

DIMETHYL SULFIDE

OVERVIEW

DMS



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Introduction

Dimethyl sulfide (DMS) is a low molecular weight, organosulfur compound that is produced industrially, while also being commonly found in nature. In fact, oceanic dimethyl sulfide is the dominant natural source for sulfur in the atmosphere (*Bates et al., 1992; Gondwe et al., 2003*). The low toxicity level of this compound is further exemplified by its use as a synthetic flavoring substance and adjuvant (*CFR 21§172.515*) in the United States.

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Physical and Chemical Properties

DMS synonyms: Methane, thiobis-; Methyl sulfide; Dimethyl monosulfide; Dimethyl thioether; DMS; Methyl Monosulfide; 2-Thiopropene; Dimethyl sulphide; Thiobismethane; (CH₃)₂S; Dimethylsulfide; Exact-S; Methyl sulphide; Methylthiomethane; Sulfure de methyle; 2-Thiopropene; UN 1164; Methylthioether; Thiopropene; Sulfide, methyl-; (Methylsulfanyl)methane

Autoignition Temperature (ASTM E 659): 206°C (403°F)

Boiling Point: 38°C (99°F)

Boiling Range (Anhydrous): 90% @37.1 +0.2° C

CAS Registry Number: 75-18-3

Coefficient of Expansion: 0.0013 ml/ml/°C.

Critical Pressure: 826 psia= 56.1 atm= 5.69 MN/sq m

[U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Manual Two. Washington, DC: U.S. Government Printing Office, Oct., 1978.]

Critical Temperature: 444 deg F= 229 deg C= 502 deg K Density/Specific Gravity: 0.847 (20°C) (water = 1)
Dielectric Constant: 12

Evaporation rate (n-butyl acetate = 1): »1.0

Flash Point (ASTM D-93, closed cup): -48° C (-54° F)

Flash Point (calculated): -34° C

Formula: C₂H₆S

Freezing Point: -98.3°C (-145°F)

Hansen Solubility Data:

Dispersion 16.1

Polar 6.4

Hydrogen Bonding 7.4

Heat of Combustion: 13,200 Btu/lb= 7340 cal/g= 457.3 K cal/mol= 307X10⁵ J/kg

[U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Manual Two. Washington, DC: U.S. Government Printing Office, Oct., 1978.]



Heat of Fusion: 30.73 cal/g

Heat of Vaporization: 194 Btu/lb= 108 cal/g= 4.52X10+5 J/kg

[U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Manual Two. Washington, DC: U.S. Government Printing Office, Oct., 1978.]

Henry' Law Constant: 1.61x10-3 atm cu-m/mol³ @ 25° C

[Gaffney JS et al; Environ Sci Technol 21: 519-23 (1987)]

Hydroxyl radical rate constant: 4.56x10-12 cu-cm/molc sec @ 25° C

[Atkinson R; Journal of Physical And Chemical Reference Data. Monograph No 1 (1989)]

Interfacial Tension, Liquid-Water: (est) 30 dynes/cm= 0.030 N/m @ 20° C; Ratio of Specific Heats of Vapor (Gas): 1.1277 @ 16°C

[U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Manual Two. Washington, DC: U.S. Government Printing Office, Oct., 1978]

IR: 6300 (Sadtler Research Laboratories Prism Collection)

[Weast, R.C. and M.J. Astle. CRC Handbook of Data on Organic Compounds. Volumes I and II. Boca Raton, FL: CRC Press Inc. 1985., p. V1 853]

Lower Explosive Limit: 2.2%

MASS: 10 (National Bureau of Standards EPA-NIH Mass Spectra Data Base, NSRDS-NBS-63)

[Weast, R.C. and M.J. Astle. CRC Handbook of Data on Organic Compounds. Volumes I and II. Boca Raton, FL: CRC Press Inc. 1985., p. V1 853]

Molar Volume: 73.2

Molecular Weight: 62.14

Octanol/Water Partition Coefficient: 0.92

Odor Threshold: less than 1 ppm

Odor: Unpleasant odor of wild radish or cabbage

[Fenaroli's Handbook of Flavor Ingredients. Volume 2. Edited, translated, and revised by T.E. Furia and N. Bellanca. 2nd ed. Cleveland: The Chemical Rubber Co., 1975., p. 406]

pH: not available



Physical form: Colorless Liquid

Refractive Index: 1.4355 @ 20° C/D; MAX ABSORPTION (ALCOHOL):
215 NM (LOG E= 3.0)

