

Dimethyl Sulfate

Properties, Uses, Storage, and Handling



The miracles of science™



NOTICE:

Dimethyl sulfate is an extremely hazardous liquid and vapor. May be fatal if inhaled. It causes severe burns to all body tissues. Lung injury and burns may be delayed. May cause cancer—based on tests with laboratory animals (see Personal Safety and First Aid on page 9 and the latest DuPont DMS Material Safety Data Sheet).

This bulletin is produced for the intent of providing general guidance in safety hazards and safeguards for dimethyl sulfate but does not presume to know all safety aspects of all potential processing conditions.

DuPont can assist qualified engineering/operations personnel in consultation regarding dimethyl sulfate safety with unloading/storage design, operation, first aid/medical treatment, and personal protective equipment issues.

The responsibility for dimethyl sulfate safe handling, operation, and processing rests ultimately with each customer.

This bulletin supersedes prior issues. Please replace all bulletins with this issue.

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Protection Agency, and the Food and Drug Administration, references herein to governmental requirements may be superseded.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 dimethyl sulfate.

Table of Contents

	Page
Product Information	1
Physical Properties	1
Chemical Properties	4
Product Stewardship	5
Regulatory Compliance	5
Uses	5
Commercial Applications	5
Methylation	6
Other Uses	8
Personal Safety and First Aid	9
Health Hazards	9
Vapor Exposure	9
Liquid Exposure	10
Safety Precautions	10
Personal Protective Equipment	10
First Aid	11
Site Facilities	12
Storage and Handling	12
Precautions in Use	12
Spills	13
Fire Hazards and Fire Fighting	13
Hazardous Chemical Reactions	13
Corrosion Hazards	14
Engineering Control of Hazards	14
Transportation Emergencies	15
Unloading and Transfer	16
Shipping Containers	16
Fittings	16
Wet Weather Recommendations	16
Portable Tanks	16
Bulk Shipments	18
Tank Cars	19
Tank Trucks	21
ISO Tanks	23
Equipment	24
Storage Tanks	24
Vent	24
Level	24
Meters	25
Hoses	25
Valves	25
Flanges	25
Piping	25
Bolts	25
Gaskets	25
O-rings	25
Pumps	25
Filters	26
Ventilation	26
Diking	26

(continued)

Table of Contents

	Page
Equipment Repairs	26
Valves and Piping	26
Tanks and Equipment	26
Waste Disposal	27
Analytical Method to Determine Dimethyl Sulfate in Air	27
Principle	27
Applicability	27
Limitations	27
Sensitivity, Precision, and Accuracy	28
Special Apparatus	28
Reagents	28
Special Safety Considerations	28
Procedure	28
Quality Control	30
Comments	30
References	30
Reference and Notes	31

Product Information

Dimethyl sulfate (DMS), CAS number 77-78-1, is a strong methylating agent used to make surfactants, fabric softeners, water treatment chemicals, pesticides, drugs, dyes, and photographic chemicals. Although used mainly for methylating, it can be used, under certain conditions, as a sulfonation agent, catalyst, solvent, and stabilizer (see "Uses," page 5).

Dimethyl sulfate, $(\text{CH}_3)_2\text{SO}_4$, is a clear, water-white liquid with a high boiling point and a high vapor density. This chemical is highly toxic and has no characteristic odor or warning property. Both the liquid and vapor cause severe burns to human tissue.

This bulletin provides general information to assist users in developing safe storage and handling procedures for dimethyl sulfate. This chemical requires extreme care in storage and handling. Although it is highly toxic, dimethyl sulfate can be handled safely if proper precautions are taken.

Do not handle or use dimethyl sulfate until you have read and understand the latest DuPont DMS Material Safety Data Sheet (MSDS).

The vapor pressure of dimethyl sulfate at 20°C (68°F) will give a saturated vapor concentration in air of 710 parts per million by volume. Higher temperatures will give correspondingly higher concentrations of vapor in air. Because of the toxic nature of dimethyl sulfate vapor, reactions should be carried out in closed equipment. Laboratory work should be done in ventilated hoods, and process areas should be outdoors or in well ventilated areas. The lack of distinct odor and water-like appearance of DMS makes spill detection difficult.

Physical Properties

Dimethyl sulfate dissolves in alcohol, ether, and benzene. It is slightly soluble in water (2.8 g/100 mL at 18°C [64.4°F]) and hydrolyzes to methyl sulfuric acid, then slowly to sulfuric acid and methanol at 18°C [64.4°F]) or above.

DuPont technical grade dimethyl sulfate meets specifications and has typical analyses as shown in **Table 1**. Additional physical properties are shown in **Table 2**. Density, vapor pressure, and viscosity are plotted against temperature in **Figures 1, 2, and 3**.

Table 1
Specifications and Typical Analyses

	Specifications	Typical Analyses*
Acidity (as H_2SO_4), wt%	0.20 max.	0.10
Assay, wt%	99.8 min.	99.9
Appearance	Clear	Pass

*This table gives typical analyses based on historical production performance. DuPont does not make any express or implied warranty that future production will demonstrate or continue to possess these typical analyses.

Table 2
Physical Properties of Pure Dimethyl Sulfate

Molecular weight	126.13
Boiling point, 760 mmHg (101.3 kPa), °C	188.8
°F	371.8
Freezing point, °C	-31.8
°F	-25.2
Specific gravity	
liquid, 20/20°C (68/68°F)	1.328
vapor, b.p. (air = 1)	4.35
Coefficient of cubical expansion	
(-18 to 38°C), av/°C	8.5×10^{-4}
(0 to 100°F), av/°F	4.7×10^{-4}
Refractive index, n_d^{20}	1.3874
Solubility in water,	
18°C (64.4°F), g/mL (mg/m ³)	0.028
Flash point (open cup), °C	116
°F	240
Flash point (closed cup) °C	83
°F	182
Autoignition temperature, °C	495
°F	923
Conductivity, µs/m	30
µ mho/cm	0.3
Critical pressure, MPa	4.88
atm	48.2
Critical temperature, °C	444
°F	830
Heat of combustion, kJ/mol	-1,509
kcal/mol	-360.6
Heat of vaporization	
25°C (77°F), kJ/mol	48.5
kcal/mol	11.6
Heat of formation (ΔH_f)	
25°C (77°F), J/mol	-735.1
kcal/mol	-175.7
Vapor density (air = 1)	4.35
Heat capacity (25°C [77°F]) Btu/lb °F, liquid	0.31
vapor	0.22

