sulfamic acid.

Hypochlorous acid reacts at low temperatures to form *N*-chlorosulfamic acid [17172-27-9] and *N,N*-dichlorosulfamic acid [17085-87-9]:

$$HSO_3NH_2 + HOCl \longrightarrow HSO_3NHCl + H_2O$$

$$HSO_3NH_2 + 2\ HOCl \longrightarrow HSO_3NCl_2 + 2\ H_2O$$

A similar reaction occurs when sodium is present with the formation of sodium *N*-chlorosulfamate [13637-90-6] and sodium *N,N*-dichlorosulfamate [13637-67-7]:

$$NaSO_3NH_2 + 2\ NaOCl \longrightarrow NaSO_3NCl_2 + 2\ NaOH$$

Sulfamoyl chloride [7778-42-9] forms from reaction with thionyl chloride (15, 16):

$$HSO_3NH_2 + SOCl_2 \longrightarrow NH_2SO_2Cl + HCl + SO_2$$

Certain metal iodides, eg, sodium, potassium, cesium, or rubidium, react with sulfamic acid to form the corresponding alkali metal triodides (17):

$$2\ HSO_3NH_2 + 3\ CsI + H_2O \longrightarrow CsI_3 + Cs_2SO_4 + (NH_4)_2\ SO_3$$

An exception exists to the monobasic nature of sulfamic acid when it dissolves in liquid ammonia. Sodium, potassium, etc. add both to the amido and sulfonic portions of the molecule to give salts, such as $NaSO_3NHNa$.

Sodium sulfate and sulfamic acid form the complex $6\ HSO_3NH_2 \cdot 5\ Na_2SO_4 \cdot 15\ H_2O$. Phosphorus pentachloride reacts with sulfamic acid to form the following complex (18):

$$HSO_3NH_2 + 2\ PCl_5 \longrightarrow PCl_3{\cdot}ClSO_2NH + Cl_2 + HCl + POCl_3$$

Sulfamic acid and its salts retard the precipitation of barium sulfate and prevent precipitation of silver and mercury salts by alkali. It has been suggested that salts of the type $AgNHSO_3K$ [15293-60-4] form with elemental metals or salts of mercury, gold, and silver (19). Upon heating such solutions, the metal deposits slowly in mirror form on the wall of a glass container. Studies of chemical and electrochemical behavior of various metals in sulfamic acid solutions are described in Reference 20.

1.1.2.2. Organic Reactions. Primary alcohols react with sulfamic acid to form alkyl ammonium sulfate salts (21–23):

$$\mathrm{ROH + HSO_3NH_2 \longrightarrow ROSO_2O{\cdot}NH_4}$$

Sulfation by sulfamic acid has been used in the preparation of detergents from dodecyl, oleyl, and other higher alcohols. It is also used in sulfating phenols and phenol–ethylene oxide condensation products. Secondary alcohols react in the presence of an amide catalyst, eg, acetamide or urea (24). Pyridine has also been used. Tertiary alcohols do not react. Reactions with phenols yield phenyl ammonium sulfates. These reactions include those of naphthols, cresol, anisole, anethole, pyrocatechol, and hydroquinone. Ammonium aryl sulfates are formed as intermediates and sulfonates are formed by subsequent rearrangement (25, 26).

$$\mathrm{C_6H_5OH + NH_2SO_3H \longrightarrow NH_4SO_3 - O - C_6H_5}$$

$$\mathrm{NH_4SO_3 - O - C_6H_5 \longrightarrow NH_4SO_3 - C_6H_4OH}$$

$$\mathrm{1,4{-}C_6H_4\,(OH)_2 + 2\;NH_2SO_3H \longrightarrow (NH_4SO_3O)_2\,C_6H_4}$$

$$\mathrm{(NH_4SO_3O)_2\,C_6H_4 \longrightarrow (NH_4SO_3)_2\,C_6H_2\,(OH)_2}$$

Studies of sulfoesterification of higher alcohols with sulfamic acid are described in Reference 26.

