KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

THIRD EDITION

VOLUME 22

SULFONATION AND SULFATION
TO
THORIUM AND THORIUM COMPOUNDS

KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

THIRD EDITION

VOLUME 22

SULFONATION AND SULFATION
TO
THORIUM AND THORIUM COMPOUNDS

A WILEY-INTERSCIENCE PUBLICATION
John Wiley & Sons
NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

Library of Congress Cataloging in Publication Data:

Main entry under title:
Encyclopedia of chemical technology.

At head of title: Kirk-Othmer.
"A Wiley-Interscience publication."
Includes bibliographies.
1. Chemistry, Technical—Dictionaries. I. Kirk, Raymond Eller, 1890-1957. II. Othmer, Donald Frederick, 1904—
III. Grayson, Martin. IV. Eckroth, David. V. Title:
Kirk-Othmer encyclopedia of chemical technology.

TP9.E685 1978 660'.03 77-15820
ISBN 0-471-02075-3

Printed in the United States of America

KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

Third Edition

VOLUME 22

Sulfonation and Sulfation
to
Thorium and Thorium Compounds

EDITORIAL STAFF FOR VOLUME 22

Executive Editor: **Martin Grayson**
Associate Editor: **David Eckroth**
Production Supervisor: **Michalina Bickford**
Editors: **Joyce Brown** **Caroline L. Eastman** **Carolyn Golojuch**
Anna Klingsberg **Mimi Wainwright**

CONTRIBUTORS TO VOLUME 22

Michael M. Abbott, *Renssalaer Polytechnic Institute, Troy, New York,* Thermodynamics
Herbert G. Arlt, Jr., *Arizona Chemical Company, Fair Lawn, New Jersey,* Tall oil
D. W. Bixby, *The Sulphur Institute, Washington, D.C.,* Sulfur
Bernard Bucholz, *Pennwalt Corporation, King of Prussia, Pennsylvania,* Thiophene
Arno Cahn, *Arno Cahn Consulting Services, Inc., Pearl River, New York,* Surfactants and detersive systems
G. T. Clark, *Eastman Kodak Co., Kingsport, Tennessee,* Disperse dyes under Thiazole dyes
Charles C. Coutant, *Oak Ridge National Laboratory, Oak Ridge, Tennessee,* Thermal pollution by power plants
John M. Derfer, *SCM Corporation, Jacksonville, Florida,* Terpenoids
Marian M. Derfer, *SCM Corporation, Jacksonville, Florida,* Terpenoids
J. R. Donovan, *Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri,* Sulfuric acid and sulfur trioxide
Robert E. Droegkamp, *Fansteel, Inc., North Chicago, Illinois,* Tantalum and tantalum compounds

E. M. Elkin, *Noranda Mines, Ltd., Montreal, Quebec, Canada,* Tellurium and tellurium compounds

Russell E. Farris *Sandoz, Inc., Martin, South Carolina,* Direct dyes under Thiazole dyes

H. L. Fike, *The Sulphur Institute, Washington, D.C.,* Sulfur compounds

J. G. Fisher, *Eastman Kodak Co., Kingsport, Tennessee,* Disperse dyes under Thiazole dyes

Alfred C. Glatz, *General Foods Corporation, Tarrytown, New York,* Thermoelectric energy conversion

Harold Graham, *Thomas J. Lipton, Inc., Englewood Cliffs, New Jersey,* Tea

R. A. Guest, *James Robinson & Company, Ltd., Hudderfield, Yorkshire, United Kingdom,* Sulfur dyes

W. James Harper, *New Zealand Dairy Research Institute, North Palmerston, New Zealand,* Synthetic and imitation dairy products

R. E. Hebeda, *CPC International, Summit-Argo, Illinois,* Syrups

Benjamin C. Hui, *Alfa Products, Danvers, Massachusetts,* Thallium and thallium compounds

Karl Kamman, *Keil Chemical Division, Ferro Corporation, Hammond, Indiana,* Sulfurization and sulfurchlorination

Leonard I. Katzin, *Consultant, Port Hueneme, California,* Thorium and thorium compounds

Otto S. Kauder, *Argus Chemical Corporation, Brooklyn, New York,* Thioglycolic acid

E. A. Knaggs, *Stepan Chemical Company, Northfield, Illinois,* Sulfonation and sulfation

John B. Lambert, *Fansteel, Inc., North Chicago, Illinois,* Tantalum and tantalum compounds.

