Paul Russi

DU PONT

DATA SHEET

CHLOROSULFONIC ACID

TECHNICAL

Chlorosulfonic acid is a clear, corrosive, straw colored liquid with a pungent odor. It reacts violently with water with evolution of heat and large quantities of dense white fumes. Hydrochloric acid and sulfuric acid are formed on decomposition.

Chlorosulfonic acid is used principally in organic synthesis as a sulfating, sulfonating or chlorosulfonating agent. Its chemical formula is $ClSO_2OH$. The CAS name is Chlorosulfuric Acid; no. 7790-94-5.

SPECIFICATIONS AND TYPICAL ANALYSES

	Spec.	Anal.*
Total chlorosulfonic acid ($ClSO_2OH$), %	98.5 min	99.2
Total chlorides as HCl, %	30.8 min	31.04
Sulfuric acid as H_2SO_4, %	1.5 max	0.35
Free SO_3, %	0.7 max	0.46
Iron† (Fe), ppm	4.0 max	2.2

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*This column gives typical analyses based on historical production performance. Du Pont does not make any express or implied warranty that this product will continue to have these typical properties.

†"as loaded" basis

PHYSICAL PROPERTIES

Molecular weight	116.531
Boiling point*, C	152
F	306
Freezing point, C	−80
F	−112
Specific gravity (15.6 C, 60 F)	1.752
Density (15.6 C, 60 F), lb/gal	14.6
Vapor pressure, mm Hg, 30 C (86 F)	0.8
38 C (100 F)	2.5
60 C (140 F)	11.0

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*With some decomposition

CHEMICAL PROPERTIES

Sulfation

$$ROH + ClSO_2OH \longrightarrow ROSO_2OH + HCl$$

Sulfonation

$$RH + ClSO_2OH \longrightarrow RSO_2OH + HCl$$

Chlorosulfonation

$$RH + 2ClSO_2OH \longrightarrow RSO_2Cl + H_2SO_4 + HCl$$

Sulfamation

$$RNH_2 + ClSO_2OH \longrightarrow RNHSO_2OH + HCl$$

Reaction with salts

$$NaCl + ClSO_2OH \longrightarrow NaOSO_2Cl + HCl$$

USES

The major use of CSA is for sulfating long chain alcohols. In addition, sulfonation reactions are made with fatty acids and aromatic compounds. Also, sulfamation reactions are carried out with aliphatic and aromatic amines. Specific areas of usage include:

- Manufacture of surfactants
- Preparation of intermediates for making dyes and pigments
- Manufacture of pesticides for protection of crops and livestock
- Manufacture of pharmaceuticals for human and veterinary medicines
- Manufacture of chemical blowing agents
- Miscellaneous chemical process applications employing organic sulfates, sulfamates or sulfamates

PERSONAL SAFETY AND FIRST AID

Health Hazards

Chlorosulfonic acid is a strong acid and powerful desiccant. Contact with the liquid acid will cause severe burns from both chemical and thermal effects. The vapor is also hazardous and is extremely irritating to the skin, eyes, nose and throat. Vapors may cause delayed lung damage. The vapor has such a sharp and penetrating odor that the inhalation of toxic quantities is unlikely unless it is impossible to escape the fumes.

NOTICE: CHLOROSULFONIC ACID CAUSES SEVERE BURNS. HARMFUL IF INHALED—MAY CAUSE DELAYED LUNG INJURY. CONTACT WITH WATER OR MOIST AIR RELEASES IRRITATING GAS. See Personal Safety and First Aid.

Chlorosulfonic acid reacts violently with water. When exposed to the atmosphere, chlorosulfonic acid fumes release hydrochloric acid fumes and sulfuric acid mist by reacting with moisture in the air. Inhalation of these fumes or mist may also cause lung injury.

The U.S. Department of Labor (OSHA) has ruled that an employee's exposure to hydrogen chloride shall not exceed the ceiling value of 5 ppm in air (7 mg/m^3) and to sulfuric acid mist in any 8-hour work shift of a 40 hour week shall not exceed the 8-hour time weighted average of 1 mg/m^3 (CFR 29, 1910.1000 Air Contaminants).[†]

Personal Protective Equipment

Personal protective equipment should be used to protect a worker whenever contact with the acid could be encountered.

The following acid-proof protective equipment for all operating and maintenance personnel should be available: chemical splash goggles, hard hat with brim, safety shoes with boots, jacket and rubber gauntlet gloves. Also, shirt and trousers of wool or ORLON[*] acrylic fiber should be worn. For emergencies or where there is a possibility of considerable exposure, a complete acid suit with hood, gloves and boots; and respiratory protective equipment such as: self-contained breathing apparatus, positive-pressure hose mask, or air-line mask should be used.

Safety Precautions

All persons handling chlorosulfonic acid should exercise care to prevent contact with skin, eyes or clothing and to prevent breathing of mists or vapors. Use with adequate ventilation and wash thoroughly after handling.

The following safety facilities should be easily available in all areas where chlorosulfonic acid is handled (unloading stations, storage areas):

Safety showers—Water should be supplied to the shower in a 2-inch line at 30 gal/min (114 L/min) through a quick-opening valve which stays open. Both the valve (actuated by a handle at hip level) and a 0.25-inch weep hole directly above the valve should be located below the frost line and surrounded by crushed rock or gravel to provide drainage.

Eye wash fountain—or other means for flushing the eyes with a gentle flow of tap water should be supplied.

First Aid

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse.

If inhaled, remove person to fresh air promptly. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

STORAGE AND HANDLING

Glass lined steel tanks are preferred for bulk storage of chlorosulfonic acid, although stainless steel tanks can be used if nominal iron pickup can be tolerated. Storage in steel tanks results in product discoloration and formation of sediment.