Amides react in certain cases to form ammonium salts of sulfonated amides (22). For example, treatment with benzamide yields ammonium *N*-benzoylsulfamate [83930-12-5], $C_6H_5CONHSO_3{\cdot}NH_4$, and treatment with ammonium sulfamate yields diammonium imidodisulfonate [13597-84-1], $HN(SO_2ONH_4)_2$. Ammonium sulfamate or sulfamic acid and ammonium carbonate dehydrate liquid or solid amides to nitriles (27).

Primary, secondary, and tertiary amines react with sulfamic acid to form ammonium salts (28):

$$\mathrm{HSO_3NH_2 + RNH_2 \longrightarrow RNH_2{\cdot}HSO_3NH_2}$$

$$\mathrm{HSO_3NH_2 + R_3N \longrightarrow R_3N{\cdot}HSO_3NH_2}$$

Guanidine salts can be prepared by reaction of thiocyanates and sulfamates (22).

Aldehydes form addition products with sulfamic acid salts. These are stable in neutral or slightly alkaline solutions but are hydrolyzed in acid and strongly alkaline solutions. With formaldehyde, the calcium salt of the methylol (hydroxymethyl) derivative [82770-57-8], $Ca(O_3SNHCH_2OH)_2$, is obtained as a crystalline solid.

Cadmium, cobalt, copper, and nickel sulfamates react with lower aliphatic aldehydes. These stable compositions are suitable for use in electroplating solutions for deposition of the respective metal (see Electroplating).

Fatty acid acyl halides react with sulfamic acid (29).

The *N*-alkyl and *N*-cyclohexyl derivatives of sulfamic acid are comparatively stable. The *N*-aryl derivatives are very unstable and can only be isolated in the salt form. A series of thiazolylsulfamic acids has been prepared.

Table 5. Literature References for Properties of Sulfamates

Compound	CAS Registry Number	References
ammonium	[7773-06-0]	32
aluminum	[10101-13-0]	(2, 32)
barium	[13770-86-0]	(27, 32, 33)
cadmium	[14017-36-8]	32
calcium	[13770-92-8]	32
cobalt	[14017-41-5]	(32, 34)
copper	[14017-38-0]	(27, 32, 35–37)
iron	[14017-39-1]	(12, 32)
lead	[32849-69-7]	(27, 32, 35)
lithium	[21856-68-8]	32
magnesium	[13770-91-7]	(32, 38)
manganese	[83929-95-7]	32
nickel	[13770-89-3]	(32, 36)
potassium	[13823-50-2]	32
silver	[14325-99-6]	(12, 15, 19, 27, 32, 33)
sodium	[13845-18-6]	32
strontium	[83929-96-8]	32
thallium	[21856-70-2]	32
uranyl	[82783-83-3]	32
zinc	[13770-90-6]	32
1:1 anilinium	[10310-62-0]	(22, 35, 39–41)
1:1 amylaminium	[82323-98-6]	40
1:1 benzylaminium	[82323-99-7]	42
1:1 hydroxylaminium	[82324-00-3]	(12, 22)
1:1 trimethylaminium	[6427-17-4]	38
1:1 hydrazinium	[39935-03-0]	(2, 12, 35, 40)
α-naphthylaminium	[83929-97-9]	(39, 40)
β-naphthylaminium	[83929-98-0]	(39, 40)
1:1 piperidinium	[82324-01-4]	43
1:1 *p*-toluidinium	[68734-85-0]	(39, 40)

Cellulose sulfated using sulfamic acid degrades less than if sulfated using sulfuric acid (23). Cellulose esters of sulfamic acids are formed by the reaction of sulfamyl halides in the presence of tertiary organic bases (see Cellulose esters).

Other organic reactions of sulfamic acid are described in the literature (30, 31).

