FIGURE 1 (*Above*). DRY SULFAMIC ACID

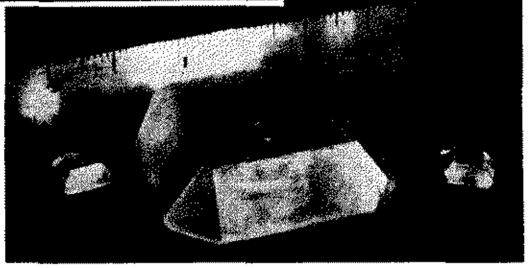

FIGURE 2 (*Right*). CRYSTALS OF SULFAMIC ACID

SULFAMIC ACID

A NEW INDUSTRIAL CHEMICAL

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A new process has been developed by which sulfamic acid is readily prepared from urea and fuming sulfuric acid. The process appears to be suitable for large-scale production, so that sulfamic acid is now potentially available as a new industrial raw material.

Sulfamic acid is a colorless, odorless, nonhygroscopic, crystalline product which may be handled and packaged commercially in a solid form. In aqueous solution it is highly ionized, forming strongly acidic solutions. Under ordinary conditions sulfamic acid is practically stable in water; at increased temperatures it is slowly hydrolyzed to ammonium acid sulfate. Similarly, alcoholysis yields ammonium alkyl sulfates. The salts of sulfamic acid are stable in neutral or alkaline solution, and such solutions may be evaporated with heating without hydrolysis of the amide group. All of the known salts of sulfamic acid, with the single exception of a basic mercury salt, are soluble in water. Salts such as lead and barium sulfamate show exceptionally high water solubility. Ammonium sulfamate shows promise as a flameproofing agent for textiles, paper, and other combustible materials.

SULFAMIC acid, HSO_3NH_2, is a strong inorganic acid available in crystalline form. It was probably first prepared over a hundred years ago (*34*) but was not isolated and identified until about sixty years ago when Berglund (*7*) prepared the acid and a number of its salts. He obtained sulfamic acid by the hydrolysis of iminodisulfonate salts with dilute acids, isolating first the soluble barium sulfamate from which the acid was then obtained. Various other syntheses for sulfamic acid, suitable only for laboratory preparations, have appeared from time to time in the literature. Recently a new process was developed independently both in this country and in Germany (*2*, *4*, *14A*) by which sulfamic acid may be produced on a commercial scale. This new process is based on the reaction of urea with fuming sulfuric acid as represented, in its simplest form, by the following equation:

$$H_2NCOHN_2 + H_2SO_4 + SO_3 \longrightarrow 2HOSO_2NH_2 + CO_2$$

In the new process urea is first dissolved in excess cold sulfuric acid. Oleum of suitable sulfur trioxide strength is then added, and the reaction is allowed to proceed under controlled conditions. During the reaction carbon dioxide is evolved, and the sulfamic acid formed precipitates from the solution. The product is isolated by filtration and purified by recrystallization from water. Since the reagents used in the process are available in unlimited quantities, it is now possible to produce sulfamic acid as a new industrial raw material. A discussion of its properties and reactions is therefore of special interest at the present time.

Dry sulfamic acid is a stable, nonhygroscopic, odorless, colorless, crystalline product (*34*). Hence it may be conveniently handled and packaged commercially in solid form (Figure 1). It readily forms large well-defined crystals (*19*, *27*, *47*) as shown in Figure 2, and it has been suggested that the formula $H_3{}^+NSO_2{-}O^-$ more accurately represents the solid form (*1*). Carefully purified crystals prepared during this investigation had a specific gravity of 2.126 (measured in toluene at 25° C.), which differs somewhat from the value 2.03 (measured in ether at 12° C.) reported in the literature (*14*). Sulfamic acid is moderately soluble in water (Figure