[Weast, R.C. (ed.). *Handbook of Chemistry and Physics*. 60th ed. Boca Raton, Florida: CRC Press Inc., 1979, p. C-505]

Solubility in Water: Max. 2% (w/v) @ 25° C

Specific Heat: @ 20° C Cp (Cal/gm/°C)=0.45

Sulfur Content: 51.5%

Surface Tension: 26.5 dynes/cm= 0.0265 N/m @ 11 deg C 23.33 dynes/cm @ 32. 9° C
19.87 dynes/cm@ 57.7° C

[U.S. Coast Guard, Department of Transportation. *CHRIS - Hazardous Chemical Data. Manual Two*. Washington, DC: U.S. Government Printing Office, Oct., 1978.]

Upper Explosive Limit: 19.7%

Vapor Density: 2.14 (Air= 1)

[Sax, N.I. *Dangerous Properties of Industrial Materials*. 5th ed. New York: Van Nostrand Rheinhold, 1979., p. 832]

Vapor Pressure @ 20° C (68° F): 530 mbar (398 mm Hg)

Vapor Pressure: 502 mm Hg @ 25° C , from experimentally-derived coefficients.

[Daubert, T.E., R.P. Danner. *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*. Washington, D.C.: Taylor and Francis, 1989.]

Viscosity at 25° C (68° F): 0.29 cps

Viscosity: Less than 32.6 Saybolt unit sec

[Clayton, G. D. and F. E. Clayton (eds.). *Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology*. 3rd ed. New York: John Wiley Sons, 1981-1982., p. 2065]

Water Soluble in DMS: Max. 0.4% (w/v) @ 25° C

Wt/vol conversion: 2.54 mg/cu m = 1 ppm

[Clayton, G. D. and F. E. Clayton (eds.). *Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology*. 3rd ed. New York: John Wiley Sons, 1981-1982., p. 2065]



Table 1 Azeotropes Formed with DMS	
Chemical	% DMS
Methanol	85
Methyl-propylether	65
Isoprene	35
2-methyl 2-butene	52
2-methyl butane	15
Pentane	45
Isopentane	15
Trimethylethylene	45

Table 2 Solvency Characteristics of DMS	
Dimethyl sulfide (DMS) is a nonpolar, stable, water-white organic solvent which is capable of dissolving a wide range of both organic and inorganic materials. In general, DMS will dissolve the following organic materials:	
Ethers	Amines
Esters	Monobasic organic acids
Alcohols	Rosins
Ketones	Polyisobutyl methacrylate
Aromatic hydrocarbons	Polystyrene
Aliphatic hydrocarbons	Polybutylene
Halogenated compounds	Polybutadiene

The following are not appreciably soluble in DMS:

- | | |
|--------------------------|-------------------|
| Aliphatic dibasic acids | Polyvinyl Acetate |
| Aromatic dibasic acids | Nylon |
| Polyethylene | Dimethyl Sulfone |
| Urea-formaldehyde resins | Sulfur |



Table 3
Solubility of Salts in Dimethyl Sulfide

(Unless otherwise noted, all determinations were made at 25° C)