B. C. Lawes, *E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware,* Sulfuric and sulfurous esters

Hillel Lieberman, *Betz Laboratories, Trevose, Pennsylvania,* Technical service

R. P. Louthan, *Phillips Petroleum Co., Bartlesville, Oklahoma,* Thiols

Jesse L. Lynn, Jr., *Lever Brothers Company, Edgewater, New Jersey,* Surfactants and detersive systems

W. S. MacGregor, *Crown Zellerbach Corp., Camus, Washington,* Sulfoxides

Robert Mazur, *GD Searle and Co., Chicago, Illinois,* Sweeteners

W. B. McCormack, *E. I. du Pont de Nemours & Co., Inc., Deepwater, New Jersey,* Sulfuric and sulfurous esters

Donald McNeil, *Technical consultant, Wilsden, Bradford, West Yorkshire, United Kingdom,* Tar and pitch

James B. McPherson, *American Cyanamid Company, Danbury, Connecticut,* Sutures

Frank P. Missell, *Universidade de São Paulo, São Paulo, Brazil,* Superconducting materials

H. T. Mulryan, *Cyprus Industrial Minerals, Englewood, Colorado,* Talc

John Norell, *Phillips Petroleum Co., Bartlesville, Oklahoma,* Thiols

M. L. Nussbaum, *Stepan Chemical Company, Northfield, Illinois,* Sulfonation and sulfation

J. V. Orle, *Crown Zellerbach Corporation, Camus, Washington,* Sulfoxides

Ludwig Rebenfeld, *Textile Research Institute, Princeton, New Jersey,* Survey under Textiles

J. M. Salomone, *Monsanto Enviro-Chem Systems, Inc., St. Louis, Missouri,* Sulfuric acid and sulfur trioxide

Mortimer Schussler, *Fansteel, Inc., North Chicago, Illinois,* Tantalum and tantalum com-

^{t} (eg, Bu^t), *t*-, *tert*-	tertiary (eg, tertiary butyl)
T	tera (prefix for 10^{12}); tesla (magnetic flux density)
t	metric ton (tonne); temperature
TAPPI	Technical Association of the Pulp and Paper Industry
tex	tex (linear density)
T_g	glass-transition temperature
tga	thermogravimetric analysis
THF	tetrahydrofuran
tlc	thin layer chromatography
TLV	threshold limit value
trans-	isomer in which substituted groups are on opposite sides of double bond between C atoms
TSCA	Toxic Substance Control Act
TWA	time-weighted average

Twad	Twaddell
UL	Underwriters' Laboratory
USDA	United States Department of Agriculture
USP	*United States Pharmacopeia*
uv	ultraviolet
V	volt (emf)
var	variable
vic-	vicinal
vol	volume (not volatile)
vs	versus
v sol	very soluble
W	watt
Wb	Weber
Wh	watt hour
WHO	World Health Organization (United Nations)
wk	week
yr	year
(*Z*)-	zusammen; together; atomic number

Non-SI (Unacceptable and Obsolete) Units		*Use*
Å	angstrom	nm
at	atmosphere, technical	Pa
atm	atmosphere, standard	Pa
b	barn	cm^2
bar[†]	bar	Pa
bbl	barrel	m^3
bhp	brake horsepower	W
Btu	British thermal unit	J
bu	bushel	m^3; L
cal	calorie	J
cfm	cubic foot per minute	m^3/s
Ci	curie	Bq
cSt	centistokes	mm^2/s
c/s	cycle per second	Hz
cu	cubic	exponential form
D	debye	C·m
den	denier	tex
dr	dram	kg
dyn	dyne	N
dyn/cm	dyne per centimeter	mN/m
erg	erg	J
eu	entropy unit	J/K
°F	degree Fahrenheit	°C; K
fc	footcandle	lx
fl	footlambert	lx
fl oz	fluid ounce	m^3; L
ft	foot	m
ft·lbf	foot pound-force	J

[†] Do not use bar (10^5Pa) or millibar (10^2Pa) because they are not SI units, and are accepted internationally only for a limited time in special fields because of existing usage.