Figure 1. Density of Dimethyl Sulfate

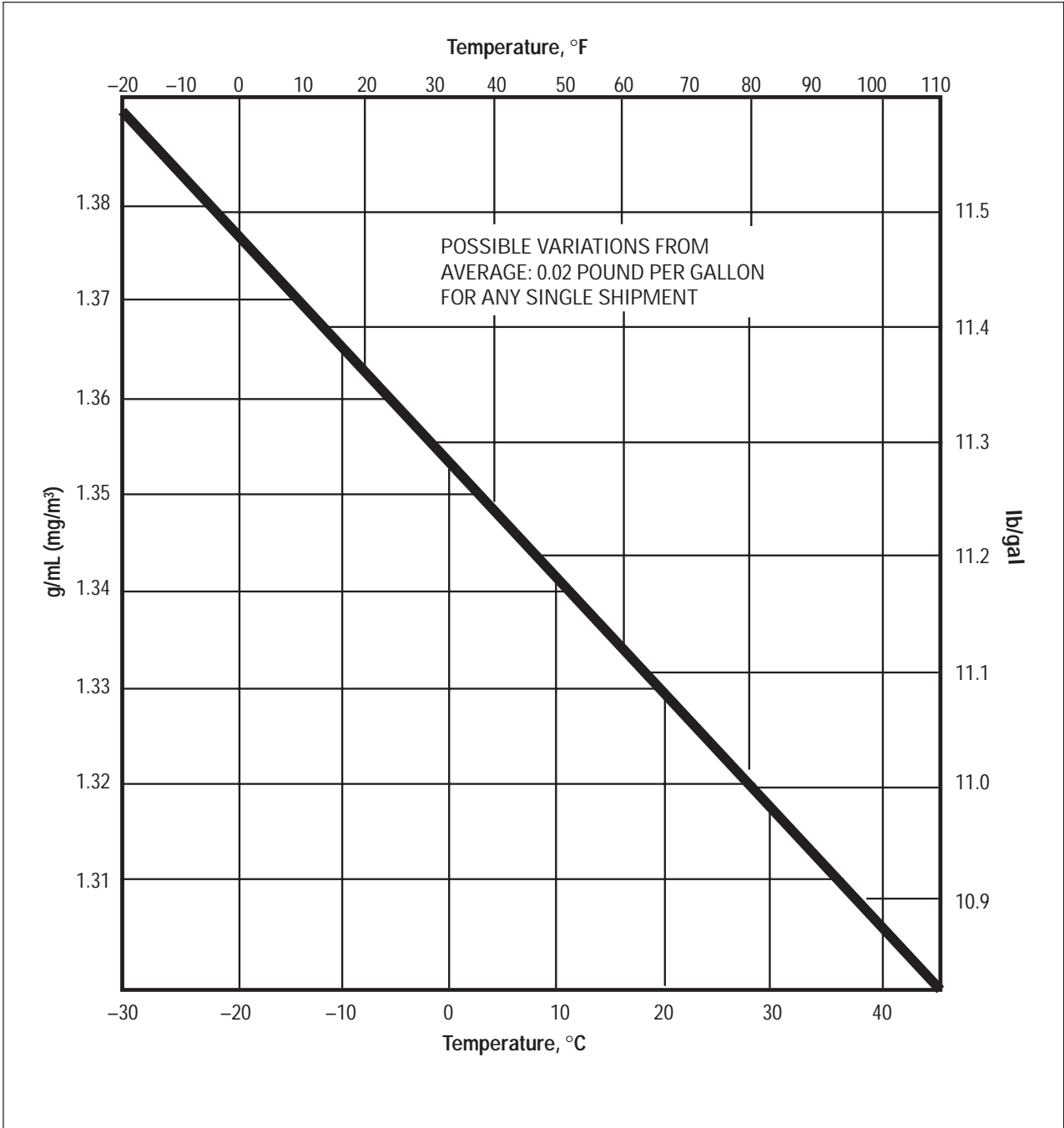


Figure 2. Vapor Pressure of Dimethyl Sulfate

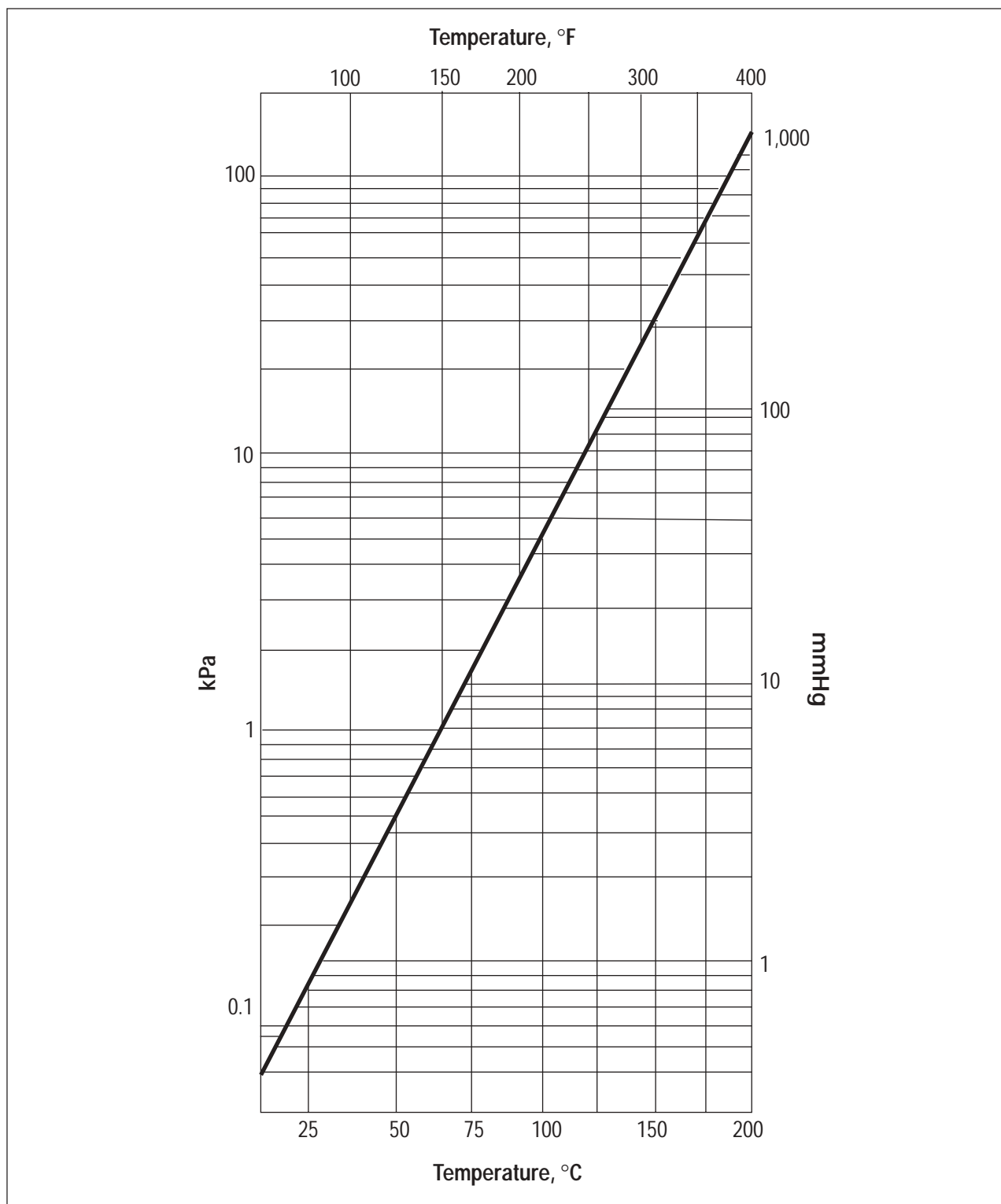


Figure 3. Viscosity of Dimethyl Sulfate

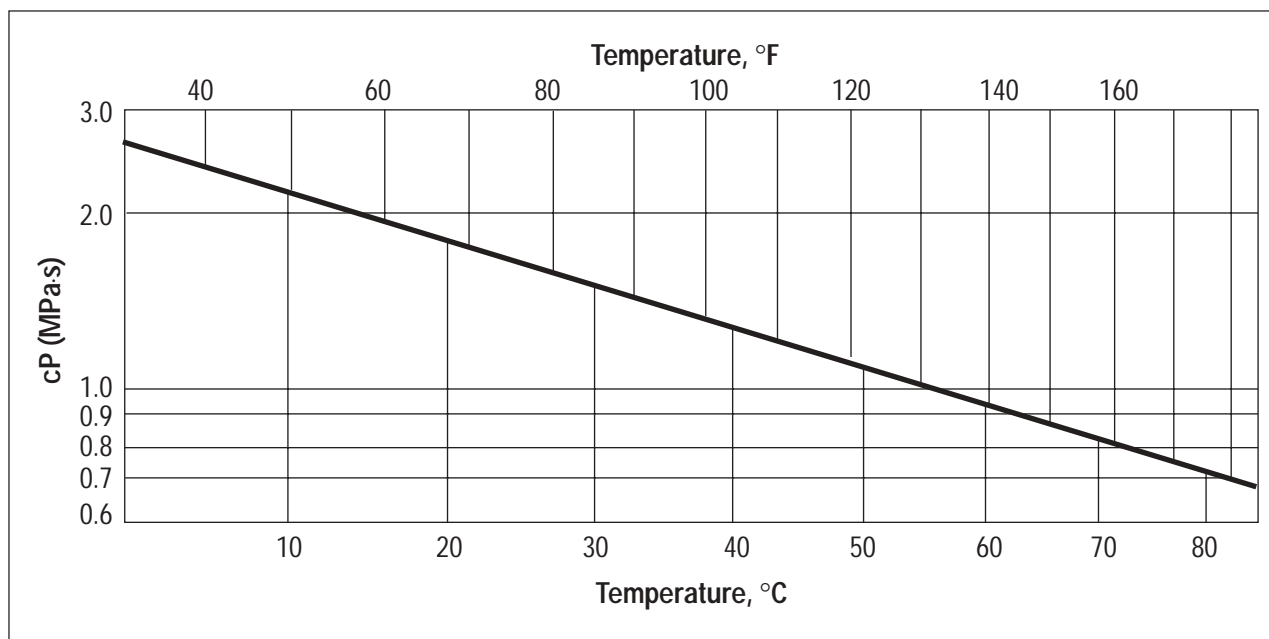
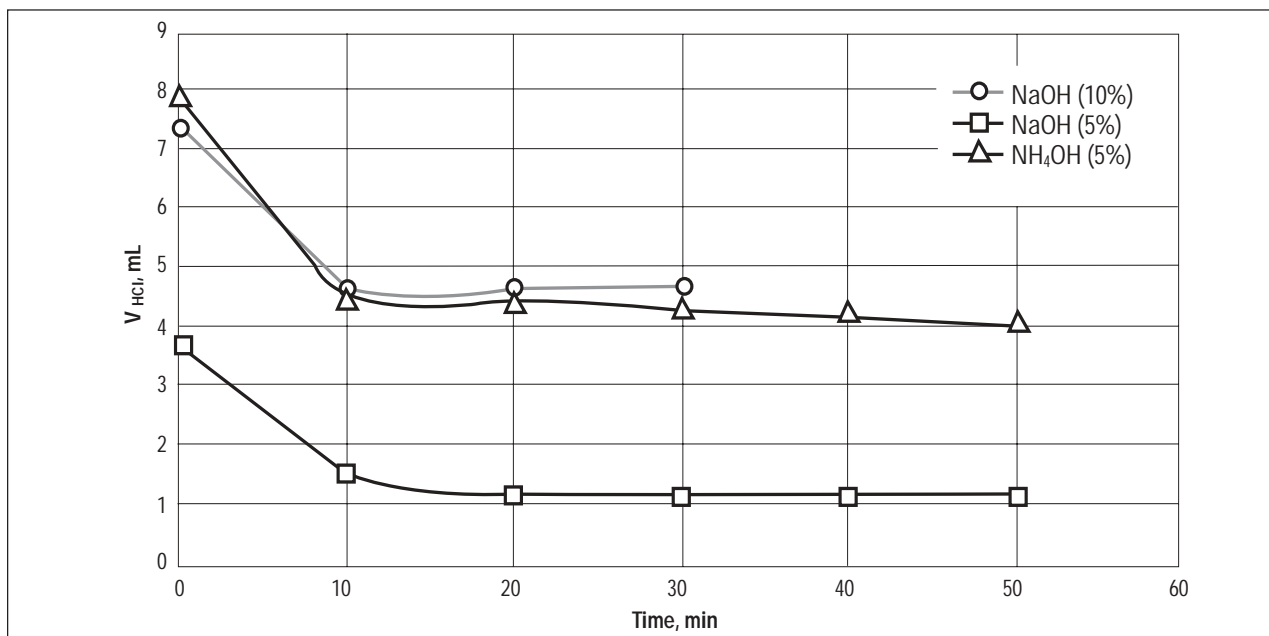


Figure 4. DMS Basic Hydrolysis (25°C [77°F])



Chemical Properties

Dimethyl sulfate hydrolyzes slowly in cold water but rapidly in warm water and acidic solutions. The hydrolysis occurs stepwise, initially forming methyl sulfuric acid, then sulfuric acid and methanol. It can be calculated that DMS hydrolyzes to methyl sulfuric acid with 99.9% completion as follows:¹

Temperature	Time
100°C (212°F)	45 sec
50°C (122°F)	20 min

Complete conversion to sulfuric acid occurs at a much slower rate. Salts of methyl sulfuric acid are formed when DMS is hydrolyzed in aqueous alkali (see **Figure 4**). Hydrolysis is rapid in aqueous ammonia. (Dilute ammonia solutions [less than 5%] are commonly used to neutralize spills and residues. Caution is necessary. Do not use concentrated aqueous ammonia. This can react with DMS with explosive violence.² Dry soda ash [Na₂CO₃] or dilute [less than 10%] caustic soda solution may also be used for neutralizing spills.) See “Spills” (page 13) for details.

Dimethyl sulfate is a strong methylating agent that reacts with active hydrogen and alkali metal salts to form substituted oxygen, nitrogen, and sulfur compounds. Usually, DMS releases only one methyl group to the reactant. Higher temperatures and concentrations are required for the second methyl group to react. Typical reactions include the preparation of tetramethyl glucosides from glucose, anisole ($C_6H_5OCH_3$) from phenol, N-methyl-p-aminophenol from p-aminophenol, and caffeine (1,3,7-trimethylxanthine) from theobromine (3,7-dimethylxanthine). Tertiary amines and DMS form quaternary ammonium compounds (see “Uses”).

Product Stewardship

DuPont fully endorses American Chemical Council’s Responsible Care® codes of Management Practices. We encourage customers to thoroughly review their safety management practices in the handling of dimethyl sulfate. In support of product stewardship, DuPont can assist in consultation on customer’s handling facilities, including unloading/storage design, personal protective equipment, first aid/medical treatment procedures, mitigation, and detection practices. For first-time dimethyl sulfate users, DuPont should be contacted before site selection has been made and/or facilities have been designed or built. DuPont personnel will visit customer sites before making the first shipment and periodically to survey unloading/handling facilities and make recommendations based on DuPont’s handling experience.