Drums of chlorosulfonic acid should be stored away from nitrates, carbides, chlorates, metallic powders and organic materials. Contact with these and other combustibles may cause fire.

Store drums with bungs up. Keep drums out of sun and away from heat.

Keep lights, fire and sparks away from storage openings. Storage periods and temperatures should be kept to a minimum.

Although chlorosulfonic acid is produced with an iron content of less than 4 ppm, the acid may pick up iron after delivery depending on the shipping container as well as elapsed time and temperature during shipment.

PACKAGES

Du Pont Chlorosulfonic Acid Technical is supplied in tank cars and tank trucks; it is also available in returnable 55-gal, 700-lb net stainless steel drums.

DOT Hazard Classification: Corrosive Material

Freight Classification: Corrosive Liquid.

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[*] Reg. U.S. Pat. & Tm. Off., Du Pont Co.

[†] Due to changing governmental regulations, such as those of the Department of Transportation, Department of Labor, U.S. Environmental Protection Agency, and the Food and Drug Administration, references herein to governmental requirements may be superseded. You should consult and follow the current governmental regulations, such as Hazard Classification, Labeling, Food Use Clearances, Worker Exposure Limitations, and Waste Disposal Procedures for the up-to-date requirements for the product described in this literature.

E. I. du Pont de Nemours & Co. (Inc.) • Wilmington, Delaware 19898

U.S. Sales Offices

CHARLOTTE NC 28230
6250 Fairview Rd., P.O. Box 30517
704-364-1550

CHICAGO IL 60631
O'Hare Plaza, Suite 760
5725 E. River Rd.
312-982-4300

CLEVELAND OH 44124
5001 Mayfield Rd.
216-382-5800

HOUSTON TX 77056
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713-877-5500

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212-971-4000

PHILADELPHIA PA (Suburban)
308 E. Lancaster Ave.
Wynnewood PA 19096
215-896-2000

SAN FRANCISCO CA 94111
Suite 3110
50 California Street
415-391-7300

International Sales Offices

IN CANADA
Du Pont Canada Inc.
Box 660
Montreal S, P.Q. H3C 2V1
514-861-3861

Du Pont Canada Inc.
P. O. Box 2300
Streetsville Postal Station
Mississauga, Ontario
L5M 2J4
416-821-5594

IN EUROPE
Du Pont de Nemours International S.A.
P.O. Box
CH-1211
Geneva 24, Switzerland
022-278111

IN THE FAR EAST
Du Pont Far East Inc.
Kowa Building No. 2
11-39 Akasaka 1-chome
Minato-ku
Tokyo 107, Japan
585-5511

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Paul Russo

DU PONT

See ... W. M. Lee, in Chemistry of Non Aqueous Solvents
Lagowski, J.J., ed. Academic Press (1967).

MATERIAL SAFETY DATA SHEET

IDENTIFICATION

Name
Chlorosulfonic Acid

Synonyms
CSA

CAS Name
Chlorosulfonic Acid

I.D. Nos./Codes NIOSH Access No. = FX5730000
Wiswesser Line Notation = H S-03G

Manufacturer/Distributor
E. I. du Pont de Nemours & Co., (Inc.)

Address
Wilmington, DE 19898

Chemical Family
Inorganic Acid

CAS Registry No.
7790-94-5

Formula:
$Cl{-}SO_2{-}OH$ or $Cl{-}SO_3{-}H$

Product Information and Emergency Phone
(302) 774-2421

Transportation Emergency Phone
(800) 424-9300

HAZARDOUS COMPONENTS

Material(s)	***Approximate %***
Chlorosulfonic Acid	99.4%

PHYSICAL DATA

Boiling Point, 760 mm Hg
155°C (311°F)

Specific Gravity
1.75 @ 16°C (60°F)

Vapor Density
4.0 (Air = 1)

% Volatiles by Vol.
100% @ B.P.

Melting Point
-80°C (-112°F)

Vapor Pressure 0.8 mm Hg @ 30°C (86°F)
2.5 mm Hg @ 37.7°C (99.9°F)

Solubility in H_2O
Complete - violent reaction

Evaporation Rate (Butyl Acetate = 1)

Form	***Appearance***	***Color***	***Odor***
Liquid	Fuming	Straw color	Pungent

pH Information
<1

Octanol/Water Partition Coefficient

FIRE AND EXPLOSION DATA

Flash Point	***Method***	***Autoignition Temperature***
Will not burn		

Fire and Explosion Hazards: Strong oxidizer. Contact with combustible materials may cause fire. Releases hazardous chlorine (Cl_2), hydrogen chloride (HCl) and sulfur dioxide (SO_2) gases when heated. Reacts violently with water-spattering acid. Leaks or spills cause dense fumes. Explosive concentrations of hydrogen gas can accumulate inside metal containers.

Extinguishing Media: Foam, dry chemical, carbon dioxide (CO_2), then use water with care from a safe distance upwind.

Special Fire Fighting Instructions: Wear protective clothing (see Protection Information). Stay upwind. DO NOT get water inside any container. Cool outside of containers with water if exposed to fire. Evacuate area. Stay upwind. If contact with smoke and fumes cannot be avoided, wear complete protective clothing with breathing air supply.

HAZARDOUS REACTIVITY

Instability Stable, but dangerously reactive.

Incompatibility: Reacts violently with water to form hydrochloric and sulfuric acids. Hazardous exothermic reaction with many organic and combustible materials, nitrates, chlorates, carbides, sulfides, cyanides, metallic powders, etc.

Decomposition: May result in dangerous temperatures and pressures, or releases dangerous gases, such as sulfuric and hydrochloric acids.

Polymerization: Will not occur.

HEALTH HAZARD INFORMATION

Exposure Limits

See attached page 3.