Non-SI (Unacceptable and Obsolete) Units		*Use*
gf den	gram-force per denier	N/tex
G	gauss	T
Gal	gal	m/s^2
gal	gallon	m^3; L
Gb	gilbert	A
gpm	gallon per minute	(m^3/s); (m^3/h)
gr	grain	kg
hp	horsepower	W
ihp	indicated horsepower	W
in.	inch	m
in. Hg	inch of mercury	Pa
in. H_2O	inch of water	Pa
in.-lbf	inch pound-force	J
kcal	kilogram-calorie	J
kgf	kilogram-force	N
kilo	for kilogram	kg
L	lambert	lx
lb	pound	kg
lbf	pound-force	N
mho	mho	S
mi	mile	m
MM	million	M
mm Hg	millimeter of mercury	Pa
mμ	millimicron	nm
mph	miles per hour	km/h
μ	micron	μm
Oe	oersted	A/m
oz	ounce	kg
ozf	ounce-force	N
η	poise	Pa·s
P	poise	Pa·s
ph	phot	lx
psi	pounds-force per square inch	Pa
psia	pounds-force per square inch absolute	Pa
psig	pounds-force per square inch gauge	Pa
qt	quart	m^3; L
°R	degree Rankine	K
rd	rad	Gy
sb	stilb	lx
SCF	standard cubic foot	m^3
sq	square	exponential form
thm	therm	J
yd	yard	m

BIBLIOGRAPHY

1. The International Bureau of Weights and Measures, BIPM (Parc de Saint-Cloud, France) is described on page 22 of Ref. 4. This bureau operates under the exclusive supervision of the International Committee of Weights and Measures (CIPM).
2. *Metric Editorial Guide* (*ANMC-78-1*) 3rd ed., American National Metric Council, 5410 Grosvenor Lane, Bethesda, Md. 20814, 1981.
3. *SI Units and Recommendations for the Use of Their Multiples and of Certain Other Units* (*ISO 1000-1981*), American National Standards Institute, 1430 Broadway, New York, N. Y. 10018, 1981.
4. Based on *ASTM E 380-82* (*Standard for Metric Practice*), American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103, 1982.
5. *Fed. Regist.*, Dec. 10, 1976 (41 FR 36414).
6. For ANSI address, see Ref. 3.

R. P. LUKENS
American Society for Testing and Materials

CONTENTS

S *continued*

SULFONATION AND SULFATION

Sulfonation and sulfation are chemical methods for introducing the SO_3 group into organic entities (1); they are closely related and usually treated jointly. Although the terms sulfonation and sulfation are often used interchangeably, the two methods differ chemically.

In sulfonation, an SO_3 group is introduced into an organic molecule, to give a product with —SO_3— linkages (sulfonates) in the form of a sulfonic acid (—SO_3H), a salt (—SO_3Na), or a sulfonyl halide (—SO_3X). Sulfonic acids are generally produced directly by reaction of an aromatic hydrocarbon with sulfuric acid, sulfur trioxide, or chlorosulfuric acid. Sulfonation of unsaturated hydrocarbons with metal sulfites or bisulfites produces the metal sulfonate salts. These reactions are referred to as sulfitation or bisulfitation. In instances where the sulfur atom, at a lower valence, is attached to a carbon atom, the sulfonation process entails oxidation. Thus, the reaction of a paraffinic hydrocarbon with sulfur dioxide and oxygen is referred to as sulfoxidation, and the reaction of sulfur dioxide and chlorine as chlorosulfonation (2). Sulfoalkylation and sulfoarylation reactions involve the addition of sulfoalkyl or a sulfoaryl group to an organic molecule.

Sulfation is defined as any process of introducing an SO_3 group into an organic compound in which the reaction product (sulfate) exhibits the characteristic —OSO_3— molecular configuration. Unlike the sulfonates, which show remarkable stability even after prolonged heating, sulfated products are unstable toward acid hydrolysis. This difference forms the basis of an analytical method to identify mixtures of these two species.

In sulfamation, also termed *N*-sulfonation, compounds of the general structure R_2NSO_3H are formed as well as the corresponding salts, acid halides, and esters. The reagents are sulfamic acid (amidosulfuric acid), SO_3–pyridine complex, SO_3–tertiary *amine complexes, SO_3–aliphatic amine adducts, and chlorine isocyanate–SO_3 complex* (3).

Sulfonation and sulfation processes are important tools for the organic chemist in the design of specific molecules. For example, the introduction of a sulfonic acid group into a specific position in an aromatic nucleus and the subsequent substitution of a hydroxyl group by alkali fusion represents a basic industrial process. On the other hand, the product-development and the application chemists are most interested in the physical and functional properties contributed by the sulfonate moiety, such as solubility, emulsification, wetting, and foaming. Just as a sulfonated emulsifier concentrates at the interface between oil and water phases, contributing to a stable emulsion, so too, in a broader sense, sulfonation and sulfation processes provide the means to interface with, modify, or bridge aqueous and organic systems. This principle is utilized in the development of water-dispersible or water-soluble dyes, flavorants, and medicinals by introducing the water-solubilizing sulfonate group.