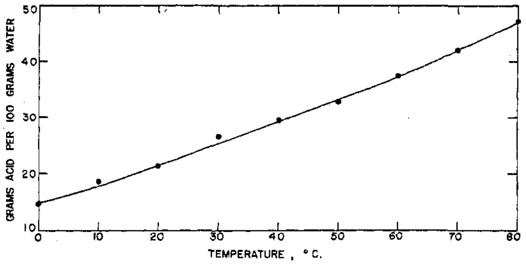

FIGURE 3. SOLUBILITY OF SULFAMIC ACID IN WATER

Temp.	Soly. per 100 Grams H_2O	Temp.	Soly. per 100 Grams H_2O
° *C.*	*Grams*	° *C.*	*Grams*
0	14.68	50	32.82
10	18.56	60	37.10
20	21.32	70	41.91
30	26.09	80	47.08
40	29.49		

3) and formamide, slightly soluble in methanol, but almost insoluble in ethanol, acetone, and ether:

Solvent	Soly. at 25° C. per 100 Grams Solvent
	Grams
Methanol	4.3
Ethanol (2% benzene)	1.7
Acetone	0.4
Ether	0.009
Formamide	20.0

Sulfamic acid is insoluble in hydrocarbons, chlorinated hydrocarbons, carbon disulfide, and sulfur dioxide. The solubility of sulfamic acid in water is decreased by the presence of sulfuric acid or sodium sulfate. Sulfamic acid is practically insoluble in 70–100 per cent sulfuric acid (Figure 4).

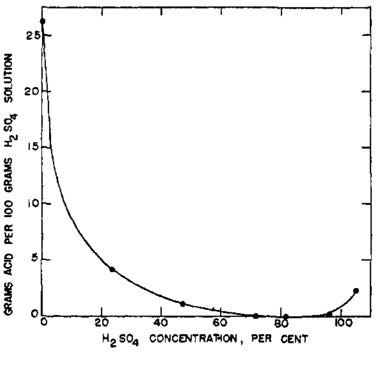

FIGURE 4. SOLUBILITY OF SULFAMIC ACID IN SULFURIC ACID SOLUTIONS AT 30° C.

H_2SO_4 Concn.	Soly. per 100 Grams H_2SO_4 Soln.
%	*Grams*
0.00	26.09[a]
23.91	4.14[a]
47.53	1.06[a]
71.80	0.00[a]
81.17	0.18[b]
96.31	0.25[b]
Fuming (21.1% SO_3)	2.38[b]

[a] Analyzed by titration and sulfate analysis.

[b] Analyzed by hydrolysis and NH_3 distillation.

Sulfamic acid is highly ionized in aqueous solution as indicated by the pH-concentration curve which falls almost midway between similar curves for hydrochloric and phosphoric acids (Figures 5 and 6). Obviously solutions of the acid also show high conductance:

Concentration	Molar Conductance at 25° C.[a] (*49*)	Calc. % Dissociation
1/32 *N*	295.8	79.1
1/64 *N*	324.9	86.9
1/128 *N*	341.9	91.4
1/256 *N*	359.2	96.0
1/512 *N*	361.9	96.8
1/1024 *N*	366.5	98.0
∞	374.0	100.0

[a] Molecular weight of 97.11 used for HSO_3NH_2, for measuremen ts at 0° C., see reference *21*.

Measurements reported in the literature (*21, 49*) indicate that the mobility of the sulfamate ion is about equal to that of the bromate or formate ion, which is lower than the mobility of halide ions or the nitrate ion but greater than that of the iodate or primary phosphate ion.

Sulfamic acid is practically stable in water solution at ordinary temperature. At elevated temperatures the acid is slowly hydrolyzed to ammonium acid sulfate (*14*). Figure 7 illustrates preliminary determinations of the rate of hydrolysis of sulfamic acid solutions of varied concentration maintained at a uniform temperature of 80° C. Salts of sulfamic acid are stable in neutral or alkaline solutions, and such solutions may be evaporated to dryness on a steam bath without hydrolysis of the amide group. Hence, the sulfamate nitrogen may be quantitatively determined by measuring the difference in ammonia nitrogen distillations prior and subsequent to an acid hydrolysis. The use of sulfamic acid as a titrimetric standard has also been suggested in the literature (*22, 24, 35*).