Salt	Solubility, (grams per 100 grams DMS)
Aluminum chloride AlCl_3	>70 g
Aluminum chloride $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	Insoluble
Ammonium bifluoride $\text{NH}_4\text{F} \cdot \text{HF}$	Insoluble
Ammonium chloride NH_4Cl	Insoluble
Ammonium chromate $(\text{NH}_4)_2\text{CrO}_4$	Insoluble
Ammonium fluoride NH_4F	Insoluble
Ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Insoluble
Antimony trichloride SbCl_3	about 1200 g
Arsenic trichloride AsCl_3	miscible in all proportions.
Arsenic trioxide As_2O_3	Insoluble
Barium chloride $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	Insoluble
Bismuth nitrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	Insoluble
Bismuth oxychloride BiOCl	Insoluble
Bismuth trichloride BiCl_3	> 125 g
Cadmium chloride CdCl_2	0.24 g
Cadmium iodide CdI_2	42.3 g at 25° C; 47.4 g at 41° C
Calcium chloride CaCl_2	Insoluble
Chromic oxide Cr_2O_3	Insoluble
Chromium acetate $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 2\text{H}_2\text{O}$	Insoluble
Chromium Chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	Insoluble
Chromium fluoride $\text{CrF}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$	Insoluble
Cobalt acetate $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$	Insoluble
Cobalt chloride CoCl_2	2.1 g at 25° C ; 26.6 g at 50° C
Cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Insoluble
Cobaltic oxide Co_2O_3	Insoluble
Columbium pentachloride CbCl_5	very soluble (evolves heat)
Cupric acetate $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	< 0.5 g
Cupric bromide CuBr_2	>10 g
Cupric chloride $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	>20 g
Cupric sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Insoluble
Cuprous chloride Cu_2Cl_2	0.31 g



Cuprous fluoride Cu_2F_2	Insoluble
Salt	Solubility, (grams per 100 grams DMS)
Cuprous iodide Cu_2I_2	> 100 g
Ferric ammonium sulfate $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Insoluble
Ferric chloride FeCl_3	about 20-30 g at 25° C
Uranyl acetate $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	Insoluble
Vanadium pentoxide V_2O_5	Insoluble
Zinc bromide ZnBr_2	70.0 g at 25° C ; 203 g at 80° C
Zinc chloride ZnCl_2	about 105 g
Zinc cyanide $\text{Zn}(\text{Cn})_2$	Insoluble

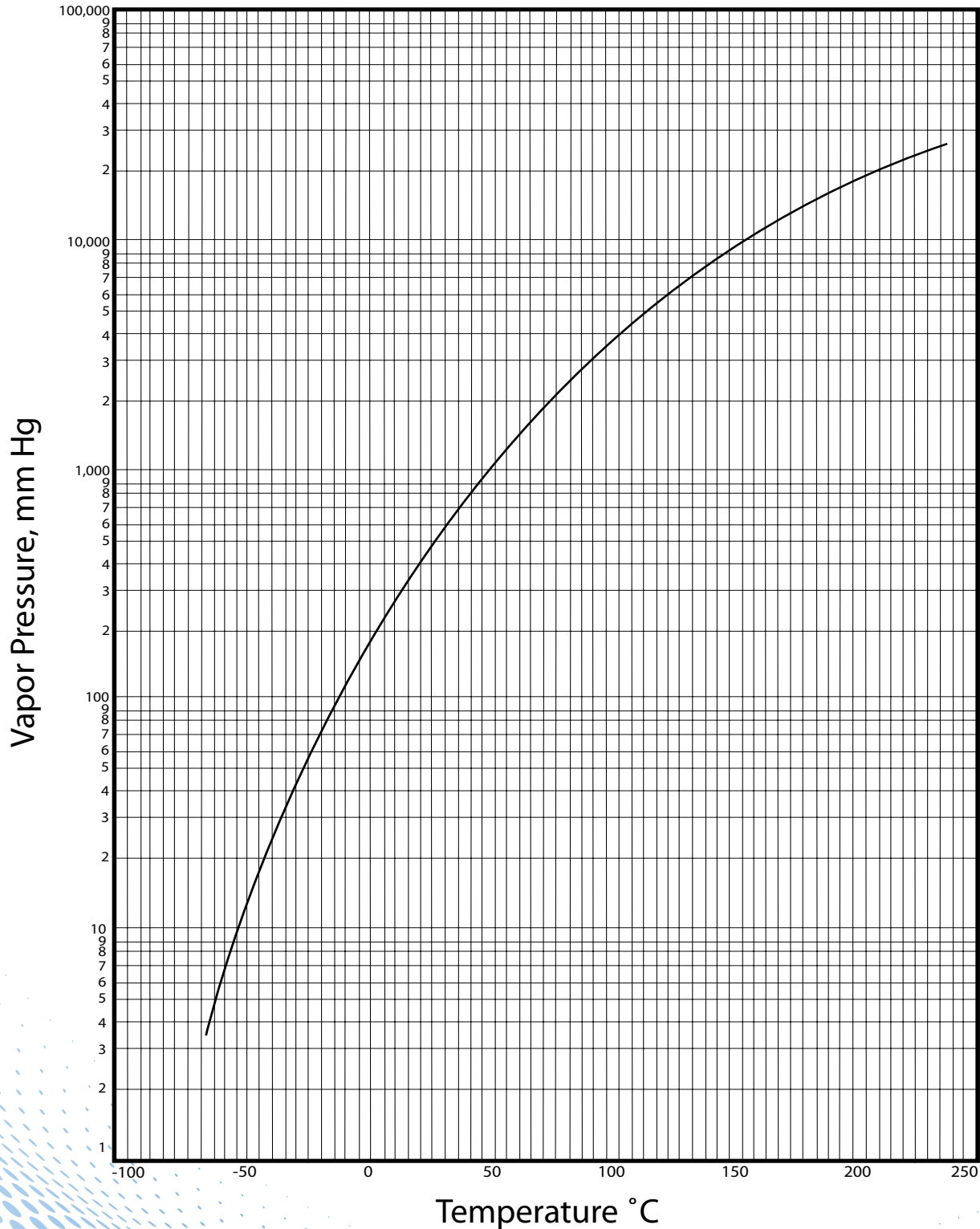
Generalizations pertaining to the solubilities of inorganic salts may be misleading and if at all possible, each specific compound should be checked for its solubility.