Sulfonation, sulfation, and sulfamation processes have led to the commercial development of new sulfonated and sulfated products. Sulfonated dyes were first developed in 1862, followed by the bisulfitation of lignin (qv) in 1866, and the oleum sulfonation of petroleum (qv) and natural occurring fats and oils in 1875 (see Fats and fatty oils). Since then, many new and improved processes have been developed contributing to today's highly efficient and complex technology. Although sulfuric acid-based sulfonation processes continue to dominate, SO_3-based processes have increased significantly over the last 15 years, including the development and utilization of continuous SO_3 film sulfonation and sulfation processes (see also Surfactants and detersive systems).

Detergent sulfonates or sulfates for use in household detergent and personal care products must have light color, little unreacted material or free oil, low inorganic salt content, and negligible odor.

Economic Aspects

It is estimated that in the United States during 1980, ca 1.6×10^6 metric tons of sulfonation, sulfation, and sulfamation products were manufactured with a market value in excess of $\$2.5 \times 10^9$, representing ca 4.5% of the total value of all synthetic organic chemical production (see Table 1). A detailed compilation of U.S. production of sulfonated and sulfated surface-active agents for 1980 is given in Table 2, whereas annual production of total surface-active agents from 1969 to 1980, as well as principal product classes are shown in Figure 1. Total surface-active agents show a modest growth during this period, with lignosulfonates and sulfated products growing faster than average (see Table 3). A comparative cost analysis for sulfonating linear detergent alkylate with sulfuric acid, oleum, or liquid SO_3 is given in Table 4. Sulfonation with SO_3 offers a 65% saving over sulfuric acid and a 39% saving over oleum. A similar comparison for the sulfation of commercial lauryl alcohol shows a 56.3% cost saving for liquid SO_3 against chlorosulfuric acid, exclusive of costs or credit created by HCl disposal or neutralization.

Table 1. Estimated U.S. Volume and Value of Sulfonation, Sulfation, and Sulfamation Products, 1980[a]

Product class	Metric tons	Volume, %	Value $	Value %
surfactants	1,338,488	82.6	1,273,278,000	50.8
dyes	56,105	3.5	398,150,000	15.9
pigments	15,966	1.0	688,950,000	27.5
medicinals	4,534	0.3	56,216,000	2.2
pesticides	68	0.004	3,299,000	0.1
cyclic intermediates	204,750	12.6	88,467,000	3.5
Total	*1,619,911*		*2,508,360,000*	

[a] Refs. 4–5, and other industry sources.