Regulatory Compliance

Dimethyl sulfate is included in the SARA Extremely Hazardous Substance, CERCLA Hazardous Material, and SARA Toxic Chemical lists. The use of dimethyl sulfate may require compliance with the above regulations; there may be additional federal, state, and local regulatory requirements.

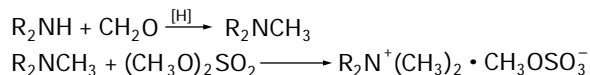
Uses

This section is divided into three parts. The first covers commercial applications of dimethyl sulfate. The second covers methylation reactions in general, as DMS is often used as a methylating agent in research laboratories; reactions were chosen to show the usefulness of DMS in chemical syntheses. The third section deals with uses other than methylation.

Commercial Applications

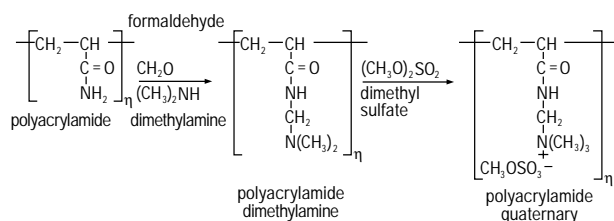
Quaternary Amines

Dimethyl sulfate is used to make quaternary fatty ammonium compounds used as surfactants and fabric softeners. An example is the quaternary salt in which R is hydrogenated tallow:



The monomethyl sulfate anion of the salt is preferred over other anions, such as chloride, because the sulfate is much less corrosive to laundry and water processing equipment. Dimethyl sulfate is preferred over methyl chloride as a methylating agent, because DMS reacts faster in higher yields and requires less costly processing equipment.

Methylated quaternary salts also serve as flocculants, which are used in water treatment, such as in sewage sludge control. An example is a quaternized Mannich base of low molecular weight polyacrylamides:³

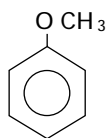


In actual practice, not all of the amide groups of the polyacrylamide are used in the Mannich reaction. The dimethylamine employed in the reaction is also a DuPont product. Information on it can be obtained by calling Product Information, 800-441-7515.

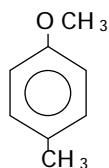


Ethers

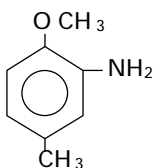
Dimethyl sulfate is used to make ethers, which in turn serve as intermediates to commercial products, such as pesticides, dyes, and fragrances. Examples of useful methyl ethers are anisole and anisole derivatives:



Anisole

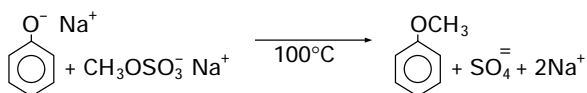
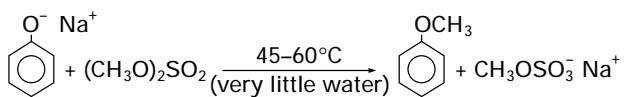


p-Methylanisole



p-Cresidine

The reaction of DMS with sodium phenolate illustrates ether synthesis.⁴ Because the phenolate ion is highly reactive in nucleophilic reactions, both methyl groups of DMS can be used:



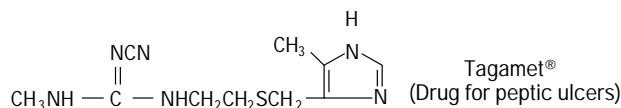
Anisole yields up to 95% can be achieved.



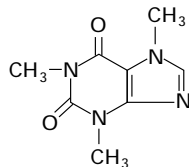
Other Products and Intermediates

Dimethyl sulfate is used to make a variety of products or intermediates to products through N-, O-, and S- alkylation reactions. These products are pharmaceuticals, agrichemicals, pesticides,

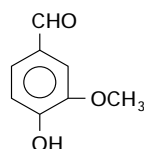
dyes, photographic chemicals, finishes, fragrances, and flavors. Examples are:



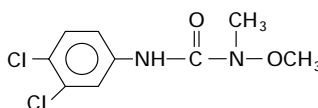
Tagamet®
(Drug for peptic ulcers)



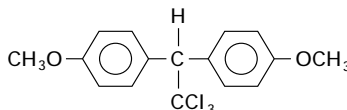
Caffeine



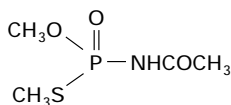
Vanillin



Linuron
(The active ingredient
in LOROX®, a herbicide)



Methoxychlor
(an insecticide)



Orthene® 5
(an insecticide)

Methylation

Because dimethyl sulfate is a strong methylating agent, it can be used to introduce a methyl group at the following reaction centers having unshared electron pairs:

- Oxygen
- Nitrogen
- Carbon
- Sulfur
- Phosphorus
- Some metals
- Heteroatoms from Groups VA and VIA

Usually a base is required, either (1) to make the reaction site more reactive, e.g., convert phenol to sodium phenolate before conversion to anisole, or (2) to neutralize the monomethyl sulfuric acid or sulfuric acid that is produced, e.g., in the methylation of aliphatic alcohols.

Usually, only one of the methyl groups of DMS reacts. For research purposes, there is no need to try to use both methyl groups. However, for commercial applications in which the reaction site is highly reactive, e.g., the sodium salt of mercaptans, it would be desirable to use both groups if possible. The chances of utilizing the second methyl group

are enhanced by employing higher reaction temperatures and by minimizing the competing reactions with water and the hydroxide ion. The competing reactions are reduced by using little or no water and by avoiding excess base. For example, base can be added as the reaction proceeds and only to the extent acid forms. Also, a reaction system of dimethylformamide/ K_2CO_3 and comparable non-aqueous solvent/base combinations can be substituted for water in many cases.

Based on rate of reaction and compared with alkyl halides, dimethyl sulfate is a much preferred alkylating agent. **Table 3** shows the relative alkylation rates with DMS and other agents in the reaction of the sodium salt of 2-methyl cyclohexanone:⁶

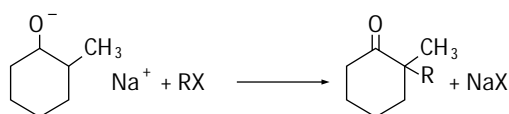
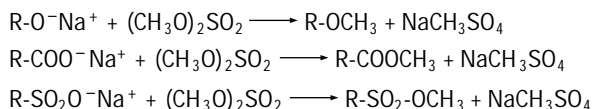


Table 3
Relative Rates of Alkylation

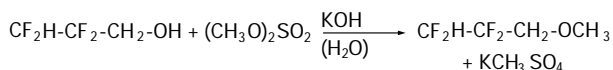
Alkylating Agent	
Butyl Bromide	1
Benzyl Chloride	17
Methyl Iodide	223
Methyl Benzene Sulfonate	970
Dimethyl Sulfate	13,300

Methylation on Oxygen

Where salts can be readily prepared, DMS methylates rapidly. Examples are:

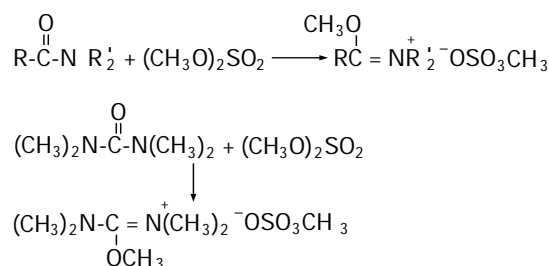


Alcohols can be methylated without first forming the alcoholate ion. An example is the synthesis of 2,2,3,3-tetrafluoropropyl methyl ether in 83% yield:⁷



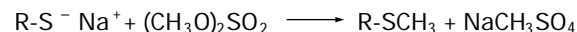
Another example is the methylation of cotton.⁸ A U.S. patent covers the methylation of substituted hydroxybenzenes in the absence of a solvent.⁹

Reaction of carboxamides gives imino ether salts:¹⁰

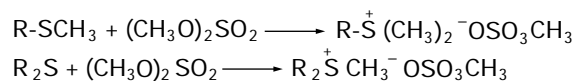


Methylation on Sulfur

Mercaptan salts are methylated rapidly with DMS:

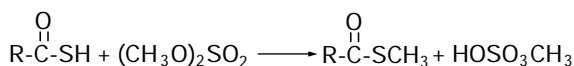


The thioethers are also reactive and can continue reaction to sulfonium salts:



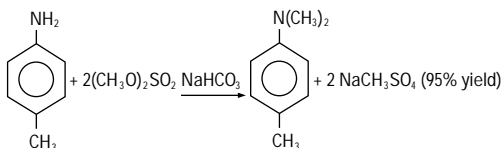
The reaction has been patented as a means of separating organosulfur compounds and fuel hydrocarbons, such as isooctane.¹¹

Another example of sulfur methylation is the preparation of thioacid esters:



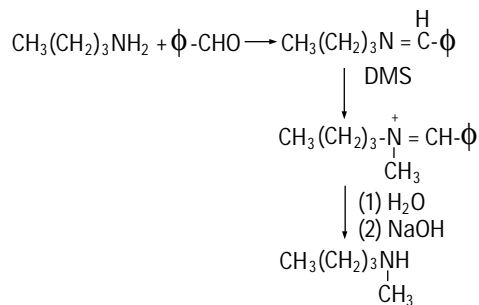
Methylation of Nitrogen

Alkylation of amines is usually employed to make tertiary amines or quaternary ammonium salts. An example is the synthesis of N, N-dimethyl-p-toluidine:¹²

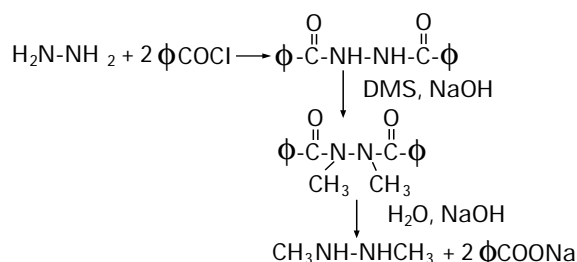


Syntheses of quaternary salts make amines more water soluble. For example, melamine resins that have been reacted with DMS are more soluble than untreated resins.¹³

It is not usually possible to stop a methylation of an amine at the monomethyl product, as it is more reactive with DMS than the starting material. Thus, blocking techniques are required when secondary amines are the desired product. The method is illustrated in the synthesis of butylmethylamine, where ϕ -CHO is benzaldehyde:¹⁴

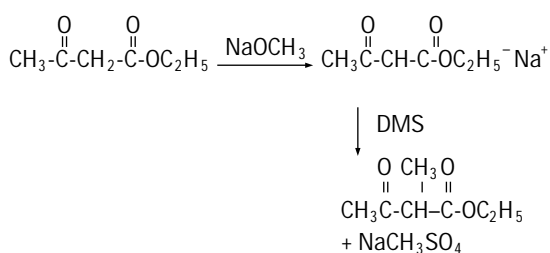


Sym-dimethylhydrazine can be synthesized from hydrazine by the method:¹⁵

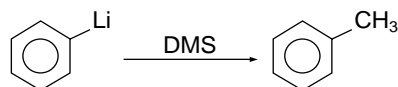


Methylation on Carbon

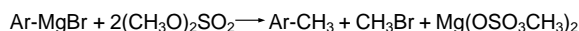
Active carbons can be methylated, as illustrated with ethyl acetoacetate:¹⁶



Also, C-methylation occurs on metallated hydrocarbons. An example is the conversion of phenyl lithium to toluene:¹⁷



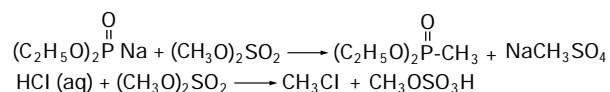
Another route is the use of Grignard derivatives:¹⁷



Aromatic hydrocarbons can be methylated by DMS in the presence of AlCl_3 in typical Friedel Crafts reaction.