Inorganic Reactions

Sulfamic acid reacts readily with basic metal oxides, hydroxides, and carbonates to yield the corresponding sulfamate salts (*7, 9, 11, 14, 15, 16, 40, 48*). Amphoteric or acidic metal oxides react less readily or not at all (*14*). Hence, salts such as sodium, barium, copper, lead, aluminum, nickel, thallium, and ferrous sulfamate are easily prepared; the bismuth, antimony, and arsenic salts are not known. Compounds containing basic amino groups likewise react to form salts of sulfamic acid. All known salts of sulfamic acid, with the single exception of a basic mercury salt (*14*), are soluble in water. Certain salts, such as the lead, barium, magnesium, and sodium salts, show exceptionally high solubility:

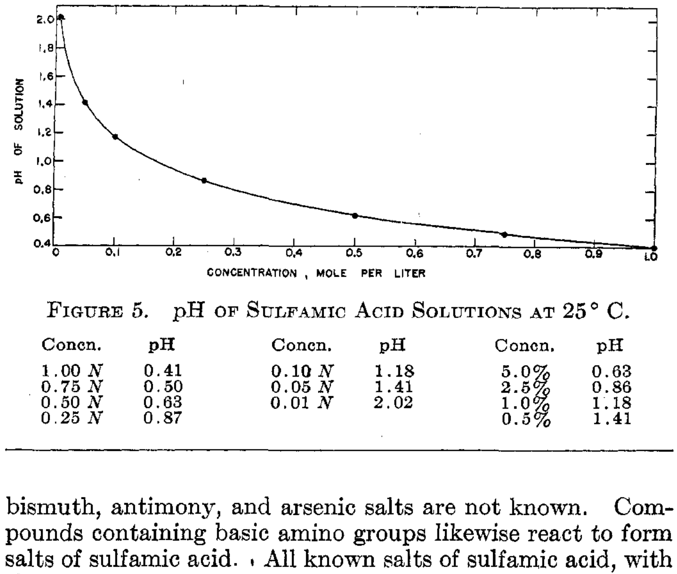

FIGURE 5. pH OF SULFAMIC ACID SOLUTIONS AT 25° C.

Concn.	pH	Concn.	pH	Concn.	pH
1.00 *N*	0.41	0.10 *N*	1.18	5.0%	0.63
0.75 *N*	0.50	0.05 *N*	1.41	2.5%	0.86
0.50 *N*	0.63	0.01 *N*	2.02	1.0%	1.18
0.25 *N*	0.87			0.5%	1.41

Sulfamate Salt	Soly., Grams/100 Grams Water at 25° C.	Sulfamate Salt	Soly., Grams/100 Grams Water at 25° C.
Ammonium	193	Barium	34.2
Sodium	106	Zinc	115
Magnesium	119	Lead	218
Calcium	67		

The high solubility of ammonium sulfamate is illustrated by Figure 8. Sulfamic acid prevents precipitation of silver, mercury, and gold by alkalies, and salts of the type of $AgHNSO_3Na$ are presumably formed in alkaline solutions (*10, 14, 25, 51*). Chloroplatinate salts form complex addition salts with sulfamic acid which are thought to exist in isomeric *cis* and *trans* forms (*28*).