Routes of Exposure and Effects Causes severe burns. Harmful if inhaled-may cause severe or delayed lung injury. Chronic overexposure to vapors or mists may damage teeth or respiratory tract.

First Aid: In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse. If swallowed, give large quantities of water. Call a physician. Never give anything by mouth to an unconscious person. If inhaled, remove to fresh air. Have patient lie down and keep quiet. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

PROTECTION INFORMATION

Ventilation Use only with ventilation adequate to maintain air concentrations below exposure limits. Fume scrubbers and mist eliminators required.

Personal Protective Equipment

See attached page 3.

Other If there is reasonable potential for contact or exposure, wear complete acid-impervious suit, hood, gloves, boots and breathing air supply.

DISPOSAL PROCEDURES

Aquatic Toxicity

TLm 96 = 100-10 ppm

Spill, Leak or Release

See attached page 3.

Waste Disposal Comply with Federal, State and local regulations. If approved, neutralized material may be drained to sewer waste disposal plant.

SHIPPING PRECAUTIONS

Transportation DOT Shipping Name: Chlorosulfonic Acid. DOT Hazard Class: Corrosive Material 49 STC Code - 49 302 04. UN No. 1754. IMCO Class 8.

Shipping Containers

Railroad tank cars, tank trucks, drums, sample bottles.

Storage Conditions

See attached page 3.

REFERENCES AND ADDITIONAL INFORMATION

Should be handled only by trained personnel; plan emergency actions in advance. Do not get in eyes, on skin, on clothing. Do not breathe vapor or mist. Keep from contact with clothing and other combustible materials to avoid fire. Wash thoroughly after handling. Before using, read: Du Pont Chlorosulfonic Acid Data Sheet. For more information, refer to Du Pont Chlorosulfonic Acid Properties, Uses, Storage and Handling Bulletin.

DATE: 12/80

CHLOROSULFONIC ACID MSDS ATTACHMENT

HEALTH HAZARD INFORMATION

Exposure Limits: Not established for chlorosulfonic acid; however, vapors react with moisture in air to form hydrochloric and sulfuric acid mists; OSHA & ACGIH have established a ceiling limit of 5 ppm or 7 mg/m^3 for hydrogen chloride, and an 8-hour Time Weighted Average of 1 mg/m^3 for sulfuric acid.

PROTECTION INFORMATION

Personal Protective Equipment: If there is any possibility of contact, wear as appropriate chemical splash goggles; safety spectacles; rubber or Neoprene® gauntlet gloves and foot gear; wool or acrylic long sleeve clothing; hard hat with brim and face shield. Have OSHA permissible respiratory protection available.

DISPOSAL PROCEDURES

Spill, Leak or Release: Evacuate area and ventilate before reentering. If necessary to enter, use self contained breathing apparatus, life line and "buddy" system. Flush away with water applied quickly to entire spill. Contain "washings" with dike, and neutralize with lime or soda ash. Use of foam will reduce fume evolution when water is added.

SHIPPING PRECAUTIONS

Storage Conditions: Keep in well ventilated area, away from heat, sparks and flame. Keep containers closed. Do not allow water to enter containers because of violent reaction. Never use pressure to empty drums. Do not wash out containers or use for other purposes. Do not store with incompatible materials (See Hazardous Reactivity Section).

DATE: 12/80

INTRODUCTION

Chlorosulfonic acid ($ClSO_2OH$) is a clear, straw-colored liquid with a pungent odor. It is a highly reactive chemical compound containing equimolar quantities of HCl and SO_3 with a molecular weight of 116.52. Its Chemical Abstract name is chlorosulfonic acid, with Registry Number (CAS) 77-94-5. It reacts violently with water evolving heat and large quantities of white fumes of hydrochloric and sulfuric acid. The uses are principally in organic synthesis as a sulfating, sulfonating or chlorosulfonating agent. It is preferred in many applications because it is a strong agent but less destructive than sulfur trioxide.

Chlorosulfonic acid (CSA) is soluble in liquid sulfur dioxide, nitrobenzene and halogenated organic solvents which also contain hydrogen. It is only slightly soluble in carbon disulfide and halogenated organics which do not contain hydrogen.

Heating chlorosulfonic acid results in the equilibrium formation of sulfuryl chloride, sulfuric acid, pyrosulfuryl mono- and dichloride and pyrosulfuric acid. There is evidence of the formation of higher polyacids, such as $HS_4O_{12}Cl$. Further heating beyond the boiling point results in decomposition into sulfur dioxide, chlorine and water. Chlorosulfonic acid is nonflammable, but it may cause ignition by contact with combustible materials. Table II lists some physical properties.

TABLE I

SPECIFICATIONS AND TYPICAL ANALYSES

	Specifications	Typical*
Total chlorosulfonic acid, %	min 98.5	99.2
Total chlorides, as HCl, %	min 30.8	31.0
Sulfuric acid, %	max 1.5	0.4
Free SO_3, %	max 0.7	0.5
Iron, as Fe, ppm	max 4.0	2.2

*The typical analyses in the above table are based on historical production performance. Du Pont does not make any express or implied warranty that future production will demonstrate or continue to possess these typical properties.

TABLE II

PHYSICAL PROPERTIES OF CHLOROSULFONIC ACID

Weight, 15.6 C (60 F), lb/gal	14.6
g/mL (Mg/m^3)	1.75
Freezing point, C	−80
F	−112
Specific gravity, 15.6 C (60 F)	1.752
Specific heat, cal/g·C (Btu/lb·F), 15-80 C (59-176 F)	0.28
kJ/kg·K	1.18
Viscosity, cP (mPa·s) −10 C (14 F)	5.5
0 C (32 F)	4.2
10 C (50 F)	3.3
20 C (68 F)	2.6
40 C (104 F)	1.7
60 C (140 F)	1.2
Vapor pressure, mm Hg, 30 C (86 F)	1.5
38 C (100 F)	2.5
60 C (140 F)	11.0
152 C (306 F), boiling point	760
Vapor density, air = 1, @216 C (421 F), approx.	2.4

The boiling point and vapor density are average values of those reported, since variations can arise from CSA's equilibrating with its decomposition products.