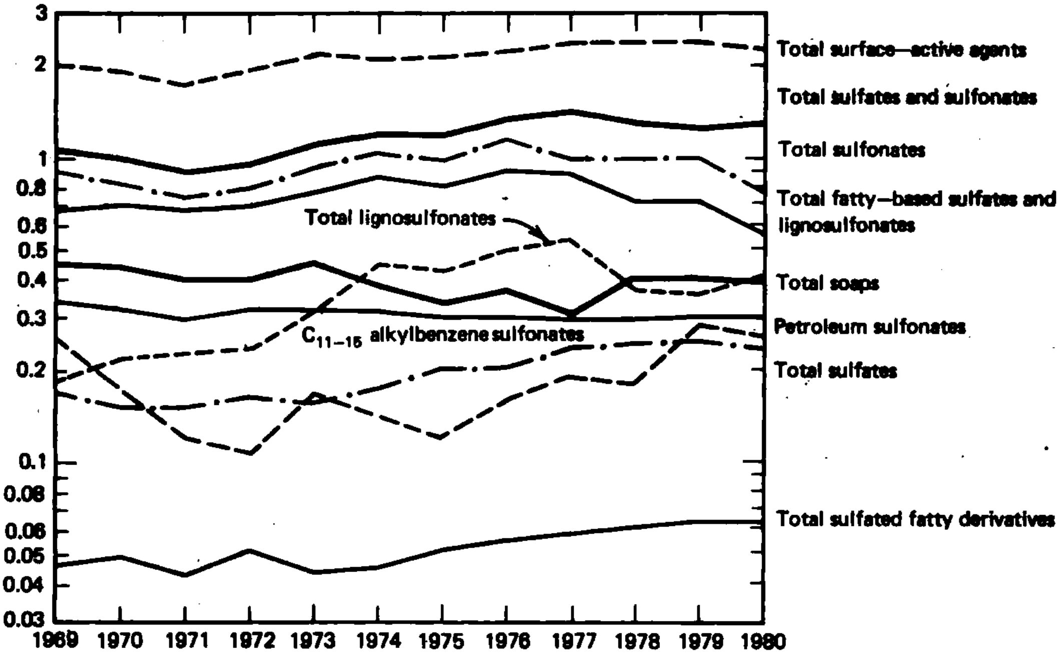


Figure 1. Annual U.S. production of surface-active agents, 10^6 metric tons.

Reagents

Sulfonation and sulfation reagents are listed in Table 5. In the 1860s, sulfuric acid was the only known sulfonating reagent; today, it and oleum are the most widely used reagents because of their convenience and low cost. Since the sulfonation of aromatic compounds with sulfuric acid produces 1 mol of water per mol of compound, 3–4 mol acid are required to obtain a suitably high conversion. This excess increases costs, but reduces viscosity and provides a good reaction medium, diluent, and heat sink. As a general rule, removal of the spent acid is required; neutralization, for example, with caustic soda results in a high sodium sulfate content which impairs the quality of the product.

Chlorosulfuric acid, usually employed in stoichiometric amounts, is another important low cost sulfonation reagent. It does, however, suffer from two drawbacks; namely, its corrosive nature, and the fact that it reacts with evolution of hydrogen

Table 2. U.S. Production of Sulfonated and Sulfated Anionic Surface-Active Agents, 1980[a,b]

Product	Metric tons	Percent of grand total	Unit value, $/t	Value, $
alkylbenzenesulfonates				
dodecylbenzenesulfonic acid	102,734		992.08	101,920,347
calcium salt	6,125		2,006.20	12,287,975
isopropylammonium salt	1,565		1,653.45	2,587,649
sodium salt	122,455		859.80	105,286,809
triethanolammonium salt	2,647		1,234.59	3,267,960
tridecylbenzenesulfonate, sodium salt	51,025		1,300.73	66,369,748
all other	7,648		1,653.47	12,645,739
Total	*294,199*	*22.00*		*304,366,227*
xylene and other aromatic sulfonates				
xylenesulfonate, ammonium salt	7,462		704.52	5,257,128
xylenesulfonate, sodium salt	15,211		947.99	14,419,876
all other	11,322		859.80	9,734,656
Total	*33,995*	*2.54*		*29,411,660*
ligninsulfonates				
calcium salt	281,631		88.18	24,834,222
iron salt	863		396.83	342,464
sodium salt	46,259		374.79	17,337,411
all other	70,394		308.65	21,727,108
Total	*399,147*	*29.85*	*154.32*	*64,241,205*
naphthalenesulfonates	9,689	*0.72*	*1,455*	*14,097,979*
naphthalenesulfonate–formaldehyde condensates[c]	*32,191*	*2.41*	*1,035*	*33,309,959*
sulfonic acids with amide linkages				
sulfosuccinamates	1,482		1,940.07	2,875,184
taurates	1,158		3,196.70	3,701,779
Total	*2,640*	*0.20*		*6,576,963*
sulfonic acids with ester or ether linkages				
sulfosuccinic acid esters, total	9,837		2,289.68	22,523,582
other sulfonic acids and salts, total	20,370		3,483.30	70,954,821
Total	*30,207*	*2.26*		*93,478,403*
other sulfonic acids and salts, total	*9,839*	*0.74*	*1,278.68*	*12,580,933*
petroleum sulfonates				
calcium salts	141,316		1,543.23	218,083,091
sodium salts	95,954		992.08	95,194,044
other petroleum salts	20,514		1,807.79	37,085,004
Total	*257,784*	*19.28*		*350,362,139*
sulfated acids, esters, and amides				
butyl oleate, sodium salt	478		992.08	474,214
isopropyloleate, sodium salt	17			
tall oil, sodium salt	1,453		617.29	896,922
all other	8,649		1,344.82	11,631,348
Total	*10,597*	*0.79*		*13,002,484*
sulfated alcohols				
dodecyl sulfonates				
ammonium salt	3,757		2,204.62	8,282,757
magnesium salt	96		3,284.88	315,348
sodium salt	8,186		2,292.80	18,768,861
triethylammonium salt	4,263		2,248.71	9,586,251
2-ethylhexyl sulfate, sodium salt	892		1,873.93	1,671,546