The halide, cyanide, and acetate salts of the metals occurring in the center of the periodic table tend to be soluble. Alkali and alkaline earth metal salts tend to be insoluble, as do most of the sulfates, carbonates, oxides, and hydrated salts. Some of the metal salts form complexes of varying degree of stability – cuprous cyanide forms a very stable complex, mercuric iodide a very easily decomposed complex.

Temperature, °C	Grams of Gas per 100 grams DMS					
	BF_3	BCl_3	HCl	NH_3	H_2S	SO_2
2	—	—	—	2.03	—	—
3	114.4	39.3	—	—	—	—
4	—	—	27.4	—	—	—
10	—	—	—	—	22.5	171.7
13	—	—	—	0.97	—	—
14	—	53.4	20.1	—	—	—
15	—	—	—	—	21.8	153
16	111.5	—	—	—	—	—
20	—	—	—	—	17.1	113
25	—	—	—	0.45	12.5	81.2
26	112.0	67.5	7.6	—	—	—



Figure 1
Vapor Pressure-Temperature





Applications for Dimethyl Sulfide

The solvency characteristics, odor, and chemical reactivity are the determining factors in the potential applications for dimethyl sulfide and its derivatives. Some of the possible applications are presented below.

Petrochemical Applications

Sulfidation Agent for Olefins Production

DMS is an essential additive in steamcracking operations. When used at trace levels, it serves to control carbon monoxide (CO) generation in the furnace. It also plays a role in managing coke formation rates, which determine furnace run lengths - and ultimately profitable plant operation. DMS is the most widely used sulfidation agent in North America. Gaylord Chemical manufactures a highly pure and consistent DMS product (Exact-S®). Exact-S® carefully controls the concentrations of impurities which are of concern to ethylene / propylene manufacturers- notably carbon disulfide.

Presulfiding of Catalysts

Gaylord Chemical manufactures DMS for use as a presulfiding agent for refinery catalysts. Dimethyl sulfide has proven to be an economical source for the organic sulfur required in hydrocracking catalysts. See bulletin 201 and *An Overview of Catalyst Sulfiding for more information.*

Ingredient in Gas Odorants

Dimethyl sulfide has a distinctive odor which is detectable in low concentrations. DMS finds use as an odorant in natural gas where it serves as a backup to mercaptan compounds. It is chemically and thermally stable and does not diminish in odor characteristics when exposed to black iron pipe and tanks. The physical properties of DMS make it easy to handle through common odorizing equipment. It boils at 37° C and is volatile enough at the concentrations required that it will not condense in transmission and distribution systems under normal operating temperatures and pressures. Dimethyl sulfide will not fractionate from liquid petroleum gas cylinders nor will it react with compressor oil to form gums, resins, and compounds with low odorizing values.