Methylation of Inorganic Compounds

Many inorganic centers can be methylated, as in the following example:¹⁸



Other Uses

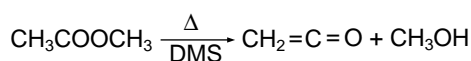
Sulfonation

Although dimethyl sulfate is mostly known as a methylating agent, it can also act as a sulfonating agent. Sulfonation will occur either by slow release of SO_3 by heating DMS or by attack at the sulfur end of the O-S bond.

Certain aromatic compounds that are highly reactive to electrophilic substitution can be sulfonated with DMS. Triphenylamine, diphenylmethanamine, anisole, and diphenyl ether give ring sulfonation on reaction with DMS at 150–190°C (302–374°F). Thallium (III) oxide or mercury (II) oxide catalyzes the DMS sulfonation of anthraquinone at 170°C (338°F).¹⁹ At 200°C (392°F), N-methyl-2-pyridones and related compounds sulfonate in the 5-position.²⁰

Catalyst

Some pyrolysis reactions are catalyzed by the presence of dimethyl sulfate. An example is the formation of ketene from methyl acetate:²¹



Also, 1,3-dihydroxypropene ether and acrolein acetals are produced by heating 1,1,3-trihydroxypropane ethers at 200–450°C (392–842°F) in the presence of DMS.²²

The alkylation of phenol with isobutylenes is promoted by the presence of catalytic amounts of DMS.²³ DMS mixed with titanium or vanadium halides acts as catalyst for the low temperature polymerization of olefins.²⁴ Telomers of ethylene and other polymerizable olefins are made by polymerization in the presence of DMS and a peroxide catalyst.²⁵ Also, a combination of certain tertiary amines and DMS is reported to initiate vinyl polymerization.²⁶

In some cases, the catalytic effect of DMS may be due to the slow release of sulfuric acid, either from hydrolysis or from heat. For example, DMS is a curing agent for furfuryl alcohol condensates, for which neutral DMS is considered a source of sulfuric acid when heated to 180°C (356°F).²⁷

Solvent

Some solvent uses of DMS have been reported. It has been used as a solvent in research on Lewis acid-aromatic hydrocarbon complexes.²⁸ DMS has been used as an electrolyte in electroplating iron.²⁹ It has served as an extraction solvent to separate phosphorus halide-hydrocarbon mixtures³⁰ and aromatic hydrocarbons from aliphatics.^{31,32}

Stabilizer

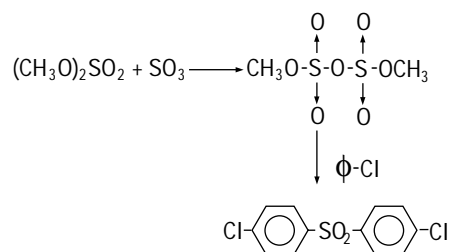
Dimethyl sulfate is reported to be a stabilizer against thiophosphate and thiophosphonate insecticides.^{33,34} Decomposition of DMS has been used with certain boron compounds to stabilize against polymerization of sulfur trioxide.³⁵

It was reported that ground wood pulp has better brightness stability when the pulp is first treated with DMS before bleaching.³⁶

Miscellaneous

As mentioned under "Catalyst," DMS can slowly release sulfuric acid. This property is useful in the separation of trivalent rare earths by a slow release into a solution of rare earth chelated with an ethylenediaminetetracetic acid and iodate anion. As the pH slowly decreases, each metal is released from the chelate in turn and precipitates as the iodate. The process yields better separations.³⁷

A mixture of DMS and SO₃ is thought to be dimethyl pyrosulfate. In reaction with chlorobenzene, 4,4-dichlorodiphenylsulfone is produced.^{38,39}



Personal Safety and First Aid

Health Hazards

In all operations involving DMS, all operating and maintenance personnel must be familiar with the potential hazards and safeguards needed to minimize the risk of injury or fume release. Personnel should be carefully trained and familiar with the latest DuPont DMS MSDS.

Dimethyl sulfate is extremely hazardous in both the liquid and vapor form because of its lack of warning properties, e.g., absence of odor, water-like appearance, and delayed biological effects. Effects may be delayed for 4 to more than 10 hr. DMS has an analgesic (numbing) effect on many body tissues; even severe exposures may not be immediately painful. Both forms are corrosive and cause burns and ulcerations of the skin, eyes, and mucous

membranes. On inhalation exposure, nose and throat irritation may occur with coughing, burning in the throat, and a choking sensation. DMS may be absorbed through the skin in sufficient amounts to cause systemic effects. Gross overexposure may cause death.

The International Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP) have listed DMS as a substance suspected or known to be carcinogenic. DuPont controls DMS as a potential carcinogen.

If exposed persons are not immediately and promptly treated, permanent eye or lung injury, or even death, may occur. Workers should be required to report promptly any exposure they encounter, in order to receive immediate first aid treatment, followed by medical attention as soon as possible. The effects of various types of exposure are summarized below.

Vapor Exposure

Effect of Vapor on Eyes

Dimethyl sulfate vapor may cause injury to the eyes and adjacent tissues that varies from slight irritation with tears to severe inflammation and edema of the eyelids and the eyeball. Irritation of the eyes may not be noted until several hours after exposure to low concentrations of the vapor. After the acute effects have subsided in severe cases, increased sensitivity to light, partial color blindness, and reduced visual acuity may persist.

An early symptom of overexposure to dimethyl sulfate vapor is a fiery red inflammation of the eyes (possibly accompanied by a delayed burning sensation). If this occurs, first aid should be given promptly, and appropriate preventive action should be taken to ascertain presence of possible leaks. Because of variation in individual susceptibility and possible delayed effects, these symptoms should not be relied on in lieu of other methods of monitoring air concentrations of DMS.

Effect of Inhaled Vapor

Dimethyl sulfate vapor is extremely irritating to all parts of the respiratory tract. This irritation may not be noted until several hours after exposure. Mild exposure leads to dry, painful cough, chest pain, and irritation of the nose and throat that may pass in 1 or 2 days, leaving only dryness of the throat. Moderate exposure causes reddening and swelling of the nasal mucous membranes and the vocal cords. The lungs and trachea are affected; there may be foamy, white sputum. With proper

treatment aimed at reducing cough, the patient may recover in a few days; otherwise, more serious injury to the lungs may follow. In 6 to 8 hours, severe exposures lead to great difficulty of breathing, with general malaise and fever as well as a rapidly developing inflammation and edema of the lungs. Severe exposures may be fatal.

Effect of Vapor on Skin

Skin exposure to high concentrations of the vapor may produce reddening and possible burns. In exposure to high vapor concentrations, dimethyl sulfate may penetrate the skin and produce systemic poisoning.

Liquid Exposure

Effect of Liquid on Eyes

Contact of liquid DMS with the eyes rapidly causes severe irritation of the eyes and eyelids. Unless the liquid is quickly removed by thorough irrigation with water, prolonged or permanent eye damage may result.

Effect of Liquid on Skin

Contact of liquid dimethyl sulfate with the skin produces initial reddening and possibly itching, followed by severe burns that may extend through the skin to the underlying tissues if the liquid is not rapidly removed. These burns may heal slowly. In lower concentrations, the corrosive action on the skin is accompanied by prolonged analgesia. Dimethyl sulfate may be absorbed through the skin, and absorption of large quantities may produce pulmonary effects, circulatory collapse, convulsions, and unconsciousness. The effects of dilute solutions may not appear for several hours.

Ingestion of Liquid

When swallowed, DMS causes severe irritation and damage to the esophagus and stomach. However, signs of injury to the digestive tract may be suppressed because of the analgesic action of dimethyl sulfate. The most prominent symptoms following ingestion are respiratory tract effects.

Safety Precautions

Do not get dimethyl sulfate in eyes, on skin, or on clothing. Do not breathe vapor; use only with adequate ventilation (see "Personal Protective Equipment.") Wash skin thoroughly after handling DMS and before eating or smoking.

Because of the health hazards of dimethyl sulfate as described above, two levels of analytical techniques should be used for air contamination. First, test kits,

such as the Dräger Multi-Gas Detector, can measure dimethyl sulfate in the air to approximately 0.005 ppm by volume. These kits are suitable for determining levels at which dimethyl sulfate poisoning may occur. The testing kits should be used routinely to spot leaks or spills that otherwise might go undetected. When positive results are obtained, immediate action should be taken to protect exposed employees (see "First Aid," p. 11).

Information about techniques for measuring personal air monitoring to 0.005 ppm, time-weighted average, are given under "Analytical Method" (page 27). This more sophisticated method is designed to monitor levels considered safe from possible chronic effects of long-term exposure to DMS.

Personal Protective Equipment

Personal protective equipment should protect the wearer in case of accidents. However, it is not a substitute for safe working conditions. The amount of protection necessary depends upon the degree of exposure during a particular task. Protective equipment should not be worn or carried beyond the operating area. After each use, the equipment should be thoroughly washed and tested for dimethyl sulfate contamination before storing.

All personnel should wear full protective clothing and air-supplied respiratory protection when unloading dimethyl sulfate shipping containers, when taking dimethyl sulfate samples, when opening equipment that may contain dimethyl sulfate, and when performing other similarly hazardous duties during which DMS vapor may be inhaled. A standby person equipped with similar protective equipment should be present to assist in an emergency.