NOTICE: CHLOROSULFONIC ACID CAUSES SEVERE BURNS. HARMFUL IF INHALED—MAY CAUSE DELAYED LUNG INJURY. CONTACT WITH WATER OR MOIST AIR RELEASES IRRITATING GAS. See Personal Safety and First Aid on page 6.

CHEMICAL REACTIONS

The major reactions of chlorosulfonic acid may be divided into three basic types which differ in the bonding order of the added—SO_3H group:

Type	Bonding Order	Example of Manufactured Compound
Sulfation	—C—O—S—	Sodium lauryl sulfate ($C_{11}H_{23}CH_2OSO_3Na$)
Sulfonation	—C—S—	Sodium phenyl sulfonate ($C_6H_5SO_3Na$)
Sulfamation	—C—N—S—	Cyclohexyl sulfamate ($C_6H_{11}NHSO_3Na$)

With CSA, chlorosulfation and chlorosulfonation reactions are also employed, where the—SO_2Cl group is attached to form chlorosulfates and sulfonyl chlorides. Examples of compounds formed:

Chlorosulfation—isopropyl chlorosulfate [$CH_3CH(CH_3)OSO_2Cl$]

Chlorosulfonation—benzenesulfonyl chloride ($C_6H_5SO_2Cl$)

See subheadings as follows for more reactions and examples.

SULFATION

Long Chain Primary Alcohols

The major application of chlorosulfonic acid is in sulfating liquid, long-chain primary alcohols such as lauryl alcohol.

$$C_{11}H_{23}CH_2OH + ClSO_3H \longrightarrow C_{11}H_{23}CH_2—O—SO_3H + HCl$$

The simple and rapid reaction produces a quality product and no solvents are needed. Continuous operation has been possible. Solid alcohols can be reacted in a solvent such as chloroform, carbon tetrachloride or tetrachloroethylene (perchloroethylene).

Long Chain Secondary Alcohols

Chlorosulfonic acid is the best sulfating agent for long-chain secondary alcohols. Sulfur trioxide, for example, causes dehydration of these alcohols.

Ethoxylated Alcohols

$$R—(CH_2—CH_2—O)_n—CH_2—CH_2OH + ClSO_3H \longrightarrow R—(CH_2—CH_2—O)_n—CH_2—CH_2—O—SO_3H + HCl$$

R can be a phenolic, aliphatic or aliphatic-substituted aromatic group.

Glycerol Diethers

$$ROCH_2—CH(OH)—CH_2OR' + ClSO_3H \longrightarrow ROCH_2—CH(OSO_3H)—CH_2OR' + HCl$$

R and R′ can be the same or different branched-chain aliphatic groups, or carboxyl groups which contain 25 or fewer carbon atoms. An example is α, α'-bis(2-ethylhexyl) glycerol ether. The reaction, which is carried out at 0 to 10 C, gives products which are useful as textile auxiliary agents.

Ester Alcohols

An example is sodium ethylene glycol monolaurate:

$$HO—CH_2—CH_2—O—CO—C_{11}H_{23} + ClSO_3H \xrightarrow[\text{in ethylene chloride}]{\text{at 10 C}} HSO_3—O—CH_2—CH_2—O—CO—C_{11}H_{23} + HCl$$

Following this reaction the acid is then neutralized with sodium hydroxide to form the sulfate. Another example is the hydroxyalkyl thiosuccinate, sulfated 20-25 minutes in CCl_4 at −5 to 0 C. The products are surfactants with a variety of applications.

Amino Alcohols

Several of these alcohols have been successfully sulfated with chlorosulfonic acid. The sulfates are being increasingly used for aminoalkylating cellulosic materials. Examples are those compounds with the structure $(RCH_2)_2NCH_2CH_2OH$ where R is an alkyl-phenyl group.

Certain amino alcohols are sulfated with chlorosulfonic acid in a halogenated solvent to give the inner salt:

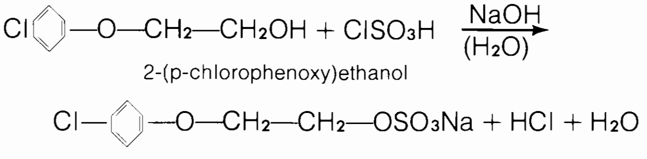
$$NH_2—CH_2—CH_2OH + ClSO_3H \longrightarrow \overset{+}{N}H_3—CH_2—CH_2—OSO_3^- + HCl$$

SULFATION WITH DIETHYL ETHER—CHLOROSULFONIC ACID COMPLEX

The diethyl ether-chlorosulfonic acid complex is a milder agent than the pure acid, and has been effectively used at 10 C with both primary and secondary alcohols, and with compounds containing functional groups.

Alcohols

ALCOHOLS WITH AN ETHER GROUP—



2-(p-chlorophenoxy)ethanol

sodium 2-(p-chlorophenoxy)ethyl sulfate

In similar reactions the appropriate alcohol produces ammonium 2-(2,4-dichlorophenoxy)ethyl sulfate, and sodium 2-(2,4-dichlorophenoxy ethoxy)ethyl sulfate. These materials exhibit herbicidal characteristics.

Sodium 1,3-bis(2-ethylhexyl)glycerol sulfate, prepared with chlorosulfonic acid in ether, is a wetting agent for cotton. Similar compounds are useful as leveling, wetting, emulsifying, and washing agents.