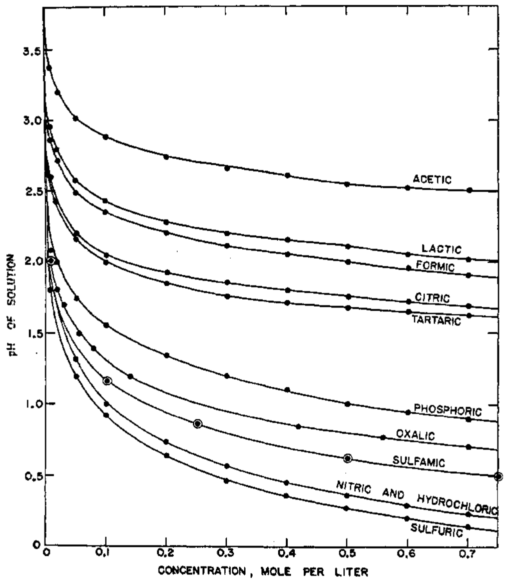

FIGURE 6. pH-CONCENTRATION CURVES FOR VARIOUS ACIDS, INCLUDING SULFAMIC ACID

At low temperature chlorine reacts with sulfamic acid or its salts to form the N-halogen derivative which at ordinary temperatures is readily hydrolyzed, yielding sulfuric acid (*53*). Bromine and chlorates in acid solution oxidize sulfamic acid to sulfuric acid with liberation of nitrogen; chromic acid, permanganic acid, and ferric chloride have no effect (*14*). Nitric acid yields nitrous oxide and sulfuric acid (*3, 14, 18*). Nitrites react rapidly with sulfamic acid, liberating nitrogen and forming sulfuric acid. This reaction may be utilized for the analytical determination of nitrites or of sulfamic acid (*5, 20*). Phosphorus pentachloride reacts with sulfamic acid to form a complex derivative having the composition $PCl_3 \cdot ClSO_2NH_2$ (*17*). Although the preparation of sulfamyl chloride by reacting thionyl chloride with sulfamic acid is reported in the literature (*17*), a recent report (*13*) does not confirm the observations previously described.

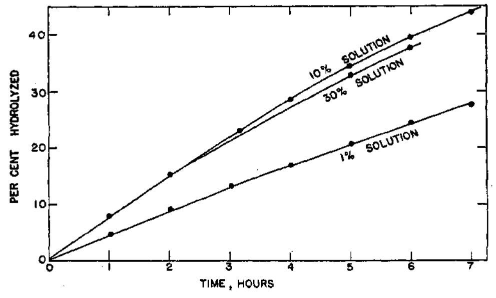

FIGURE 7. HYDROLYSIS OF SULFAMIC ACID IN AQUEOUS SOLUTIONS AT 80° C.

Time, Hours	% Hydrolyzed at Concn. of: 1%	10%	30%
1	4.54	7.75	7.85
2	9.07	15.07	15.14
3.1	13.29	...	21.98
3.16	...	22.67	...
4	16.86	28.28	27.49
5	20.61	34.27	32.79
6	24.18	39.51	37.49
7	27.29	43.66	...

Organic Reactions

Primary alcohols react smoothly with sulfamic acid upon heating and yield the corresponding alkyl ester of ammonium acid sulfate (*8, 14, 29, 31, 33, 40*). For example, methanol refluxed with sulfamic acid for several hours yields ammonium methyl sulfate. Similar reactions are obtained with long-chain primary alcohols, glycols, and glycerol. Secondary and tertiary alcohol groups do not react with sulfamic acid.

Alkylation of sulfamic acid by ordinary procedures yields the esters of dialkyl sulfamic acid, $ROSO_2NR_2$, which readily rearrange into the betaine structure, $R_3N \cdot SO_3$, if the alkyl groups are small (*12, 13, 18, 29, 30, 40, 54*). The benzyl ester of benzyl sulfamic acid, prepared by reacting sodium sulfamate with benzyl chloride in the presence of excess alkali, is stable (*54*) and may be hydrolyzed to give monobenzyl sulfamic acid. The true esters are insoluble in water, whereas the betaines are saltlike solids which are readily soluble.

Aldehydes react readily with sulfamic acid, yielding products which are decomposed by water or, in certain cases, by acid or alkaline solutions (*29*). The reactions are best carried out in neutral solutions or, if necessary, in alcohol solutions using an alcohol-soluble sulfamate such as the trimethyl amine salt. The products obtained have the general structure represented by the formula $R \cdot CHOH \cdot NHSO_3M$ or $RCH{:}NSO_3M$, where M represents a metal or ammonium group and R represents hydrogen or an organic group. Addition reactions of sulfamates with benzaldehyde, cinnamic aldehyde, vanillin, anisaldehyde, citral, maltose, glucose, furfural, acetaldehyde, and formaldehyde have been reported in the literature (*23, 50, 52*).