1.2. Sulfamates

Sulfamates are formed readily by the reaction of sulfamic acid and the appropriate metal or its oxide, hydroxide, or carbonate. Approximate heats of neutralization are –54.61 kJ/mol (−13.05 kcal/mol) for the NaOH reaction and −47.83 kJ/mol (−11.43 kcal/mol) for NH_4OH at 26–30°C. Sulfamates prepared from weak bases form acidic solutions, whereas those prepared from strong bases produce neutral solutions. The pH of 5 wt % solution of ammonium sulfamate is 5.2. Crystals of ammonium sulfamate deliquesce at relative humidity of 70% and higher. Both ammonium sulfamate [7773-06-0] and potassium sulfamate [13823-50-2] liberate ammonia at elevated temperatures and form the corresponding imidodisulfonate (12). Inorganic sulfamates are quite water-soluble, except for the basic mercury salt. Some relative solubilities of sulfamates at 25°C in 100 g of water are ammonium, 103 g; sodium, 106 g; magnesium, 119 g; calcium, 67 g; barium, 34.2 g; zinc, 115 g; and lead, 218 g. The properties of a number of sulfamates may be found in the literature (see Table 5).

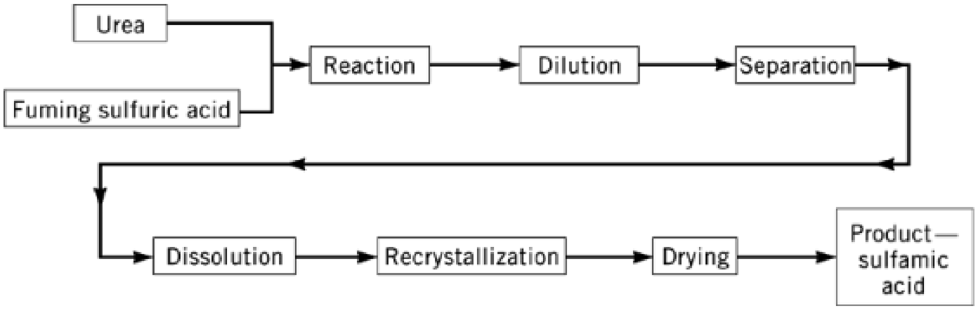

Fig. 1. Schematic flow diagram of the sulfamic acid process.

2. Manufacture

2.1. Sulfamic Acid

Sulfamic acid is manufactured by the reaction of urea and fuming sulfuric acid (3, 4, 44). This reaction is considered to take place in two steps involving an aminocarbonylsulfamic acid intermediate:

$$NH_2CONH_2 + SO_3 \longrightarrow [HSO_3NHCONH_2]$$

$$[HSO_3NHCONH_2] + H_2SO_4 \longrightarrow 2\ HSO_3NH_2 + CO_2$$

The overall reaction is as follows:

$$NH_2CONH_2 + SO_3 + H_2SO_4 \longrightarrow 2\ HSO_3NH_2 + CO_2$$

Urea reacts with fuming sulfuric acid in an exothermic reaction that needs agitation and cooling. After completion of the reaction, excess sulfur trioxide is removed by dilution or by other methods (45, 46). A flow diagram of the process is shown in Figure 1.

In the sulfamic acid process, electrical energy is needed for removal of reaction heat, filtration, fluid transportation, etc. Consumption is about 300 kWh/t of sulfamic acid. Consumption of steam, used for the heat exchanger, crystallizer, and drier, is from 1000 to 1500 kg/t of sulfamic acid.

The reaction between urea and fuming sulfuric acid is rapid and exothermic. It may proceed with violent boiling unless the reaction temperature is controlled. The reactants are strongly acidic. Therefore, operators should wear suitable protective gear to guard against chemical hazard. Special stainless steel, rubber lining, fiber-reinforced plastics, and polyvinyl chloride and carbon equipment are used.

The reaction takes place at atmospheric pressure. For stable control of the reaction rate, the reaction is first carried out at a temperature of 50°C and then at 60°C. Overall, this batch reaction takes about 9 hours. After completion of reaction, the slurry is diluted to about 70% sulfuric acid solution, and crude sulfamic acid crystals are separated by centrifuge. The crystals are dissolved in mother liquor to make a saturated solution at 60°C and the solution is concentrated under vacuum at 40°C. Purified sulfamic acid is obtained by recrystallization.