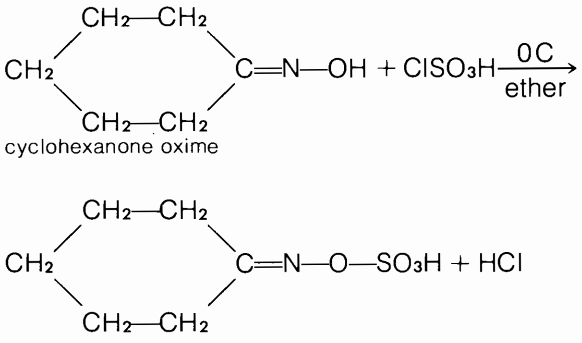
ALCOHOLS WITH AN AMIDE GROUP—2-hydroxy-4,6,6-trimethylheptanenitrile, when treated with concentrated sulfuric acid at 30-60 C, yields the hydroxycarboxamide. The amide reacts with chlorosulfonic acid in ether at 0-40 C, and following neutralization, forms the sulfate, a useful wetting, penetrating, emulsifying, and dispersing agent.

ALCOHOLS WITH A NITRO GROUP—Nitroheptadecyl alcohol, when reacted with chlorosulfonic acid in ether at 20 C followed by neutralization, yields a useful wetting agent.

THIO-ALCOHOLS—2-(alkylthio)ethanols(8-18 carbon atoms in the alkyl group) react with chlorosulfonic acid in ether to yield the sulfate following neutralization. These sulfates have proved valuable as surfactants, nematocides and fungicides. An example is the 2-(dodecylthio)ethyl sulfate.

Ketoximes

These compounds are as easily sulfated as the alcohols, using chlorosulfonic acid in ether at 0 C.



cyclohexanone oxime

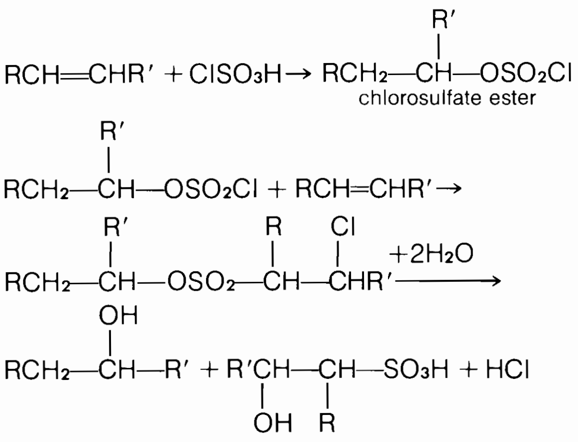
SULFONATION

Aromatic Hydrocarbons

$(C_6H_5)_2 + ClSO_3H \rightarrow C_6H_5—C_6H_4SO_3H + HCl$

Alkenes

Chlorosulfonic acid with an excess of alkene and with a non-polar solvent or without a solvent, forms secondary alcohols and hydroxy sulfonic acids.



$$RCH{=}CHR' + ClSO_3H \rightarrow RCH_2—\overset{R'}{\overset{|}{C}}H—OSO_2Cl$$

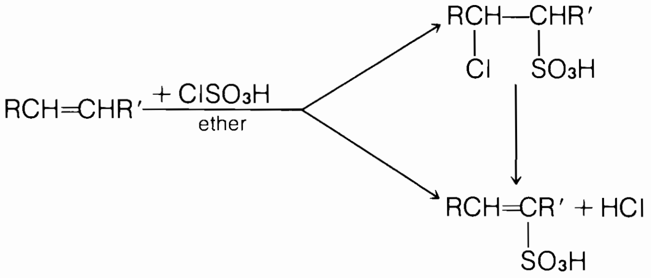
chlorosulfate ester

$$RCH_2—\overset{R'}{\overset{|}{C}}H—OSO_2Cl + RCH{=}CHR' \rightarrow$$

$$RCH_2—\overset{R'}{\overset{|}{C}}H—OSO_2—\overset{R}{\overset{|}{C}}H—\overset{Cl}{\overset{|}{C}}HR' \xrightarrow{+2H_2O}$$

$$RCH_2—\overset{OH}{\overset{|}{C}}H—R' + R'\underset{\underset{OH}{|}}{C}H—\underset{\underset{R}{|}}{C}H—SO_3H + HCl$$

With polar solvents the alkene and chlorosulfonic acid give chlorinated acids or alkene sulfonic acids.



$$RCH{=}CHR' \xrightarrow[\text{ether}]{+ClSO_3H} \underset{\underset{Cl}{|}}{RCH}—\underset{\underset{SO_3H}{|}}{CHR'} \rightarrow RCH{=}\underset{\underset{SO_3H}{|}}{C}R' + HCl$$

$$RCH{=}CHR' \xrightarrow[\text{ether}]{+ClSO_3H} RCH{=}\underset{\underset{SO_3H}{|}}{C}R' + HCl$$

Long Chain Fatty Acids and Esters

$R—CH_2—COOH + ClSO_3H \rightarrow$
$RCH(SO_3H)COOH + HCl$

SULFAMATION

Aliphatic and aromatic amines react with chlorosulfonic acid to give sulfamic acids or their salts.

$2C_6H_5NH_2 + ClSO_3H \rightarrow$
$C_6H_5NH—SO_3H \cdot C_6H_5NH_2 + HCl$

SULFONYL CHLORIDES

Sulfonyl chlorides are those compounds in which an $—SO_2Cl$ group is attached to an aromatic ring (a chlorosulfonate) or to an alkoxy group (a chlorosulfate).