Minor incidental contact with DMS is difficult to detect on protective equipment but has caused serious burns following equipment removal. Upon completion of an activity requiring a full protective suit, the person should rinse the suit under a safety shower. The standby person should then assist washing the suit with a brush and mild detergent solution prior to rinsing under the safety shower again. The suit should then be checked with a Dräger tube for presence of DMS before removing. Change gloves as necessary during protective equipment removal. Rewash suit, hood, and gloves. Don dry protective equipment if re-entry to the DMS area is necessary. Store all protective equipment in the DMS use area.

Equipment suggested for handling dimethyl sulfate is as follows:

- **Chemical Goggles**—Gas-tight goggles should be worn whenever there is even minimal danger of contact with dimethyl sulfate liquid or vapor. Face shields should also be worn when complete face protection is desirable.
- **Respiratory Protection**—Whenever atmospheric contamination by dimethyl sulfate vapor is possible, personnel should wear a self-contained breathing apparatus or air line mask.
- **Safety Hats**—A safety hat or a hat of nonabsorbent material should be worn to protect against the danger of overhead leaks.
- **Shoes**—Rubber shoes with safety caps or rubber boots (over safety shoes) should be used. Other materials such as leather will absorb DMS and should not be used.
- **Protective Suits**—Suits and hoods made of butyl rubber should be worn for hazardous duties. Coverall suits, hoods, and boots should always be available in the area for use in emergencies.
- **Gloves**—Gloves made of butyl or neoprene rubber should be worn whenever contact with dimethyl sulfate is possible. Plastic or rubber-coated fabric gloves should not be used when working with dimethyl sulfate, because the inside of the gloves might become contaminated; this contamination is difficult to remove and offers a possible hazard to the next user. Leather gloves should not be used because they absorb DMS and offer no protection. Gloves should be washed with soap and running water before removal.



DMS Personal Protective Equipment

First Aid

Speed in removing the patient from a contaminated atmosphere and in removing dimethyl sulfate from the skin or eyes is most important. To avoid serious injury, first aid must always be started immediately for contact with DMS in any form. For all affected persons, call a physician, even if there is no evidence of injury as effects can be delayed for more than 10 hr. Give the physician a detailed account of the accident.

First Aid for Vapor Exposure

Irritation by dimethyl sulfate may not be noted for several hours after exposure. Any worker exposed to dimethyl sulfate should be moved immediately to fresh air; call a physician.

The eyes should be flushed immediately with running water for at least 15 min. If oxygen is available with trained personnel to administer it, the patient should be given 100% oxygen (preferably exhaled against a positive pressure of not more than 6 cm [2-3/8 in] of water). Oxygen inhalation should be instituted, even if there are no signs of injury and should be carried on for 30 min of each hour for 6 hr.

If respiration is weak or fails, give artificial respiration or use oxygen inhalation through suitable equipment.

If excessive coughing due to the action of dimethyl sulfate upon the upper respiratory tract makes it difficult to use a mask, an oxygen tent should be used, giving the patient oxygen under atmospheric pressure.

Because the administration of oxygen should be continuous (1 hr maximum for continuous treatment with 100% oxygen),

a small portable oxygen tank plus mask should be available for use during transfer of a patient from the plant to a hospital.

Caution

It may not be advisable to administer oxygen under positive pressure in the presence of impending or existing cardiovascular failure.

First Aid for Exposure to Liquid

Remember that the action of dimethyl sulfate on the skin or eyes may be delayed for several hours after contact. First aid must be instituted as quickly as possible after contact. Flush the eyes with running water for at least 15 min. Remove all contaminated clothing immediately, including shoes. Destroy shoes. Wash contaminated clothing before reuse. Wash DMS off the skin under a shower with plenty of cool water for at least 15 min. Treat the affected areas at once with an ice water pack. Avoid freezing the skin. A solution of three parts rubbing alcohol to one part water may help relieve pain and the severity of the burn.

First Aid for Eye Contact

If liquid dimethyl sulfate has entered the eyes or if they have been exposed to strong concentrations of the vapor, they should be flushed immediately with plenty of water for at least 15 min. The eyes should be held open during the irrigation to ensure contact of water with all the tissues of the surface of the eye and lids.

Promptly call a physician, preferably an eye specialist. If a physician is not immediately available, the eye irrigation should be continued for a second period of 15 min. No oils or oily ointments should be instilled, unless ordered by the physician.

First Aid for Ingestion

Ingestion of dimethyl sulfate is unlikely in industrial uses; however, should it occur, the following first aid measures should be undertaken. Dilute the DMS immediately by giving large quantities of milk of magnesia, aluminum hydroxide gel, milk or water to drink; beaten eggs may be given as a demulcent. Do not give a solution of baking soda. Contact a physician. **DO NOT INDUCE VOMITING. NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON.**

Suggestions to Physicians

There is no specific antidote for the treatment of dimethyl sulfate intoxication. Effective treatments include the following:

- Administration of oxygen
- Nebulized bronchial dilator such as isoproterenol or epinephrine for bronchial spasm
- In the more severe cases, intravenous hydrocortisone followed by oral steroid therapy such as prednisone for several days
- Broad spectrum antibiotics if superimposed bacterial pneumonia is suspected
- Nebulized nonirritant bronchial detergents to moisten the bronchial mucosa and increase mucous secretion
- Tracheotomy as indicated

Because of the risk of delayed occurrence of pulmonary edema, the importance of careful observation of a patient thought to have inhaled dimethyl sulfate vapor cannot be overemphasized. The effects of dimethyl sulfate exposure could appear more than 10 hr after exposure.

Site Facilities

At loading stations and storage and handling areas, the following safety equipment should be easily accessible:

- **Safety Showers**—Freeze-proof water should be supplied to the shower by a 2-in line (minimum pressure 30 psig) through a quick-opening valve that stays open. Both the valve (actuated by a handle at hip level) and a 0.25-in deep hole directly above the valve should be located below the frost line and surrounded by crushed rock or gravel to provide drainage. If the valve is located above the frost line, it should be electrically traced and insulated. Shower locations should be appropriately identified by lights and/or signs, and access to the showers must not be obstructed in any manner. Safety showers should be tested on a periodic recorded basis.
- **Water Hydrant and Hose**—Provide a water monitor or some means of spraying water fog onto a dimethyl sulfate spill.
- **Eye Wash Stations**—Each station should provide a means of gently irrigating the eye with a constant, controllable stream of cool water. It should be close to a safety shower or part of the shower system. The station should be self-draining to ensure operability in subfreezing weather.
- **Fire Extinguishers**—Provide a carbon dioxide or dry chemical fire extinguisher for small fires. For large fires, use alcohol-resistant foam plus water spray or fog.
- **Neutralizing Solution**—Dilute caustic or ammonia aqueous solution to neutralize spills or decontaminate equipment.

Storage and Handling

Precautions in Use

All employees should be instructed in the handling hazards of DMS and the precautions that must be employed to handle dimethyl sulfate safely.

Areas where DMS is used should be clearly identified, and entry to these areas should be limited to operating personnel and authorized persons.

All persons entering the area should wear personal protective equipment (see “Personal Protective Equipment” [page 10]). Minimal protection should include eye protection, head covering, and rubber gloves. As the degree of exposure increases, depending on the task to be performed, full rubber suits and self-contained breathing apparatus may be required.

Safety equipment should be readily accessible for emergency use. Keep areas around safety showers, fire extinguishers, personal protective equipment, and stairways open and clear at all times.

Adequate ventilation should be provided in working rooms. Ventilation should ensure a substantial air flow away from all work areas. Ventilating equipment should be designed to handle the heavy dimethyl sulfate vapor.

It is important to know that air concentrations are below allowable levels, both in routine operation and in suspect conditions. The concentration of DMS in air can be measured by various techniques, as described under “Safety Precautions” (page 10) and “Analytical Method” (page 27).

No wooden ladders, wooden sample carriers, or other wooden equipment should be permitted in the area. All tools in contact with dimethyl sulfate must be decontaminated by immersion in dilute (2–5%) caustic, soda ash, or ammonia solution.

The use of absorbent materials such as rags, paper, and wood in handling or using dimethyl sulfate should be prevented. If such material is contaminated with dimethyl sulfate, it must be decontaminated with caustic, soda ash, or ammonia solution, followed by washing and then disposed of as hazardous waste.

Because dimethyl sulfate contaminated with moisture will hydrolyze to methyl sulfuric acid and then eventually to sulfuric acid and methanol, it must be stored in closed containers or blanketed with an atmosphere of dry air or nitrogen at all times. Small quantities should be stored in tightly closed, properly labeled containers. Glass bottles should be used only for in-plant samples suitably protected in secondary containers. They should be carefully identified, carried in a sturdy metal carrier, and should not be left unattended, unless in a specially identified metal container surrounded by a layer of soda ash. Keep containers of dimethyl sulfate out of the sun and away from heat.

Spills

Dimethyl sulfate’s absence of odor and water-like appearance may cause a spill to go unnoticed. If any water-like liquid is visible, assume a leak or spill has occurred and test for the presence of DMS using a tester kit. Proper personal protective equipment should be worn when performing the test.

Spills of dimethyl sulfate should not be left unattended. They should be contained, and runoff to sewers avoided. Minor spills should be flooded with water to dilute and hydrolyze the dimethyl sulfate. The area should be covered with dilute (less than 10%) caustic soda solution or dilute (less than 5%) ammonia solution. Soda ash may also be sprinkled over the surface if wetted with a gentle spray of water. The neutralizing agent should remain on the affected area for 24 hr (final neutralization is slow) and then washed away. Only personnel wearing protective equipment should perform these operations.

Comply with federal, state, and local regulations on reporting releases.

Fire Hazards and Fire Fighting

Dimethyl sulfate is an OSHA Class III A combustible liquid. Every precaution should be taken to prevent exposure of DMS to heat, open flames, sparks and other sources of ignition. Electrically ground all equipment. Follow applicable National Fire Protection Association Codes and OSHA Title 29 CFR 1910.106 for regulations on storing and handling flammable and combustible materials.

In fighting fires involving dimethyl sulfate, water spray may be used to blanket the fire and to cool other tanks and equipment containing DMS. Foam, carbon dioxide, or dry chemical is also effective. When fighting such a fire, all personnel must be upwind of the fire. Flammable, toxic vapor will be given off at the elevated temperatures that may be encountered in a fire. Firefighters should wear self-contained breathing apparatus and full protective clothing as discussed under “Personal Protective Equipment” (page 10).

Hazardous Chemical Reactions

Dimethyl sulfate and concentrated aqueous ammonia react with extreme violence.²

In the preparation of methyl azide, dimethyl sulfate reacts with sodium azide with explosive violence. Hydrazoic acid, which forms below pH 5, is a powerful explosive.⁴⁰

Corrosion Hazards

Dimethyl sulfate is inert to iron and steel and mildly corrosive to copper, brass, and copper alloys. Steel is normally considered the material of choice for storage and handling of dry dimethyl sulfate. When iron content of DMS is critical, stainless steels of the 300 series are used. DMS is hydrolyzed by water to produce methanol and sulfuric acid. Therefore, unless moisture or water vapor is excluded from the system, dimethyl sulfate will exhibit corrosion characteristics similar to those of sulfuric acid.