The yield of sulfamic acid varies with operating conditions. An overall yield of about 90% is obtained in the Nissan process. Losses are approximately 6% in the reaction stage, 3% in recrystallization, and 1% in other sections. The manufacture of ammonium sulfamate also is described in German and Japanese patents (47, 48).

2.2. By-Products and Waste Disposal

A by-product of sulfamic acid manufacturing is fuming sulfuric acid or dilute sulfuric acid. The amount of sulfuric acid (as 100% H_2SO_4) is 1–1.5 times as much by weight as the sulfamic acid product. This by-product also contains ammonium salts and is therefore normally used as raw material for fertilizer (see Fertilizers).

The off-gas from the reactor contains CO_2, SO_3, and H_2SO_4. The SO_3 is removed by absorption (qv) into concentrated sulfuric acid solution or by other means. The CO_2 and H_2SO_4 vapor is removed by absorption into water or alkaline solution.

3. Economic Aspects

Until the 1970s, the main production countries of sulfamic acid were the United States, several European countries, and Japan. The large amounts of dilute sulfuric acid by-product generated led to the difficult situation of by-product acid disposal. Concomitantly, the start of chemical production in developing Asian countries caused successional sulfamic acid production withdrawal in the 1980s. As of the mid-1990s production countries are Japan, Taiwan, Indonesia, India, and China. The 1995 world production capacity was ca 96,000 metric tons.

In Japan, sulfamic acid is produced and supplied in crystal form. It is packaged in 25-kg net weight paper bags and in 600-kg, 700-kg, and 750-kg resinous flexible containers. The truckload price (fob Japan) is \$1–2/kg. Three principal uses of sulfamic acid are in chemical cleaning, as sulfonation reagent, and for use in synthetic sweetener.

Ammonium sulfamate is also produced and commercially available in Japan. It is packed in 25-kg net weight paper bags and 500-kg resinous flexible containers. The truckload price (fob Japan) is \$1.5–\$3/kg. Other sulfamates, eg, nickel sulfamate and aluminum sulfamate, are commercially available. The primary salts manufactured from sulfamic acid in the United States are the ammonium and nickel sulfamates. These salts of sulfamic acid are used mainly in electroplating.

4. Specifications and Analysis

4.1. Sulfamic Acid

Specifications and typical analyses of commercially available sulfamic acid are listed in Table 6.

The assay determination of sulfamic acid is made by titration of an accurately prepared sulfamic acid solution using sodium nitrite solution and an external potassium iodide starch-paste indicator. It is based on the reaction

$$HSO_3NH_2 + NaNO_2 \longrightarrow NaHSO_4 + H_2O + N_2$$

Standard 1/10 *N* nitrite is used to titrate a solution prepared by dissolving 10–100 mg of sulfamic acid and about 6 mL of $(1+1)$ H_2SO_4 in 300 mL of distilled water at 40–50°C. At the end point, the colorless external potassium iodide starch-paste indicator changes to blue. A 1-mL solution of 1/10*N* $NaNO_2$ is equivalent to

Table 6. Specifications and Analyses of Commercially Available Sulfamic Acid[a]

	Crystalline material	
Property	Specifications[b]	Typical analyses[c]
sulfamic acid, wt %	99.5[d]	99.9
ignition residue, wt %	0.05	0.0002
Fe, wt %	0.001	0.0001
heavy metal (as Pb), wt %	0.001	0.0001
chloride, wt %	0.002	0.0001
sulfate, wt %	0.05	0.01
nitrate, wt %	0.0001	<0.0001
solution appearance	transparent and colorless	transparent and colorless
moisture, wt %	0.1	0.01
particle size		
1680 μm stop, wt %	1.0	0.6
250 μm pass, wt %	30.0	24.6

[a] Values for product manufactured by Nissan Chemical Industries, Ltd.
[b] Values are maximum unless otherwise noted.
[c] Values given are typical. Numbers for individual batches may vary.
[d] Value is minimum.