Chlorosulfonates

A chlorosulfonate is formed in a two-stage reaction when an excess of chlorosulfonic acid is reacted with the aromatic hydrocarbon:

$C_6H_6 + ClSO_3H \rightarrow C_6H_5SO_3H + HCl$
$C_6H_5SO_3H + ClSO_3H \rightarrow C_6H_5SO_2Cl + H_2SO_4$

This reaction can also be carried out very conveniently by using a mixture of chlorosulfonic acid and sulfur trioxide. The interreaction of the sulfur trioxide eliminates the evolution of HCl:

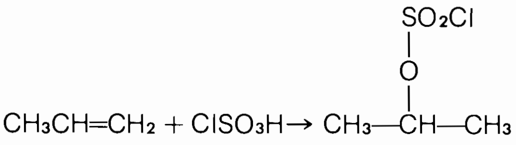
$C_6H_6 + SO_3/ClSO_3H \xrightarrow{\text{low temp}}$
$C_6H_5SO_3H + ClSO_3H \rightarrow C_6H_5SO_2Cl + H_2SO_4$

Chlorosulfates

A chlorosulfate is formed when an excess of chlorosulfonic acid is reacted with an alcohol:

$ROH + 2ClSO_3H \rightarrow R—O—SO_2Cl + HCl + H_2SO_4$

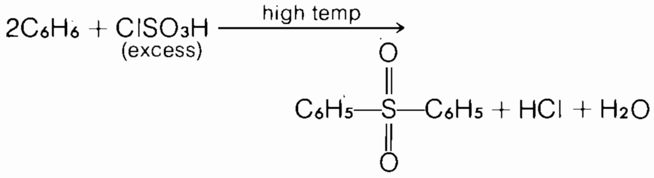
A chlorosulfate is also formed when a stoichiometric equivalent of chlorosulfonic acid is reacted with an alkene:



$$CH_3CH{=}CH_2 + ClSO_3H \rightarrow CH_3—\overset{\overset{\overset{SO_2Cl}{|}}{O}}{\overset{|}{C}}H—CH_3$$

SULFONES

When an excess of chlorosulfonic acid is reacted with an aromatic hydrocarbon at elevated temperatures, the sulfone is formed:



$$2C_6H_6 + \underset{\text{(excess)}}{ClSO_3H} \xrightarrow{\text{high temp}} C_6H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-C_6H_5 + HCl + H_2O$$

Sulfones are also made by reacting sulfonyl chlorides with hydrocarbons in the presence of $AlCl_3$ (Friedel-Crafts synthesis). This synthesis can be employed to make unsymmetrical sulfones.

INORGANIC REACTIONS

Under anhydrous conditions chlorosulfonic acid reacts as a monobasic acid with sodium chloride to form sodium chlorosulfate and hydrogen chloride:

$$NaCl + ClSO_3H \rightarrow NaOSO_2Cl + HCl$$

Phosphorous pentoxide and phosphorous pentachloride form pyrosulfuryl dichloride with chlorosulfonic acid.

$$P_2O_5 + 6ClSO_3H \rightarrow 3Cl_2S_2O_5 + 2H_3PO_4$$
$$PCl_5 + 2ClSO_3H \rightarrow Cl_2S_2O_5 + POCl_3 + 2HCl$$

CONDENSATIONS

Chlorosulfonic acid, because of its affinity for water, is an excellent dehydrating or condensing agent.

USES AND APPLICATIONS

Chlorosulfonic acid is used most widely for sulfating liquid long chain alcohols. The reaction is relatively simple and rapid and goes to completion through the loss of HCl. CSA is a strong agent, but reacts more moderately than sulfur trioxide with good yields and color. Solid alcohols as well as ethoxylated alcohols, ester alcohols and long chain hydroxy amides can be sulfated in halogenated solvents. Sulfation with CSA generally requires close to stoichiometric amounts, thus minimizing purification problems. Long chain fatty acids and aromatic compounds can be sulfonated with CSA, and sulfamation reactions can be carried out with aliphatic and aromatic amines. Specific reactions are improved in some cases by the use of solvents, additives or CSA complexes with other agents such as SO_3, ethers, amides and tertiary amines.

SURFACTANTS

The major commercial use for chlorosulfonic acid is for sulfation or sulfonating operations in the manufacture of a variety of cleaning and wetting agent products. Usually these materials are of a proprietary nature for use in shampoos and other personal care products or for formulating commercial laundry detergents and wetting agents.

DYES & PIGMENTS

Chlorosulfonic acid is used as a sulfonating or chlorosulfonating agent to prepare intermediates for the manufacture of numerous dyes and pigments. It also is employed as a solvent or reaction medium for dyestuffs that are difficult to solubilize.

PHARMACEUTICALS

Manufacturers of various medicinals use CSA as a reactant in intermediate steps of synthesis processes. The major categories of these products are sulfonamides (anti-infectives) and benzothiadiazines (diuretics). They are used in both human and veterinary medicine as well as for preparation of animal feed additives.

CHEMICAL BLOWING AGENTS

Products to expand volume and reduce density of rubbers and plastics are made with CSA. These products fall chiefly in the categories of sulfonhydrazides and semi-carbazides.

PESTICIDES

A number of proprietary pesticides utilize CSA as chlorosulfonating or sulfonating agents in the manufacturing process. Ultimately these products find usage for protection of livestock, for weed control and in treatment of vegetable, fruit and other crops.