Fuel Additive

Ethylene oxide containing 1 wt. % dimethyl sulfide may be used as a monopropellant for rocket motors. The use of DMS prevents exhaust nozzle fouling and carbon deposition on the firing chamber surfaces.⁵

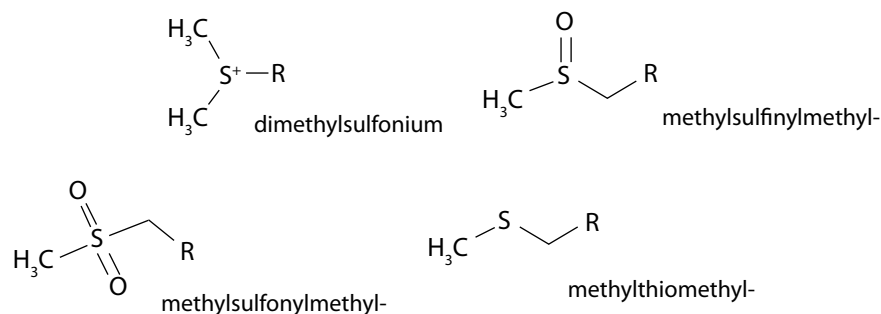
Extraction Solvent

Dimethyl sulfide, a simple thioether, has a distinct advantage as an extraction solvent in that it does not form dangerous peroxides. In addition, DMS has a low affinity for mineral acids and will not extract these from water solutions. The low water solubility of DMS is another important factor in its use as a replacement for ethers.

Use in Fine Chemical Synthesis

Chemical Reactant

DMS will undergo several types of reactions and may be used as a source / for the following reactive groups:



Additional details concerning these and other reactions are presented in Bulletin 203B, "Chemical Reactions of Dimethyl Sulfide."

Reaction Medium

Dimethyl sulfide is inert to most reaction components and has a wide range of solubilities for both organic and inorganic materials, including many gases. These characteristics are the basis for its use as a nonaqueous reaction medium. DMS is particularly useful for utilizing soluble gases since lower operating pressures are possible.

Preparation of Carbonyl Cyanide

Carbonyl cyanide can be prepared easily and safely by reacting tetracyanoethylene oxide with DMS. Additional information on this preparation will be found in Bulletin 203B, "Chemical Reactions of Dimethyl Sulfide".

Catalyst Modifications

The presence of DMS can alter the course of reaction in certain catalytic processes.

A. Selective Hydrogenation

Ethylene which is produced by pyrolysis of natural gas contains varying amounts of acetylene. For most uses of ethylene, the acetylene must be removed. Hydrogenation using a palladium catalyst has been used to accomplish acetylene removal, but this is always accompanied by undesired hydrogenation of ethylene to ethane. When DMS is added to the mixture, it has been found that the hydrogenation of ethylene is suppressed while that of acetylene proceeds normally. The DMS is not decomposed by the treatment and does not have a permanent effect on the catalyst.³



B. Diolefin Polymerization

Materials consisting of a combination of an organometallic reducing agent and a reducible compound of a heavy metal have been found to serve very well as catalysts for polymerization of diolefins such as butadiene and isoprene. The polymers so produced have a structure predominantly of the *cis*-1, 4 configuration. While these polymers are very useful for some purposes, for other applications it is desirable to produce polymers having *trans*-1, 4 configurations. It has been found that such polymers can be produced if the catalyst is modified by the addition of DMS. To insure the 1, 4 configuration, it is also necessary to use iodine either as part of the organometallic reducing agent or as part of the heavy metal reducible compound.⁴

Polymer

Ion Exchange Resins

Strong basic ion exchange resins have been prepared by chloromethylating bead form copolymers of styrene and divinyl benzene followed by reaction with dimethyl sulfide. Treatment with alkali produces a basic resin containing benzyldimethylsulfonium groups.