9.709 mg of sulfamic acid. The 1/10 *N* nitrite titrant solution is standardized using primary standard-grade sulfamic acid. For sulfamate assay determination, the same procedure is used as for sulfamic acid.

For crystal sulfamic acid assay, a simplified procedure of neutralization titration with sodium hydroxide solution may be used. At the end point, Bromothymol Blue (BTB) indicator changes color from yellow to yellowish green. A 1-mL solution of 1/2*N* NaOH is equivalent to 0.0485 g of sulfamic acid.

5. Health and Safety Factors

Contact with sulfamic acid and its solutions can cause eye burns and irritate the nose, throat, and skin. Workers should wear cup-type, rubber, or soft plastic-framed goggles, equipped with approved impact-resistant glass or plastic lenses. Goggles should be carefully fitted to ensure maximum protection and comfort. Exposure to the skin can be minimized by wearing rubber gloves when handling sulfamic acid and its solutions, and hands should be washed thoroughly after handling. Breathing of the dust should be avoided and adequate ventilation should be provided.

In case of eye contact, the eyes should be flushed immediately using plenty of water for at least 15 min and a physician should be consulted. Exposed skin should also be flushed copiously with water. Anyone who has ingested the acid should immediately drink large amounts of water and consult a physician.

Toxicity data for the acid are as follows: oral LD_{50} (rats), 1600 mg/kg; and oral LD_{50} (mice), 3100 mg/kg (49). The physiological effects of sulfamic acid and ammonium sulfamate are described in Reference 50.

6. Uses

6.1. Sulfamic Acid

6.1.1. Removal of Residues from Industrial Processing Equipment

Properties of sulfamic acid that make it particularly well suited for scale-removal operations and chemical cleaning include the following: the acid is available in dry form, permitting convenient transportation, storage, handling, and packaging operations; it is a strong acid in aqueous solutions and is effective in solubilizing hard-water scales; sulfamic acid is nonvolatile and chloride-free; aqueous solutions do not emit objectionable or corrosive fumes and can be used on stainless steel generating no chloride stress corrosion; the acid is readily reactive with most deposits to form highly water-soluble compounds that are water rinsable; redeposition of dissolved solids is minimized. Sulfamic acid is less corrosive than many other strong acids on most materials of construction (see Table 3). Moreover, sulfamic acid is compatible with corrosion inhibitors, wetting agents, pH indicators, and other components of dry-cleaning formulations. The acid does not have a high toxicity rating, but all suppliers recommend caution in handling and recommend personal protection to avoid any injury.

Acid cleaners based on sulfamic acid are used in a large variety of applications, eg, air-conditioning systems; marine equipment, including salt water stills; wells (water, oil, and gas); household equipment, eg, copper-ware, steam irons, humidifiers, dishwashers, toilet bowls, and brick and other masonry; tartar removal of false teeth (50); dairy equipment, eg, pasteurizers, evaporators, preheaters, and storage tanks; industrial boilers, condensers, heat exchangers, and preheaters; food-processing equipment; brewery equipment (see Beer); sugar evaporators; and paper-mill equipment (see also Evaporation; Metal surface treatments; Pulp).

6.1.2. Manufacture of Dyes and Pigments and pH Adjustment

Use of sulfamic acid in the manufacture of dyes and pigments involves removal of excess nitrite from diazotization reactions (see Azo dyes) and is based on the following reaction:

$$NO_2^- + HSO_3NH_2 \longrightarrow HSO_4^- + N_2 + H_2O$$

Sulfamic acid is also used in some dyeing operations for pH adjustment; however, it is useful in lowering pH levels in a variety of other systems. The low pH persists at elevated temperatures and there are no objectionable fumes.

