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SULFAMIC ACID • INDUSTRIAL APPLICATIONS

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THE recent development of a practical process for commercial-scale manufacture of sulfamic acid (HSO_2NH_2) has stimulated a wide interest in this new industrial chemical. A number of industrial uses based on the unique chemical and physical properties of the acid have already been developed. These point to a gradually expanding production to supply an increasing demand. A number of promising commercial applications are discussed in the present paper. The rather extensive literature was reviewed in a previous publication (5), and therefore only references of direct interest have been included here.

It has long been known that nitrites react rapidly with sulfamic acid to yield nitrogen and sulfuric acid. A novel industrial application of this reaction is the removal of excess nitrite following diazotization reactions, for example, in dye and lake color manufacture. Sulfamic acid is two to six times more effective, on a weight basis, than urea which is commonly used for such purposes. Moreover, higher concentrations of nitrite may be employed, and the time required for excess nitrite removal in most cases may be shortened from a period of hours to a period of a few minutes. The reaction of sulfamic acid with nitrites is practically instantaneous, and only theoretical quantities of the acid are required. Cleaner shades of color with greater uniformity between batches are made possible through this use of sulfamic acid. It is of interest that the above mentioned results have been substantiated by recently published data (13) showing that analytical procedures based on colorimetric diazotization methods have given improved accuracy when the excess nitrite was removed by means of ammonium sulfamate.

A previous publication (5) mentions the advantages of ammonium sulfamate as a flameproofing agent for textiles, paper, and similar articles. Sulfamates, generally, show good flameproofing characteristics (6) and are free from stiffening action or any tendency to crystallize on the surface of the treated article upon aging. For example, sulfamates are well suited for flameproofing certain types of regenerated cellulose film (7). In this application the sulfamates show a remarkable compatibility with cellulose and do not crystallize or otherwise affect the transparency of these films even on prolonged aging. Further evaluation of other sulfamate salts has indicated that, on an equal weight basis, calcium sulfamate, $\text{Ca}(\text{SO}_2\text{NH}_2)_2 \cdot 4\text{H}_2\text{O}$, is only slightly less efficient as a flameproofing agent than ammonium sulfamate, and that it is free from corrosive action on copper, brass, and bronze under laboratory test conditions. The calcium salt is comparatively nonhygroscopic, shows no tendency to effloresce on a treated surface, and does not cause yellowing of paper upon storage under adverse conditions.

In the leather industry sulfamic acid offers attractive possibilities in deliming and pickling operations (8). The solid nature of the acid facilitates handling while the high solubility of its salts allows their rapid and complete extraction when desired. Sulfamic acid should prove worthy of study as a replacement for all or part of the more common acids now employed in chrome tanning baths because of the inherent differences between the sulfamate ion and the sulfate or chloride ions (12).

A NUMBER of promising applications for sulfamic acid take advantage of its solid, odorless, and nonhygroscopic nature. The pure acid, preferably mixed with an inert binding substance, may readily be pressed into pellet forms of comparatively uniform composition and weight. Such pellets have a large variety of applications and are especially suitable for consumer usage where specific quantities, based on a number of pellets, may be recommended in the directions supplied by the manufacturer. In certain instances sulfamic acid has been included as an ingredient in dry chemical mixtures which show no appreciable reaction until water is added to the composition. For many such purposes it is essential that a solid nonhygroscopic acid be employed which preferably contains no water of crystallization. These include abrasive mixtures for cleaning metals, ceramics, etc., and compositions suitable for the production of various gases such as carbon dioxide, hydrogen, hydrogen sulfide, and nitrogen.

A recent publication by Audrieth *et al.* (4) reports excellent results obtained by using sulfamic acid as a primary acid standard. The acid is highly recommended because it is nonhygroscopic and shows sharp end points with a variety of indicators. The latter results confirm previous observations that the acid is highly ionized in aqueous solution.