Table 2 *(continued)*

Product	Metric tons	Percent of grand total	Unit value, \$/t	Value, \$
mixed linear alcohol sulfates, sodium salts	24,412		2,182.57	53,280,899
octyl sulfate, sodium salt	123		3,130.56	385,059
all other	67,213		2,270.76	152,624,592
Total	*108,942*	*8.15*		*244,915,313*
sulfated ethers				
alkylphenols, ethoxylated, sulfated	2,526		2,377.75	6,006,197
dodecyl alcohol, ethoxylated, sulfated, ammonium salt	1,909		1,168.45	2,230,571
dodecyl alcohol, ethoxylated, sulfated, sodium salt	6,958		1.962.11	13,652,361
mixed linear alcohols, ethoxylated, sulfated ammonium salt	38,897		837.76	32,586,351
all other	60,684		1,918.02	116,393,128
Total	*110,974*	*8.30*		*170,868,606*
natural fats and oils, sulfated				
castor oil, sodium salt	2,396		1,234.59	2,958,078
cod oil, sodium salt	746		573.20	427,607
herring oil, sodium salt	844		639.33	539,596
neat's-foot oil, sodium salt	613		683.43	418,943
tallow, sodium salt	1,260		595.25	750,015
Total	*5,859*	*0.44*		*5,094,238*
all other anionic surface-active agents				
sulfated and sulfonated, total	*31,061*	*2.32*	*771.62*	*23,967,289*
Grand total	*1,337,098*		*951.28 (avg)*	*1,366,273,398*

[a] Refs. 4–5.

[b] 100% pure.

[c] Tanning agents.

Table 3. U.S. Production Growth Rates for Surface-Active Agents, Soaps, and Sulfonated and Sulfated Products, 1969–1979

Products	%
surface-active agents, total	+14.6
soaps	−8.5
sulfonates, total	+10.7
alkylbenzenesulfonates	−12.1
lignosulfonates	+91.8
fatty acid-based sulfonates	+34.0
petroleum sulfonates	+5.3
sulfates, total	+47.6

chloride, which presents a disposal problem. Alternatively, the hydrogen chloride may be absorbed in a water scrubber and sold as a commercial grade or recycled.

Stabilized liquid sulfur trioxide, introduced commercially as a sulfonation/sulfation reagent in 1947 (7), is second only to oleum; in the United States, in fact, it is preferred to oleum for detergent manufacture. Because of its extreme reactivity, special

Table 4. Cost of Sulfonation/Sulfation Agents

Agent	kg required	\$/kg agent[a]	\$/t substrate	Total cost, \$
sulfonating agent				
for 1 t linear alkylate (LA)				
H_2SO_4	7292	0.0818	81.86	122.79
oleum	5590	0.0890	89.02	102.38
SO_3, stabilized	1730	0.2095	209.44	74.56
sulfating agent				
for 1 t fatty alcohol				
chlorosulfuric acid	281.6	0.3308	330.69	191.80
SO_3, stabilized	1944.4	0.2095	209.44	83.77

[a] Based on quoted prices as of May 3, 1982.

handling and processing methods are required in order to avoid overreaction, oxidation, and charring. The extreme reactivity of liquid SO_3 can be moderated with solvents such as liquid SO_2, low boiling halogenated hydrocarbons, and paraffins. The reactivity of SO_3 is best controlled by dilution of gaseous SO_3 with nitrogen, SO_2, or dry air. Commercial sulfonation/sulfation processes generally employ a 2–8% SO_3–dry air mixture, or sometimes converter gas at 8% SO_3 concentration. Liquid SO_3 is continuously vaporized into a dry air stream to produce the desired mixture, or provided directly from a sulfur burner equipped with a catalytic converter (see below). Sulfur trioxide may also be obtained from oleum.

Sulfur trioxide occurs in three polymeric forms, known as alpha-, beta-, and gamma-SO_3 (see Table 6). Only the gamma polymer is liquid at room temperature; it can be stabilized to prevent conversion to the beta form, which is caused by small amounts of moisture. Unstabilized sulfur trioxide must be protected from freezing and moisture; otherwise, polymerization and solidification may create serious process problems.