6.1.3. Paper-Pulp Bleaching

Sulfamic acid additions to chlorination bleaching stages are effective in reducing pulp-strength degradation associated with high temperatures (52) (see Bleaching agents). Other benefits are noted when sulfamic acid is added to the hypochlorite bleaching stage (53), including reduction of pulp-strength losses as a result of high temperature or low pH; increased production by means of higher temperatures and lower pHs at the same pulp-strength level; savings in chemical costs, eg, lower consumption of buffer, caustic soda, and higher priced bleaching agents; and improved efficiency through reducing effects of variation in temperature and pH.

6.1.4. Chlorine Vehicle and Stabilizer

Sulfamic acid reacts with hypochlorous acid to produce N-chlorosulfamic acids, compounds in which the chlorine is still active but more stable than in hypochlorite form. The commercial interest in this area is for chlorinated water systems in paper mills, ie, for slimicides, cooling towers, and similar applications (54) (see Industrial antimicrobial agents).

6.1.5. Analytical and Laboratory Operations

Sulfamic acid has been recommended as a reference standard in acidimetry (55). It can be purified by recrystallization to give a stable product that is 99.95 wt % pure. The reaction with nitrite as used in the sulfamic acid analytical method has also been adapted for determination of nitrites with the acid as the reagent. This reaction is used commercially in other systems for removal of nitrous acid impurities, eg, in sulfuric and hydrochloric acid purification operations.

6.1.6. *Sulfation and Sulfamation*

Sulfamic acid can be regarded as an ammonia–SO_3 complex and has been used thus commercially, always in anhydrous systems. Sulfation of mono-, ie, primary and secondary, alcohols; polyhydric alcohols; unsaturated alcohols; phenols; and phenolethylene oxide condensation products has been performed with sulfamic acid (see Sulfonation and sulfation). The best-known application of sulfamic acid for sulfamation is the preparation of sodium cyclohexylsulfamate [139-05-9], which is a synthetic sweetener (see Sweeteners).

6.2. Sulfamates

6.2.1. *Ammonium Sulfamate*

A number of flame retardants used for cellulosic materials, including fabrics and paper products, are based on ammonium sulfamate (56). These products are water-soluble and therefore nondurable if treated fabrics are washed or exposed to weathering conditions. For most fabric and paper constructions, efficient flame retardancy can be provided with no apparent effect on color or appearance and without stiffening or adverse effects on the feel of the fabrics. A wide variety of materials are treated, including hazardous work-area clothing, drapes, curtains, decorative materials, blankets, sheets, and specialty industrial papers (57).

Ammonium sulfamate is highly effective in nonselective herbicides to control weeds, brush, stumps, and trees (58) (see Herbicides).

6.2.2. *Other*

Nickel sulfamate is made by the combination of nickel carbonate and sulfamic acid. It is almost exclusively used in the plating industry, with its solutions used for both plating and electroforming. The principal value of this system is low internal stress in deposits and high plating rates. Other sulfamates used in plating solutions include the salts of cobalt, cadmium, ferrous iron, and lead (see Electroplating). Ferrous sulfamate is used in nuclear fuel processing solutions (59). Certain amine sulfamates impart softening properties to papers and textiles. Such materials exhibit long effective service, particularly at low humidity (see Quaternary ammonium compounds).

Calcium sulfamate and magnesium sulfamate are used effectively as a stiffening promoter of concrete and hydraulic cement (see Cement). Compared to calcium chloride [10043-52-4], which is commonly used as stiffening promoter, these sulfamates do not contain chloride and are not alkaline. Therefore highly durable concrete is made using these sulfamates (60, 61). These sulfamates and sulfamic acid are also used with the ground injection material the main component of which is water glass, to help easy adjustment of gelation time and increasing firmness of ground (62–64). Crystallization of ammonium sulfate [7783-20-2] from its mother liquor with addition of guanidine sulfamate [51528-20-2] as crystal habit modifier produces bigger and spherically shaped granular crystals (65, 66). Sulfamates of alkaline metals are used as additives in chromium tanning of hides (67).

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