Because DMS has some solvent-type properties, the use of plastic materials, coatings, and other non-metals is not recommended.

Engineering Control of Hazards

Proper design of storage and handling systems from point of delivery to point of consumption and proper operating and maintenance procedures are essential to safeguard against serious incidents.

Design factors to consider include:

- A tight system that minimizes plant and community exposure potential.
- Location of storage tank and unloading spot(s) relative to other chemicals and working areas. Dimethyl sulfate is combustible and should be stored and used in areas protected from flames, sparks, and excessive heat. Plants handling dimethyl sulfate should preferably be located away from densely populated areas or major highways.
- Means of confining accidental leaks, a proper drainage system, and a spill and leak cleanup procedure that is consistent with plant and regulatory agency requirements.
- Provision for more than one escape route in the event of fire or release of dimethyl sulfate fumes.
- Readily accessible safety showers, eye wash stations, breathing air supply, evacuation alarms, public address systems, and other emergency equipment such as fire hydrants, fog nozzles, and monitors.
- Means of detecting dimethyl sulfate leaks while they are still small through the use of detector kits.
- Lines, tanks, and equipment that have been opened to the air must be purged with nitrogen or dry air before use in dimethyl sulfate service.
- Storage tanks and equipment must be electrically grounded.
- Tank vents should be equipped with suitable flame arrestors. Fill pipes should extend to within 6 in of tank bottoms.
- Electrical equipment, wiring, and fixtures must meet the requirements of National Electrical Code, Article 500.
- OSHA regulations pertaining to storage and handling of flammable and combustible liquids are given in 29 CFR 1910.106. Similar requirements are given in NFPA 30 from the National Fire Protection Association.
- Vents and pressure relief devices must be designed to handle pressure limitations and volumes of vapor that could be expected in emergency fire conditions.
- The process and storage tank vents should be located so that hazardous vapors given off during fires or emergency conditions will not harm personnel or increase the fire hazard.
- Suitable scrubbing facilities for venting/evacuating unloading, storage, and handling facilities.
- Provisions should be made to allow deinventory of dimethyl sulfate equipment/storage to other vessels in the event of leaks.
- The number of nozzles on the storage tank should be minimized. Top outlets are preferred to avoid leaks. The outlet nozzle should be of heavy-duty construction with a remotely actuated valve mounted directly to the nozzle.
- Appropriate, remotely operated actuated valves should be installed to allow isolation of equipment in the event of a dimethyl sulfate leak. Installation of an excess flow valve should be considered.
- Avoid using small diameter piping (less than 1 in), except for fit-up to instruments, because small diameter piping is not mechanically very strong. A small line can break if hit by another object.
- Adequate lighting and appropriate alarms and interlocks. Redundant systems should be provided for critical alarms, interlocks, and level measurements.
- Piping systems should be sloped and provisions made for blowing the line clear with nitrogen. Screwed fittings should not be used except for fit-up to instruments.
- Means of isolating tank car or tank truck with remote-controlled block valves in the event of a hose failure. Motion detectors for the tank car or truck should also be installed to shut down the unloading operation if the cargo tank is inadvertently moved while hooked up.

- Depending on site-specific considerations, such as proximity to the community, consider providing water monitors (manual or remote-controlled) and water curtains to allow mitigation of dimethyl sulfate in an emergency situation.
- Flange guards should be installed to avoid spraying DMS if a leak occurs. Flange guards that change to a bright color in the presence of an acid are commercially available.

Operating and maintenance factors to consider include:

- Inspection and thickness testing of equipment and piping on a periodic basis, at least every 2 yr or as determined by previous inspection history. Up-to-date isometric dimethyl sulfate piping drawings, with testing points, should be used to correlate test data to equipment in the plant. Particular attention should be paid to high-temperature and high-velocity areas.
- Internal inspections of dimethyl sulfate storage and process vessels should be made periodically. New vessels should be inspected after 5 yr of service. The frequency of inspections will depend on previous inspection history and the type of steel of which the tank is made, generally every 5 yr for older vessels and every 7–10 yr for newer vessels. Due to the highly toxic nature of DMS, internal inspections are usually made from outside the tank. Acoustic emission (AE) testing of storage tanks can be used to pinpoint potential problem areas that can be examined more closely.
- Regular inspection and periodic replacement (annually) of unloading hoses.
- Inspection and testing of the electrical grounding system with a megmeter to ensure overall resistance of the system to ground is less than 10 ohms.
- Clearly written unloading, storage, and handling instructions, including checklists to ensure that correct procedures are followed so that spills are avoided.
- Material of construction verification for critical equipment (valves, bolts, etc.), whose failure could cause a major spill.
- Regular inspection and/or testing of alarms, interlocks, pressure relief valves, and rupture disks.
- An administrative system that ensures equipment inspections are completed and results are documented.
- Conducting periodic process hazards reviewed, which closely examine procedures, equipment layout, past incidents, etc., and make changes to improve equipment reliability and personnel safety.

- Labeling of lines and equipment that contain dimethyl sulfate.
- Thorough training and regular retraining of personnel in the important aspects of handling dimethyl sulfate. These include:
 - use of personal protective equipment
 - hazards resulting from improper handling of DMS
 - prevention and detection of leaks
 - maintenance procedures, including equipment decontamination
 - emergency procedures
 - cleanup procedures
 - first aid and medical treatment procedures
- Performing a consequence analysis of credible and worst-case incidents; model vapor cloud effects on the surrounding community. Some locations may want to complete a quantitative risk assessment (QRA) to help determine the ranking of hazard/risk reduction programs.

Transportation Emergencies

If a shipment of DuPont DMS is involved in an accident or emergency anywhere in the continental United States, make a toll-free telephone call to the American Chemical Council Chemical Transportation Emergency Center (CHEMTREC) in Washington, DC:

800-424-9300

The information specialist on duty will ask the name and location of the caller, the name of the shipper, the product, the shipping point and destination, what happened, the nature of any injuries, weather conditions, proximity to populated areas, etc. The specialist will then give the caller recommendations for controlling the emergency situation until the shipper's specialist can relay help. CHEMTREC will immediately advise DuPont of the emergency, and one of our specialists will contact the caller promptly.

In Canada, call:

DuPont Canada, Inc.
Maitland, Ontario
(613) 348-3616

In Mexico, call:

DuPont Mexico S.A. de C.V.
Mexico City, MX
55-5722-1000

Unloading and Transfer

Shipping Containers

DuPont ships dimethyl sulfate in portable tanks, tank trucks, tank cars, and ISO containers. The U.S. Department of Transportation (DOT) classifies DMS as a 6.1 (Poison) with a secondary hazard of 8 (Corrosive). Shipping papers must also designate DMS as a Poison Inhalation Hazard, Hazard Zone B. All containers must be marked as prescribed by DOT regulations.

Fittings

Tank trucks are normally unloaded at the rear bumper using the 2 in, 150 lb flanges for both the liquid and vapor return fittings. Tank cars use 1000 lb Weco fittings (Figure 206 in catalog), 1½ in for liquid and 1 in for vapor, available from FMC Corporation, (281) 591-4000. ISO tanks use 2000 lb Huber Yale fittings, 1½ in for liquid and 1 in for vapor, available from Sturm Engineering, (304) 736-3476. Portable tanks use 4,000 lb Huber Yale fittings, both 1 in, available from R&M Energy Systems, (800) 858-4158.

Caution

When unloading containers of DMS, a full chemical-proof suit with hood and breathing air supply should be worn (see “Personal Protective Equipment” [page 10]).

Wet Weather Recommendations

DuPont recommends that DMS be unloaded from cargo tanks under dry weather conditions. The chance of a serious, accidental exposure to DMS increases significantly in wet weather. Special precautions are necessary when rain, snow, or ice conditions prevail or when there is enough wetness to make DMS leakage difficult to distinguish.

If unloading cannot be deferred until dry weather conditions prevail, a weather cover should be provided over the unloading area, specifically the connections and unloading hose, so that DMS leaks can be detected.



DMS Portable Tank



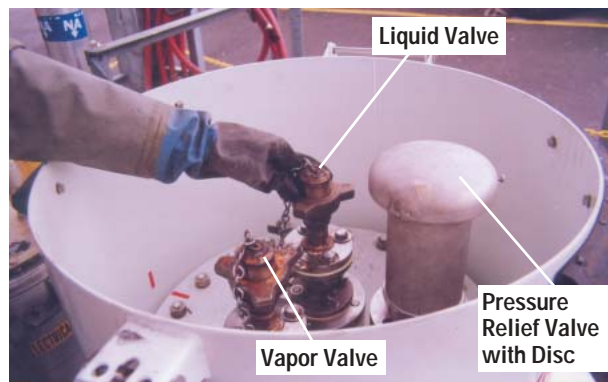
DMS Portable Tank and Special Flatbed Truck

The unloading area should be curbed or sloped so that drainage water that could contain DMS can be collected and neutralized with dilute alkali or ammonia solution.

The unloading operation should be closely monitored by customer supervision to ensure that any leakage is detected and any contaminated drainage water is properly neutralized.

Portable Tanks

DuPont ships dimethyl sulfate in DOT 51, IMO type 1 returnable stainless steel portable tanks. The tanks contain up to 2,200 lb (net) DMS and have a tare weight of 1,800 lb. The tanks are equipped with a 1-in liquid fitting, a 1-in vapor return fitting, and a combination rupture disc/relief valve assembly set for 160 psi (see **Figure 5**).