The extreme reactivity of SO_3 may also be moderated by complexing with Lewis bases, eg, dioxane, DMF, pyridine, THF, dimethyl sulfoxide, trialkyl phosphates, and organic bases and amines such as trimethylamine; triethylamine; *N*,*N*-dimethylaniline; *N*,*N*-diethylaniline; morpholine; and quinoline. The reactivity of such complexes is inversely proportional to their stability, and consequently they can be selected for a wide variety of processing conditions. For example, the SO_3–trimethylamine complex is very stable, melting at 239°C. It is soluble in many solvents, including water, in which it is sufficiently stable to be used for sulfation. At present, SO_3-adducts are not commercially available. In general, the complexing agent must be removed after the reaction is completed.

A mixture of gaseous sulfur dioxide and chlorine is a useful reagent for reactions known as sulfochlorination. The actual reagent is believed to be sulfuryl chloride which also can be prepared by heating chlorosulfuric acid in the presence of catalysts, or from sulfur dioxide and chlorine in the presence of activated carbon or camphor. Sulfuryl chloride is soluble in glacial acetic acid and is readily decomposed by hot water or alkalies. Its bp is ca 69.2°C and it is extremely corrosive and toxic.

In sulfoxidation, sulfur dioxide and oxygen, catalyzed by uv radiation, convert *paraffins to sulfonic acids:*

$$2\,RH + 2\,SO_2 + O_2 \xrightarrow{h\nu} 2\,RSO_2OH \qquad (1)$$

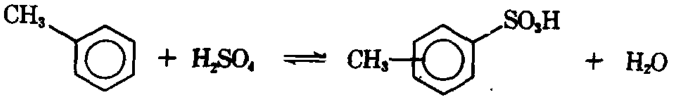
Economic considerations heavily influence the choice of reagent. Although both sulfuric acid and oleum are cheaper than SO_3, a large excess of both reagents is required, which creates substantial quantities of spent acid that have to be discarded or recycled, and affects the economics of the process. In contrast, SO_3 and chlorosulfuric acid usually react stoichiometrically to give products containing very little sulfuric acid; consequently, the neutralized product contains only small amounts of sodium sulfate.

Sodium sulfite and bisulfite are also useful sulfonation agents; they offer economic advantages and versatility (see below).

Sulfonation

The sulfonation of benzene and short-chain alkylbenzenes, such as toluene, the xylenes, cumene, and ethylbenzene, is an important commercial process that is carried out in a number of ways, using sulfuric acid, oleum, or sulfur trioxide. The sulfur trioxide route presents potential fire and explosion hazards and produces by-product sulfones that impair product solubility. Precise process control is essential, and the sulfones are removed by extraction.

The reaction of toluene with 97% sulfuric acid is highly exothermic:



(2)

If excess acid is employed, the sulfonic acid can be extracted. However in other industrial processes, particularly in the sulfonation of xylenes, a large excess of the organic compound is used. The reaction is generally carried out under reflux and the water formed is distilled until the sulfuric acid has been completely consumed. The sulfonic acid is isolated by neutralization with caustic soda, and the excess xylene is separated and recycled. Toluene sulfonation yields 62% *para*-, 32% *ortho*-, and ca 6% *meta*-toluenesulfonic acid (8). The yield of meta isomer can be increased by raising the reaction temperature and increasing the strength of the sulfuric acid. Thus, 97.4% sulfuric acid at 100°C for 2.7 h gave a maximum meta isomer yield of 33%, with 47.3% para and 19.7% ortho isomers (9).

Sulfonated toluene, xylene, and cumene, primarily in the form of ammonium and sodium salts, are important hydrotropes or coupling agents in the manufacture of liquid cleaners and surfactant compositions, and serve as key crisping agents in drum and spray-drying operations.

Phenol from Benzene. For many years, phenol (qv) was manufactured principally via the sulfonation of benzene. The process was cumbersome and involved a large number of separate steps, and the production of 1 kg phenol, required 4.3 kg benzene:

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O \qquad (3)$$

$$2\ C_6H_5SO_3H + Na_2SO_3 \rightarrow 2\ C_6H_5SO_3Na + H_2SO_3 \qquad (4)$$

$$C_6H_5SO_3Na + 2\ NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O \qquad (5)$$

$$2\ C_6H_5ONa + H_2SO_3 \rightarrow 2\ C_6H_5OH + Na_2SO_3 \qquad (6)$$