Modification of Nylon Fibers

A physical and chemical modification of nylon fibers and fabrics may be accomplished by immersion in a solution of DMS and zinc chloride. This treatment will delustre the fibers and make them more receptive to dyeing. It is also claimed that the fiber surfaces will have a higher coefficient of friction, a more rapid moisture pickup, and increased opacity.¹

Fiber Spinning

Polyvinyl chloride polymers can be dry spun or extruded after treatment with DMS and a ketone solvent. Aging of the polymer-solvent mixture produces a viscous solution which can be extruded directly into an atmosphere such that the solvent evaporates readily. Both DMS and the ketone solvent are necessary with their proportions determined by the K value of the polymer.²

Applications in the Life Sciences

Food and Beverage Component

Dimethyl Sulfide is present above its flavor threshold in most beers. Because of its low flavor threshold, 10 - 150 ppb, it is a primary flavor and aroma compound that makes a significant contribution to beer character, especially in lager beers. Other food applications include non-alcoholic beverages, ice cream, candy, baked goods, gelatins and puddings, and syrups. The use levels are in parts per million.



STORAGE AND HANDLING

Dimethyl sulfide is a highly flammable liquid with a flash point of -34°C and an autoignition temperature of 206°C . As a general rule, the same precautions should be employed in the handling of DMS as are used with diethyl ether. *See Bulletin 202B - DMS Bulk Trailer Unloading* for more detailed instructions on handling that specific packaging option.

As with any highly flammable material, DMS should be stored in tightly closed containers, in a cool place, and away from strong oxidizing agents or open flames. If operations are to be conducted in closed spaces, explosion-proof electrical switches and motors are suggested, such as will meet specifications of Class 1, Group C, Division 1 of the National Electrical Code. It is also suggested that consideration be given to maintaining an inert atmosphere in the head space when loading or unloading storage tanks or drums.

Drums must be grounded before the DMS can be transferred. Suitable methods include gravity flow or pressure unloading with an inert gas. For gravity unloading, piping may be of mild steel or even polyethylene tubing, again being sure that the drum and storage tank are properly grounded and electrically interconnected. With this method of unloading, air venting the drum should be satisfactory. In the event of pressure unloading, in no instance should air or oxygen be used for pressurizing. In current operations, nitrogen has proven very satisfactory for this type of handling.

Storage tanks must be suitable for flammable liquids and may be mild or stainless steel, or aluminum. Nozzles should be flanged and located on top of the tank or vessel whenever possible. Do not expose storage tanks to heat, sparks, or open flames.

Heating coils are not recommended; inadvertent use of heating coils could result in excess vapor generation and tank overpressure. Vents should be adequate to accommodate flow rates during unloading. Vapor controls such as conservation vents, relief valves, floating roofs, scrubbers, carbon absorbers or flares may be required for safety, environmental or odor control purposes. A nitrogen blanket is the preferred atmosphere. Unloading by nitrogen pressure is recommended. Pumping is satisfactory with an inert purge on the transferring vessel and the storage tank. *Never use air or oxygen for pressuring.*

Piping of mild or stainless steel; flanged construction is recommended for 2" and larger sizes with valves of mild steel, cast iron or stainless steel. Flanges in pipelines carrying DMS should be electrically jumpered so as not to rely on the bolts as conductors. The piping should be designed so that liquid velocities do not exceed 10 feet per second and the entry of DMS into tanks should be at the bottom through a dip tube to avoid static electricity. Do not allow DMS to fall through a vapor space.

Hose of stainless steel wire covering either a Teflon liner or a stainless steel bellows is preferred.

Couplings: Hose fittings should be non-sparking brass or aluminum; an Acme type screw on LPG type fitting is an option.



Gaskets and O-rings should be of Teflon[®], Gylon[®] PTFE, or Kalrez[®] or similar material. Glass- filled TFE and graphite-filled or TFE-filled spiral wound stainless steel gaskets may also be used for piping and equipment flanges.

Pumps may be mild steel or stainless steel with mechanical seals to avoid leaks.

Electrical equipment should be suitable for a Class I hazardous location (Article 500 of the National Electric Code). Specific installations determine whether Division 1 (normally hazardous) or Division 2 (potentially hazardous) location is indicated.

Bibliography

1. R. J. Herschler; U. S. Patent 3,023, 074, Feb. 27, 1962.
2. F. Siclari and A. Bellano; Italian Patent 508, 513, Jan. 10, 1955.
3. L. K. Frevel and L. J. Kressley; U. S. Patent 3,075,024, Jan. 22, 1963.
4. R. A. Stewart and E. Lasis; U. S. Patent 3,196,143, July 20, 1965.
5. H. B. Welirnan; U. S. Patent 3, 236, 046, Feb. 22, 1966.



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