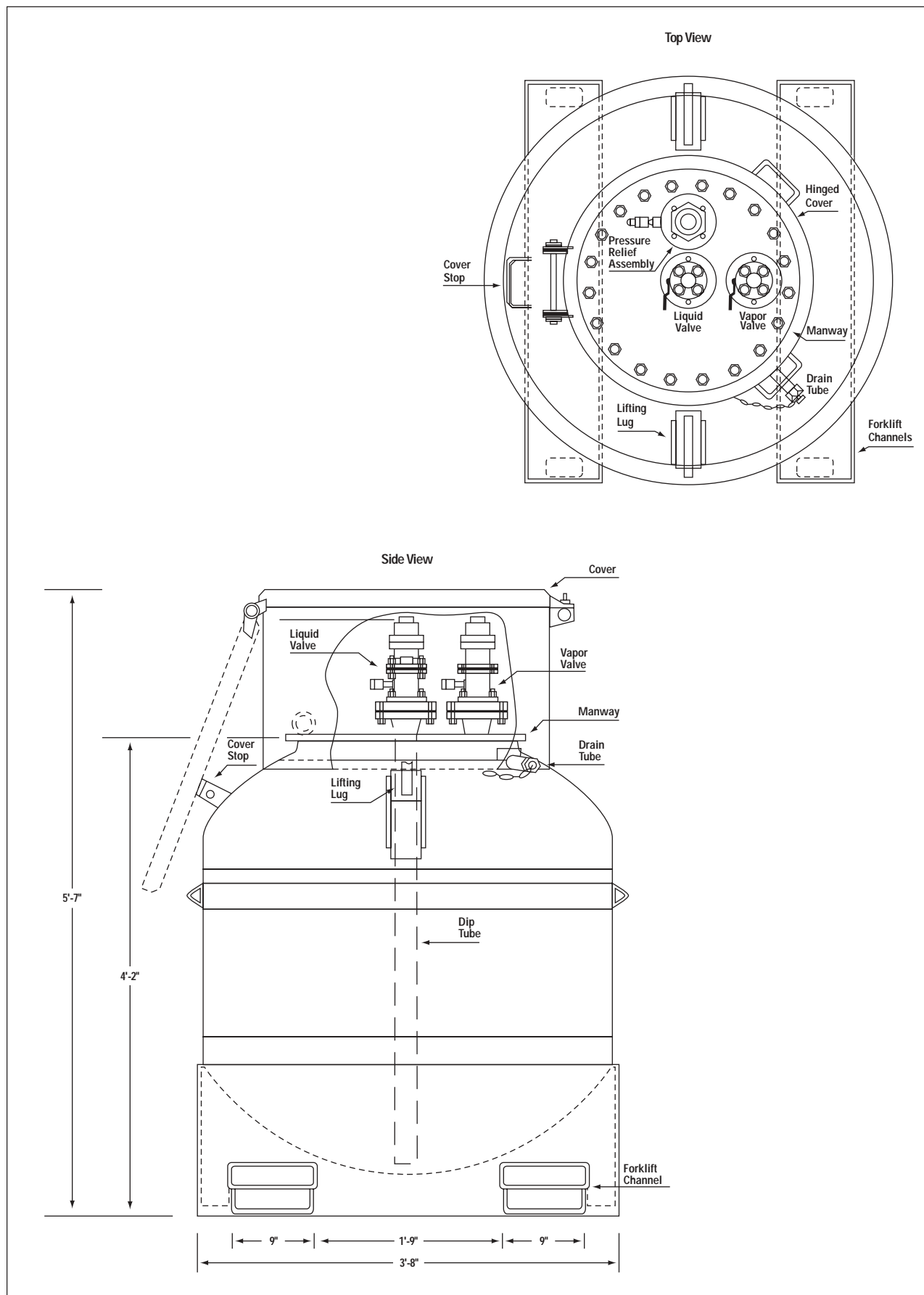


DMS Portable Tank Fittings

Portable tanks are shipped on a dedicated DuPont flatbed truck specially equipped to handle the tanks. The customer must supply a fork truck or crane to receive the tanks. The tanks are supplied with fork truck channels and lifting lugs for this purpose.

Avoid handling portable tanks in wet weather or if they are damp, because any DMS leakage might be mistaken for water. Tanks should preferably be stored under an open roofed-in area, out of the sun and away from heat.

Figure 5. Dimethyl Sulfate Portable Tank



Prior to unloading a tank, check the level in the receiving vessel to be sure it can hold the amount of DMS to be transferred. Vacuum or pump unloading is preferred to pressure unloading, because a leak could be more easily controlled. If pressure unloading is required, dry air or nitrogen should be used at the minimum pressure needed to transfer the material. Pressure should not exceed 145 psig, the maximum allowable working pressure of portable tanks.

After a portable tank has been emptied, relieve any pressure in the tank, close the valves, replace and tighten the caps, and secure the cover. In order to protect the handlers and truckers on the return trip, it is essential that this procedure be completed and double checked and that the tank be tagged to ensure compliance.

An empty tank must NOT be washed out. The tank will still contain a small residue of liquid and vapor, which would present a hazard in return transportation comparable to a full container.

According to DOT regulations, containers that last contained a hazardous material, and that have not been cleaned or purged, must be labeled, marked, and certified as if they were full. Shipping papers should reflect this requirement by using the notation: "Residue Last Contained Dimethyl Sulfate—6.1 (Poison), 8 (Corrosive), UN 1595, Poison—Inhalation Hazard, Hazard Zone B."

DuPont Portable Tank Shipping Policy

DMS deliveries are made only by drivers who have been trained and are equipped to safely handle this product in DuPont-dedicated trucks. These drivers ensure the safe transportation of full tanks to the customers and the return of empty tanks to the producing location.

Use of dedicated trucks and trained personnel provides proper controls and minimizes the exposure of the customer, the carrier, and the public to this hazardous product.

Restricted Deliveries

Due to limitations on delivery equipment and driver availability, prescheduling of delivery dates is necessary. The following information is a guide when ordering DMS:

- Truckload shipments can normally be delivered on the date requested. Customers are notified when the order is placed with the Customer Service Center if there is a conflict in scheduling.

- Less-than-truckload (LTL) orders are consolidated with other orders to make a full truckload. These combined shipments are made at least once a month. However, shipments may be made more frequently, depending upon the number of orders DuPont receives in a given month.
- DuPont can make an LTL emergency shipment if equipment is available and the customer agrees to pay for exclusive use of the DuPont truck. Our service representative receiving the order can supply the approximate cost of such a delivery.
- Empty tanks are picked up when new orders are delivered. Only with special justification will DuPont arrange for pickup of empties other than when a new order is delivered. *Empty tanks should be thoroughly dry*, that is, free of outside water when presented to our drivers for pickup. Do not return empty tanks via common carrier.

Bulk Shipments

Tank trucks are supplied with their own submerged pumps to allow pump unloading. For safety reasons, pump unloading of tank cars is preferred over pressure unloading. This puts the unloading hose and pipe under suction pressure, so that any leak can be stopped promptly without having to vent the tank car of padding pressure. It may be necessary to supply a nominal amount of dry air or nitrogen for pump priming or to avoid creating a vacuum in the tank car being unloaded. In this case, the pressure should be the minimum needed for effective pump operation, with appropriate valving and controls for emergency shutoff of air or nitrogen supply and depressurizing. When pumping from a tank car without padding with pressure, ensure that the car is adequately vented to prevent collapse. This is done using a closed-loop unloading system with vapors from the storage tank vented back to the tank car.

When pump unloading is employed, only pumps without seals should be considered to avoid pump leakage. Because pump unloading will not completely empty lines and hose, care must be exercised in pump location and valving to avoid spillage. A means to purge lines with dry air or nitrogen should be provided.

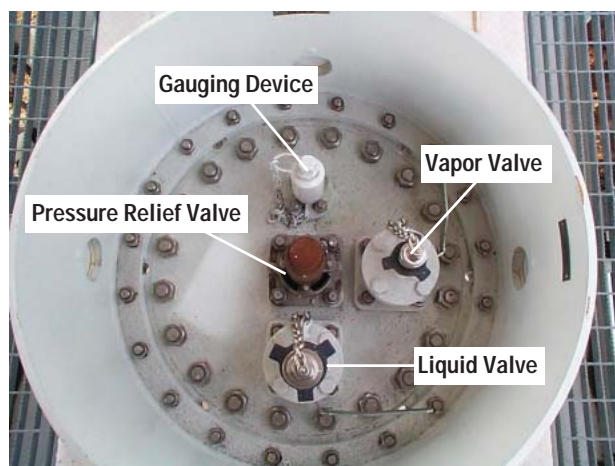
If dry, compressed air or nitrogen is used in place of pumping, pressure must not exceed 30 psig, and connections must include safeguards to ensure that this pressure is not exceeded. The supply valve should be remotely located or barricaded to protect the operator against leaks at fittings when the tank car is pressurized. Safety shutoff of air supply

should also be provided for use in event of a tank or pipeline leak. A pressure relief valve should be installed downstream of the pressure regulator.

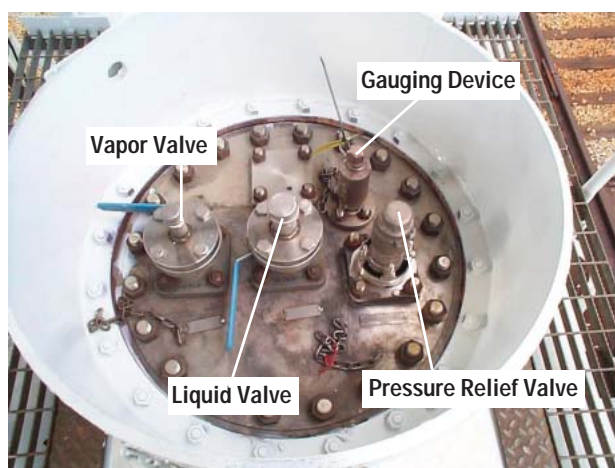
Prior to unloading, the area should be roped off and caution signs posted to keep out unauthorized personnel. Tank trucks and cars must be attended during unloading operations.

Tank Cars

DuPont ships dimethyl sulfate in dedicated 105J500W tank cars containing 165,000 lb (DUPX 20501–20506) or 130,000 lb (DUPX 12515–12520) of product. These cars are top unloaded using a pump. Vapors from the storage tank are returned to the car through the vent line (see **Figures 6 and 9**).

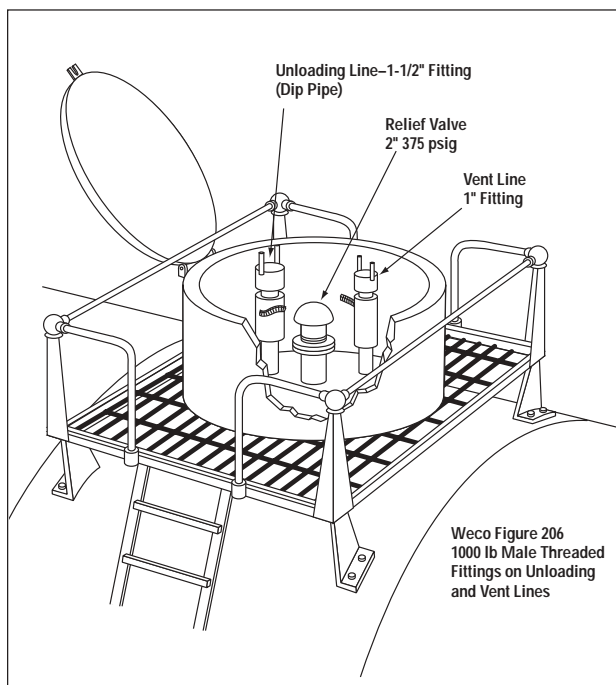


17,000 gal Tank Car Fittings (DUPX 20501–20506)



12,800 gal Tank Car Fittings (DUPX 12515–12520)

Figure 6. Typical Dome Arrangement—Dimethyl Sulfate Cars



When the tank car of dimethyl sulfate arrives, be sure to check its number against the shipping papers to confirm you have the proper car. The product tags on the valves should also read “Dimethyl Sulfate.” Prior to unloading the tank car, be sure the storage tank can take the entire delivery.