OTHER USES

The wide range of use of organic sulfates, sulfonates and sulfamates creates many in-process applications for CSA. The following partial listing gives product types and use areas which now or can require CSA in the manufacturing process:

- Plasticizers (from toluene sulfonyl chloride)
- Resins
- Catalysts for polymerization, esterification and other organic reactions
- Alkylation processes
- Hydrogen chloride and carbon monoxide (from formic acid)
- Synthetic tanning agents

PERSONAL SAFETY AND FIRST AID

HEALTH HAZARDS

Chlorosulfonic acid is a strong acid and powerful desiccant. Contact with the liquid acid will cause severe burns from both chemical and thermal effects. The vapor is also hazardous and is extremely irritating to the skin, eyes, nose and throat. Vapors may cause delayed lung damage. The vapor has such a sharp and penetrating odor that the inhalation of toxic quantities is unlikely unless it is impossible to escape the fumes.

Chlorosulfonic acid reacts violently with water. When exposed to the atmosphere, chlorosulfonic acid fumes release hydrochloric acid fumes and sulfuric acid mist by reacting with moisture in the air. Inhalation of these fumes or mist may also cause lung injury.

The U.S. Department of Labor (OSHA) has ruled that an employee's exposure to hydrogen chloride shall not exceed the ceiling value of 5 ppm in air (7 mg/m^3) and to sulfuric acid mist in any 8-hour work shift of a 40 hour week shall not exceed the 8-hour time weighted average of 1 mg/m^3 (CFR 29, 1910.1000 Air Contaminants).†

SAFETY PRECAUTIONS

All persons handling chlorosulfonic acid should exercise care to prevent contact with skin, eyes or clothing and to prevent breathing of mists or vapors. Use with adequate ventilation and wash thoroughly after handling.

PERSONAL PROTECTIVE EQUIPMENT

Personal protective equipment should be used to protect workers whenever contact with acid could be encountered. However, it should not be considered a substitute for safe working conditions and practices.

The minimum protection suggested for operating and maintenance personnel includes:

- chemical safety goggles or face shield
- hard hat
- safety shoes
- long sleeved shirt and trousers of wool, DACRON® polyester fiber or ORLON® acrylic fiber

A rubber apron and rubber or plastic-coated gauntlets long enough to cover the forearm provide additional protection when there is a possibility of body contact. In emergencies or in performing work where there is possibility of considerable exposure (such as taking samples, opening equipment, or performing tasks during which inhalation of vapor or mist may occur), a full rubber suit with hood, boots and gloves should be worn. Air should be supplied to the hood until the absence of fumes in the work area has been established.

Proper selection and care of respiratory protective equipment is an essential part of respiratory protection. Standby respiratory equipment is necessary in areas where chlorosulfonic acid is handled (unloading stations, storage areas, etc.). For additional information about respiratory protective equipment see: ANSI, American National Standard Practices For Respiratory Protection No. Z 88.2-1969 or OSHA Standard 1910.134, Respiratory Protection.

Site Facilities

The following safety facilities should be easily available in all areas where chlorosulfonic acid is handled (unloading stations, storage areas):

Safety showers—Water should be supplied to the shower in a 2-inch line at 30 gal/min (114 L/min) through a quick-opening valve which stays open. Both the valve (actuated by a handle at hip level) and a 0.25-inch weep hole directly above the valve should be located below the frost line and surrounded by crushed rock or gravel to provide drainage.

Eye wash fountain—or other means for flushing the eyes with a gentle flow of tap water should be supplied.

FIRST AID

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. Wash clothing before reuse.

If inhaled, remove person to fresh air promptly. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

HANDLING PRECAUTIONS

SPILLS AND LEAKS

Prevention of spills and leaks of chlorosulfonic acid should be carefully considered in the design and oper-

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†Due to changing governmental regulations, such as those of the Department of Transportation, Department of Labor, U.S. Environmental Protection Agency, and the Food and Drug Administration, references herein to governmental requirements may be superseded. You should consult and follow the current governmental regulations, such as Hazard Classification, Labeling, Food Use Clearances, Worker Exposure Limitations, and Waste Disposal Procedures for the up-to-date requirements for the product described in this literature.

ation of facilities handling this acid. Factors important in spill prevention include facilities design, facilities monitoring, detailed operating and unloading procedures, and employee training and education. See further discussion of factors to consider in design under Engineering Control of Hazards.

Even with the best efforts aimed at preventing spills, they may still occur, so consideration should be given to possible problem areas such as: vessels, piping, unloading areas, etc. Chlorosulfonic acid spills should be contained, and run-off to sewers and waterways prevented. Drainage to sewers should be avoided because the violent reaction with water can result in sewer damage. However, containing the leakage in a dike around the tank may make it difficult, if not impossible, to determine the source of the leak because of excessive fuming. It is best to evaluate the drainage pattern and install diversion diking that contains the spillage in such a location that the leak can be controlled.

Depending on the magnitude of the spill, control can be best achieved by absorption in expanded clay, diatomaceous earth, dry sand or other non-reactive absorbants. Such materials with the absorbed acid can then be removed from the area for burial, controlled dilution with water or neutralization with alkali, in accordance with applicable federal, state or local regulations.

Spills in unconfined, outdoor areas can be controlled by the use of water fog or mechanical foam. This permits the dilution of the spill to non-fuming strengths of sulfuric acid for subsequent neutralization. Large volumes of sulfuric acid mist and HCl gas are evolved during the water fog or foam treatment until the strong acid has been sufficiently diluted. A solid stream of water should not be used because of violent spattering from the reaction of chlorosulfonic acid with water. If small spills are flushed with water, the water should be added from a distance and the person flushing should be upwind and provided with self-contained breathing apparatus. No one should be allowed downwind of the contaminated area while flushing is taking place.

For suppressing fumes from chlorosulfonic acid in a dry diked confined area, the application of white mineral oil to the surface of the acid is effective. The mineral oil forms a seal over the liquid chlorosulfonic acid and essentially stops the fuming. The liquid chlorosulfonic acid beneath the seal can be pumped out and recovered.