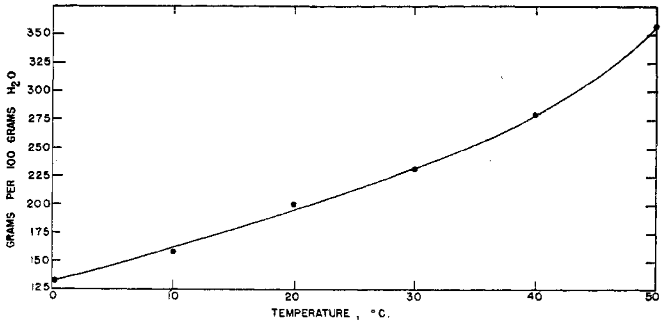

FIGURE 8. SOLUBILITY OF AMMONIUM SULFAMATE IN WATER

Temp. ° C.	Soly. per 100 Grams H_2O Grams	Temp. ° C.	Soly. per 100 Grams H_2O Grams
0.2	134.8	30	232.4
10	166.6	40	279.5
20	200.2	50	357

Amides may react with sulfamic acid in certain cases to form the ammonium salt of the sulfonated amide. For example, benzamide reacted with sulfamic acid forms the ammonium salt of benzoyl sulfamic acid, $C_6H_5CONHSO_3NH_4$ (*2, 6, 32*). According to the patent literature (*26*) fatty acid chlorides may be reacted with sulfamic acid to form corresponding sulfonated amides. Sulfamic acid fused with ammonium sulfamate yields the ammonium salt of imino disulfonic acid, $HN(SO_3NH_4)_2$ (*2*). However, the above reactions are not broadly applicable because of complicated side reactions which often occur.

Phenols, naphthols, and related compounds (cresols, anisole, anethole, carbinol base, pyrocatechol, resorcinol, hydroquinone, etc.) react with sulfamic acid under suitable conditions to give aromatic sulfonated derivatives (*8, 24, 42, 43, 46*). It was reported that ammonium phenyl sulfate is first formed as an intermediate in the reaction (*24*). Thus phenol heated with sulfamic acid at 100° C. is stated to give ammonium phenyl sulfate which, upon heating at 150–160° C., gives the ammonium salt of *p*-phenol sulfonic acid. β-Naphthol at 160° C. yields the ammonium salt of 2-naphthol-6-sulfonic acid (*24*).

Unsaturated compounds, such as anethole and isosafrole (*43, 44*), are reported to react to a limited extent with sulfamic acid. Styrene heated at 150° C. for one hour with sulfamic acid is reported to give ammonium styryl sulfonate, $C_6H_5CH{:}CHSO_3NH_4$, from which the free acid (melting at 55° C.) may be isolated (*44*).

Aromatic amine addition salts of sulfamic acid may in certain cases be rearranged, first, into ammonium salts of substituted sulfamic acids and then into the ring sulfonated derivatives of aromatic amines. For example, aniline sulfamate refluxed in excess aniline forms ammonium phenyl sulfamate which, on further heating by fusion, yields the ammonium salt of *p*-sulfanilic acid (*36, 39, 40, 45*) as represented by the following equations:

$$C_6H_5NH\cdot HSO_3NH_2 \longrightarrow C_6H_5NHSO_3NH_4 \longrightarrow p\text{-}NH_2C_6H_4SO_3NH_4$$

Phenylhydrazine is reported to react similarly, yielding a quantitative amount of the ammonium salt of phenylhydrazine sulfonic acid, $C_6H_5NHNHSO_3NH_4$. Upon oxidation the latter product yields $C_6H_5N{:}NSO_3NH_4$, from which the free benzene azosulfonic acid and its silver salt were prepared (*40*). Diphenylhydrazine does not react. Aliphatic amines react with difficulty and yield the alkyl amine salt of the alkyl-substituted sulfamic acid. For example, excess isoamyl amine heated with sulfamic acid at 200° C. for 3–4 hours yields the isoamyl amine salt of isoamyl sulfamic acid (*39, 41*). The naphthyl amines react similarly to aniline, but the intermediates are thought to rearrange readily into ring sulfonated derivatives (*45*). The reactions of benzyl amine piperidine, chloroanilines, and pseudocumidine are also described in the literature (*36, 37, 38, 41*).