As expected, sulfamic acid readily forms salts with various basic amines. In general, such salts are considerably more soluble than the corresponding sulfates and frequently show greater solubility than corresponding salts of ordinary inorganic acids. A comparison of the solubility of the sulfamates and sulfates of quinine and strychnine in water at 25° C. is as follows (in grams per 100 grams of water):

	Sulfamate	Sulfate	Bisulfate
Quinine	22.4	0.14	11.1 (hydrated)
Strychnine	4.95	3.2	

Similarly, the salts of basic dyestuffs and polymeric natural or synthetic resins containing basic amino groups show maximum solubility in the form of sulfamic acid salts in many cases. Such products (sulfamates) may often be isolated as crystalline solids which retain their solubility on storage because sulfamic acid is entirely nonvolatile. Nicotine sulfamate shows somewhat greater efficiency as an insecticide than the pure sulfate. Sulfamic acid has been suggested for the extraction and purification of alkaloids. Following extraction, the alkaloid sulfamate may be converted into the corresponding sulfate simply by heating the acidified sulfamate solution.

THE sulfamates of organic amines are easily prepared by treating an aqueous or alcoholic solution of the amine with a calculated quantity of sulfamic acid, followed by isolation of the salt either by evaporation or by precipitation through the addition of solvents such as acetone or ether. Ammonium sulfamate or substituted ammonium sulfamates are soluble in formamide, substituted formamides, and polyhydric alcohols such as glycol and glycerol. In general, such salts also show high solubility in water or diluted methanol. The sulfamates of ethanalamines, diethylenetriamine, and triethylenetra-

mine are liquid under ordinary conditions. A number of sulfamates, their melting points, and the results of their analysis are listed in Table I (3).

TABLE I. ANALYSES OF ORGANIC SULFAMATES

Salt	Composition	% SO ₂	
		Ob- tained ° C.	Calcd.
Aluminum	Al(SO ₂ NH ₂) ₂ · 18H ₂ O	...	45.96 45.07
Barium	Ba(SO ₂ NH ₂) ₂	...	59.42 58.29
Calcium	Ca(SO ₂ NH ₂) ₂ · 4H ₂ O	...	64.20 63.15
Copper	Cu(SO ₂ NH ₂) ₂ · 2H ₂ O	...	64.04 65.86
Lead	Pb(SO ₂ NH ₂) ₂ · 2H ₂ O	...	43.42 44.18
Magnesium	Mg(SO ₂ NH ₂) ₂ · 4H ₂ O	...	67.34 66.66
Potassium	KSO ₂ NH ₂	192	71.64 71.11
Zinc	Zn(SO ₂ NH ₂) ₂ · 4H ₂ O	...	59.20 58.29
Ammonia	NH ₄ SO ₂ NH ₂	131	85.92 84.21
n-Amylamine	C ₈ H ₁₇ NH ₂ · HSO ₂ NH ₂	136	52.75 52.17
Aniline	C ₆ H ₅ NH ₂ · HSO ₂ NH ₂	155	50.68 50.52
n-Butylamine	C ₄ H ₉ NH ₂ · HSO ₂ NH ₂	109	57.09 56.47
Dicyclohexylamine	(C ₆ H ₁₁) ₂ NH · HSO ₂ NH ₂	160	36.14 34.53
Ethylenediamine	H ₂ NCH ₂ CH ₂ NH ₂ · 2HSO ₂ NH ₂	157	75.58 75.29
Octadecenyamine	C ₁₈ H ₃₅ NH ₂ · HSO ₂ NH ₂	93	26.36 26.37
Piperidine	C ₅ H ₁₀ NH ₂ · HSO ₂ NH ₂	62	52.63 52.46
Pyridine	C ₅ H ₅ NHSO ₂ NH ₂	79	54.30 54.54
Octadecylamine	C ₁₈ H ₃₇ NH ₂ · HSO ₂ NH ₂	112	26.36 26.23
Strychnine	C ₂₁ H ₃₂ N ₂ O ₂ · HSO ₂ NH ₂	...	22.15 22.27