SPILL CONTROL

Users are urged to determine which of the methods of control is best suited for their plant and equipment. It is important that appropriate equipment be available and suitably located to handle a leak or spill without delay. Personnel should be provided with appropriate personal protective equipment and instructed in equipment location and operation. It is desirable to incorporate a spill handling procedure into a plant's disaster plan so that the appropriate regulatory agencies are promptly notified and public relations contacts are properly carried out. It is useful to review spill handling procedures with the local fire department.

Du Pont can provide a film showing spill control measures, that may be helpful in instructing new users who are not familiar with the handling of chlorosulfonic acid. The four techniques demonstrated in the film are summarized in Figure 1.

FIGURE 1 CSA SPILL CONTROL FILM

1. **ABSORBENT CLAY**
   - 2 volumes of dry absorbent per volume of acid
   - For small spills or line or equipment drain situation
   - Primary purpose to locate source of spill
2. **WATER FOG NOZZLE**
   - Open or unconfined areas
   - Fine spray combines with the acid smoothly to convert to H_2SO_4 less than 100% in strength and HCl gas
   - No violent spattering
   - Avoids solid stream of water
   - Operator comes fairly close to source of spill
   - Requires 5 minutes to dispose 25 gallons (95 liters)
3. **WATER-POWERED FOAM GENERATOR**
   - Open or unconfined areas
   - Can be set up to operate remotely
   - Occasional violent eruptions as water in foam separates out and contacts the acid
   - Requires 2 minutes to dispose 25 gallons (95 liters)
4. **WHITE MINERAL OIL**
   - Confined or diked area
   - Forms a durable seal over the acid so that it can be pumped from beneath the seal

HAZARDOUS CHEMICAL REACTIONS

Water or caustic solutions should never be added to CSA because of violent reaction and spattering.

Chlorosulfonic acid reacts readily with many other compounds. Many of these reactions are well known and have been employed safely for many years. For a compilation of reactions reported to be potentially hazardous, refer to NFPA 491M, "Manual of Hazardous Chemical Reactions".

CSA reacts with organic and inorganic reducing materials with rapid generation of heat. CSA is a powerful dehydrating agent and readily chars many organic substances. On contact with combustible materials such as wood shavings, the heat produced by dehydration may be sufficient to cause fire.

CSA also reacts with carbonates to generate carbon dioxide gas and with cyanides and sulfides to form poisonous hydrogen cyanide and hydrogen sulfide gases respectively. Thus, there is not only the danger of violent eruption that could result in acid burns, but also the possibility of generating explosive or poisonous atmospheres which could present additional hazards. For these reasons, CSA should be used strictly in accordance with the directions prepared by qualified technical personnel.

Many lubricants are attacked by CSA. Use only silicone or fluorocarbon-based lubricants.

CORROSION HAZARDS

CSA attacks cast iron, brass, bronze and most other non-ferrous metals. Glass-lined steel is the preferred material of construction for chlorosulfonic acid. Stainless steel is resistant to corrosive attack in the liquid phase. Steel is moderately resistant to CSA, but there is appreciable iron pick-up, discoloration, and sludge formation. TEFLON® is the only known resistant plastic material. Rubber, neoprene, polyester and PVC are all readily attacked by CSA and, therefore should never be used in this service.

CSA absorbs moisture rapidly on exposure to air, which normally forms dense white fumes. Such fumes consisting of HCl and H_2SO_4 acid can cause severe corrosion damage to metal surfaces such as tanks and pipe lines.

FIRE AND EXPLOSION HAZARD

CSA is nonflammable. It is highly reactive and capable of igniting finely divided combustible materials on contact or may cause spontaneous combustion in contact with such organic materials as sawdust and oily rags.

When diluted to non-fuming concentrations, the hydrochloric acid and sulfuric acids so formed attack many metals to release flammable hydrogen gas. Therefore, no open flames, open lights or matches should be allowed in or around acid containers or lines.

Fire Fighting

In case of fire, use dry chemical or carbon dioxide extinguishing methods. Water can be used on combustibles burning in the vicinity of CSA but care must be exercised not to apply water directly to CSA to avoid rapid evolution of heat and violent spattering. Cool tank with water if exposed to fire, but do not get water into tank.

High pressure water fog or mechanical foam can also be used to keep tank cool if exposed to fire. Do not allow water or water containing foam to contact CSA in a confined area such as a tank because it may cause violent eruptions that could result in structural failure.

ENGINEERING CONTROL OF HAZARDS

Proper design of the storage and handling system from the point of delivery to the point of consumption is necessary to safeguard against the hazards of chlorosulfonic acid. Factors to consider in design include:

1. Location of storage tank relative to other chemicals and working areas.
2. A tight system which minimizes the chances of a leak.
3. Means of confining accidental leaks as well as proper drainage and cleanup of leaks consistent with plant and regulatory requirements.
4. Provision for more than one escape route in event of fire, explosion or accidental release of fumes.
5. Easily accessible safety showers, fire fighting and other emergency equipment such as foam generators and foam, fog nozzles, respiratory apparatus.
6. Provision for venting storage and unloading facilities to recovery or abatement facilities in order to prevent exceeding the allowable limits set by government (OSHA) pollution regulations (29 CFR 1910.1000 Air Contaminants) or safety standards for ground level concentrations.
7. Storage tanks should preferably not have operating bottom outlets. Sufficient corrosion allowance should be allowed to give long term life.
8. Storage and handling facilities should be equipped with appropriate alarms, interlocks, remote operated valves, emergency shut-down buttons and relief devices.
9. Storage tanks and piping should be inspected and tested for thickness on a periodic basis, annually or as required by local ordinances. It is recommended that an internal inspection be made at least every 5 years.
10. Unloading and transfer instructions should be written with particular emphasis on how to avoid spills. Check lists for unloaders, handlers and