Potential Applications

One of the most promising potential industrial applications for sulfamic acid is the use of certain of its salts as flameproofing agents for fabrics, paper, and other combustible materials. Ammonium sulfamate is unique among orthodox flameproofing salts because it does not cause stiffening or otherwise adversely affect the handle and feel of fabrics, paper, and the like, and because it shows no tendency to effloresce to the surface upon prolonged storage. Sulfamates may be applied by impregnation as water solutions. They are not removed by dry cleaning treatments. Other advantages of importance in specific applications have been noted. In several systems ammonium sulfamate has shown less tendency to coagulate colloidal solutions than other inorganic salts.

Sulfamic acid, by virtue of its unusual properties, represents an important addition to the group of commercial acids represented by lactic, acetic, formic, tartaric, oxalic, and similar acids, and should be especially useful for applications in which a highly ionized nonvolatile acid is desired or where precipitation of insoluble salts must be avoided. Moreover, the nonhygroscopic crystalline nature of sulfamic acid, which facilitates handling and storage, is a distinct advantage of this new industrial chemical.

A variety of additional industrial applications for sulfamic acid and its derivatives may be expected on the basis of the above-mentioned properties and reactions. For example, the salts of sulfamic acid have novel solubility characteristics; in many cases they are more soluble than the corresponding salts of other inorganic acids. Perhaps the most outstanding example is lead sulfamate, a saturated solution of which at 25° C. contains 68.5 per cent of the salt and has a density of 2.18 (d_4^{25}). In a number of cases sulfamates showed a definite retarding effect on the precipitation of basic compounds when alkali was added to metal salt solutions. Sulfamic acid also showed a peptizing action on suspended particles of inorganic solids. The salts of aromatic amines are unusual because they may be rearranged into substituted sulfamic acids, followed by further rearrangement into ring-sulfonated derivatives. Such reactions offer possibilities in the preparation of various intermediates in organic syntheses.

Sulfamic acid should find extensive use as an analytical reagent. It was previously recommended as a standard for titrimetric work because it is a nonhygroscopic crystalline acid which gives sharp end points with ordinary titration indicators. Sulfamic acid should be particularly useful for the determination of nitrites, even in the presence of nitrates. Such analyses may be carried out by measuring either the nitrogen evolved by the reaction or the sulfate which is formed.

Acknowledgment

The helpful criticism and assistance of G. D. Patterson and J. K. Hunt in this investigation are appreciated by the author.

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THE MAN WHO COULD MAKE GOLD

By
George Howe

A list of Reproductions Nos. 1 to 60 appeared in our issue of January, 1936, page 129; the list of Nos. 61 to 72 appeared in our issue of January, 1937, page 74; Nos. 73 to 84 are listed in January, 1938, page 70, where also is shown No. 85 and details for obtaining photographic copies of the originals. No. 86 appears on page 145, February issue, No. 87 on page 269, March issue, No. 88 on page 427, April issue, and No. 89 on page 500, May issue. The photographs of these paintings are supplied in black and white only.

No. 90 in the Berolzheimer series of Alchemical and Historical Reproductions is a very recent India ink drawing made to illustrate the story "The Man Who Could Make Gold" in the December 11, 1937, issue of *Collier's Weekly*.

We extend our thanks to *Collier's* and its Art Department, and to Mr. Howe for the ready permission to reproduce this.

It is evident that the alchemist depicted is undertaking a metallurgical transmutation, with the usual results, probably volatilization and oxidation of a large part of the base metal used.

It is most remarkable how persistent and optimistic these alchemists were, in the face of repeated failure, loss of materials, and *no gold*, for most of them were sincere in their efforts, only a few being rank charlatans. We owe them a great debt for their pioneer work which has made modern metallurgy possible.

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