It was previously shown that many of the inorganic sulfamates, such as the lead and barium salts, show high solubility in water. Many of the sulfamates are hydrated as is indicated by the analytical data included in Table I. The compositions shown are in agreement with the literature with the exception of the lead salt which was reported as monohydrated (2) and the magnesium salt which was reported as a trihydrate (14). The hydrated salts recorded in Table I were dried at about 20 per cent relative humidity, and the anhydrous salts were dried in a vacuum desiccator (15 mm.) over calcium chloride. The aluminum salt may be prepared by reacting aluminum sulfide with a suspension of sulfamic acid in a minimum quantity of water, followed by a filtration of the solution and isolation of the salt. Since the hydrated sulfamates are not readily crystallized by the addition of methanol, they are best separated by evaporation of their aqueous or alcoholic solutions under reduced pressure.

The solubility of various salts suggests that sulfamic acid may be useful in the extraction or purifications of certain ores and minerals (1, 11). A further separation of the extracted metals might be accomplished simply by heating the acid extraction solution and thereby converting the sulfamates into soluble and insoluble sulfates. Other possible applications include the use of heavy metal sulfamates for electroplating and of sulfamic acid for anodizing aluminum and aluminum alloys. In the field of agriculture sulfamic acid has been suggested as a means for modifying the alkalinity of soils. The solid nature of the acid would facilitate its handling and application. In addition, potentially available nitrogen would be added to the soil.

Sulfamic acid behaves as a dibasic acid when dissolved in liquid ammonia. Thus sodium and potassium metal react with alkali metal salts to form N-alkali metal derivatives represented by the formula, NaSO₂NHNa. Ammonium sulfamate first reacts with the formation of sodium sulfamate, and further reaction with sodium causes replacement of the amide hydrogen (3). Upon addition to water the amide metal is hydrolyzed to hydroxide which may be titrated quantitatively with standard acid.

IT IS well known that formaldehyde and aldehydes, in general, form addition products with sulfamic acid salts. Such compounds are stable in neutral or weakly alkaline solution although the reaction is readily reversed by acid and strong alkali. Methylol derivatives of the alkali metal sulfamates are best prepared by adding excess formaldehyde solution to

cold concentrated solutions of the sulfamate and keeping the temperature preferably below 10° C. After standing for several hours the methylol derivative may be precipitated from solution as a soft sticky mass by the addition of methanol. Attempts to analyze the product, after drying in a desiccator, gave inconsistent results. The methylol derivative of calcium sulfamate is readily obtained in crystalline form by adding excess formaldehyde (37 per cent) to a concentrated solution of calcium sulfamate at room temperature, allowing the solution to stand for about an hour, and then precipitating the methylol derivative by the addition of several volumes of methanol and acetone. Analysis indicated that the product (reprecipitated and washed with methanol and acetone) contained one methylol group per amide group; found, 8.21 per cent carbon, 2.84 hydrogen, 46.76 ash (CaSO₄); calculated for Ca(SO₂NHCH₂OH)₂, 8.22 per cent carbon, 2.76 hydrogen, 46.57 ash. The product carbonized when heated on a spatula over a free flame. It slowly reduced a heated ammoniacal silver nitrate solution to give the silver mirror test. Nitrous acid reacted only exceedingly slowly with the compound to liberate nitrogen. Heating an aqueous solution of the compound at 100° C. for an hour gave only slight hydrolysis to calcium sulfate. The methylol sulfamates are thought to show reactions similar to both formaldehyde and the methylol amides. Hence, such derivatives should show promise in a wide range of industrial applications.

Although sulfamic acid has long been known, fundamental data concerning the properties of the acid, its salts, and derivatives are incomplete (5). For example, information concerning free energy of the acid and the sulfamate ion is not available, the solubilities of many salts have not been reported, and the composition of possible hydrated salts is unknown; further study of various complex salts therefore appears desirable. The literature on sulfamyl chloride is indefinite and confusing (9, 10). Additional investigations concerning the rearrangement of aryl ammonium sulfamates and the preparation of aldehyde-sulfamate addition products might lead to new derivatives and extended uses. It is anticipated that as additional information on sulfamic acid and its derivatives becomes available, other industrial applications will be developed permitting manufacture on a major scale.

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