Tank Car Placement and Unloading

Refer to the Bureau of Explosives Tariff No. BOE-6000, “Hazardous Material Regulation of the Department of Transportation,” for specifics on tank car placements.

Check and inspect tank car outlets for leakage or broken or missing seals. Report any damage or tampering by telephone to the DuPont Customer Service Center (see back cover). You will be advised of the proper procedure for accepting or returning the shipment.

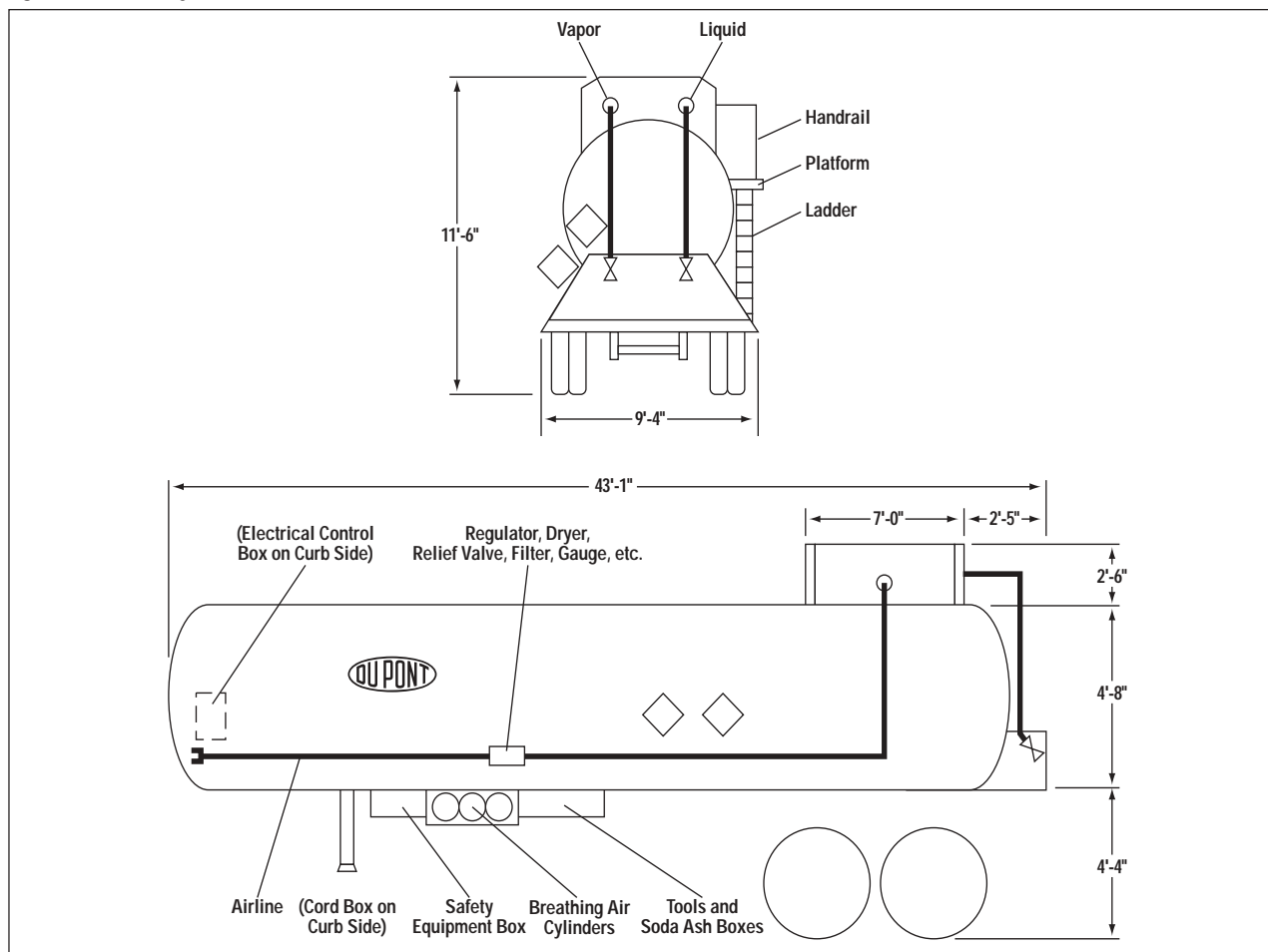
All of the following should be considered and planned *before* unloading a dimethyl sulfate tank car:

- The car should be spotted accurately at the unloading station. The unloading track should be level.
- The storage tank can accommodate an entire car load.
- Brakes should be set and wheels chocked on all cars being unloaded.
- Blue caution signs should be placed during the unloading operation (49 CFR 174.67) and the area barricaded.
- The unloading track should be protected by derails at the open end(s) of the siding, approximately one car-length from the car.
- The car should be electrically grounded.
- The unloading hoses should be visually inspected and the test date current.
- The nearest safety shower and eyewash fountain should be checked.
- Dimethyl sulfate unloading operations should be conducted by properly trained and instructed personnel.
- Unloading operations should be performed only in daytime, unless adequate lighting is provided.
- The car should be attended during the entire period of unloading.



DMS Tank Truck

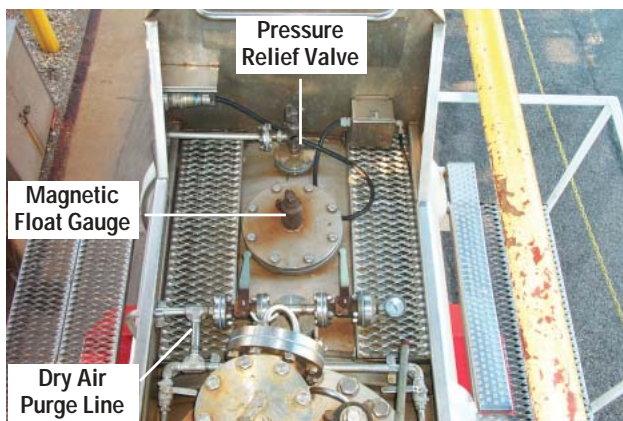
Figure 7. Dimethyl Sulfate Tank Truck



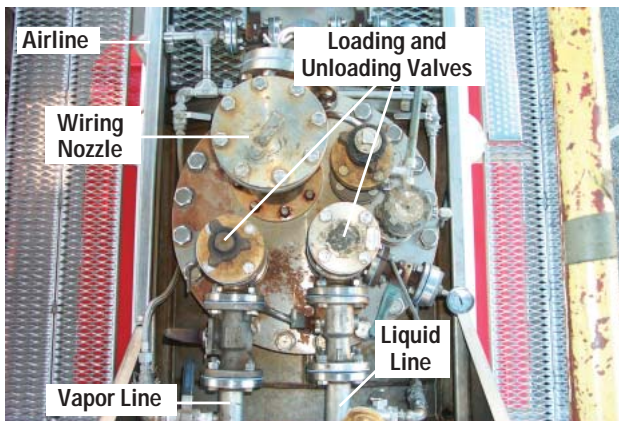
- The person performing the unloading operations should wear personal protective equipment (refer to the PPE section).
- The unloading line should be disconnected as soon as the car is empty and the hoses are blown clear with nitrogen.

DuPont caution signs, which list safety information and DuPont telephone numbers.

If any difficulties were encountered during unloading, or any defects noted in the tank car, advise the DuPont Customer Service Center promptly (see back cover).



DMS Tank Truck Fittings



Release of Tank Car

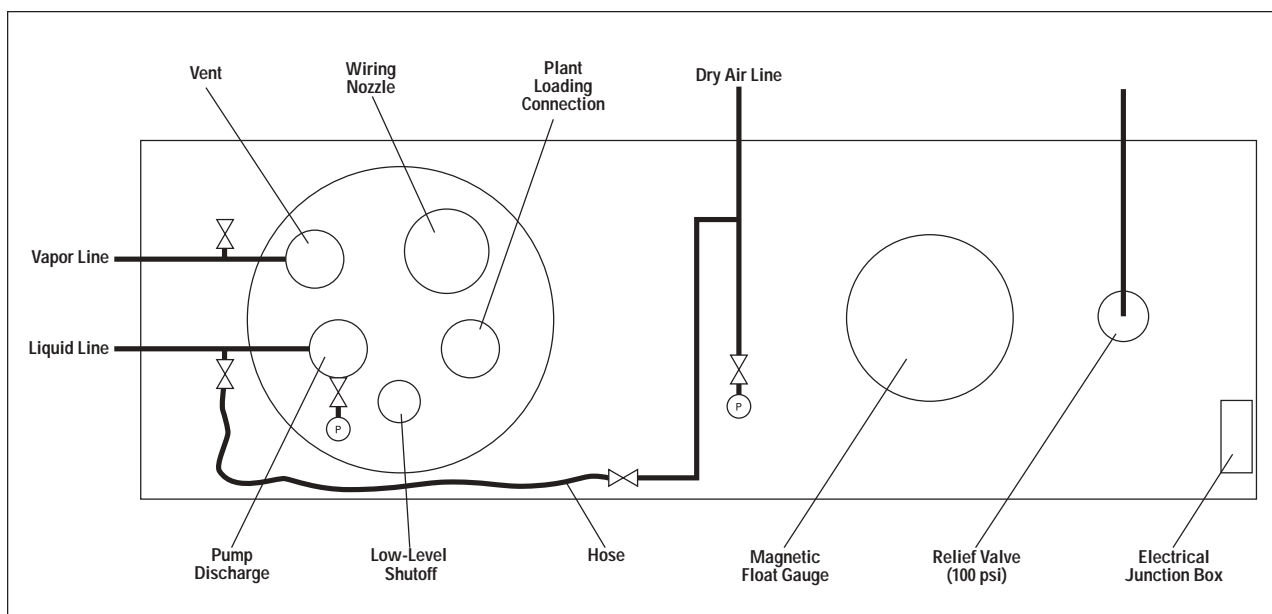
Emptied tank cars should be returned to the shipper promptly. DOT regulations require that all car openings be tightly closed in the same manner as if the car were full.

Before release, be sure the placards on the sides and ends of the car are still legible. Do NOT remove the

Tank Trucks

DuPont supplies DMS in dedicated MC-312 tank trucks equipped with a submerged pump and vapor return fittings. There are liquid and vapor return fittings in the rear of the truck at both the top of the trailer and at bumper level (see **Figures 7 and 8**). The vapor return line enables equalizing pressure by returning vapors back to the truck as the storage

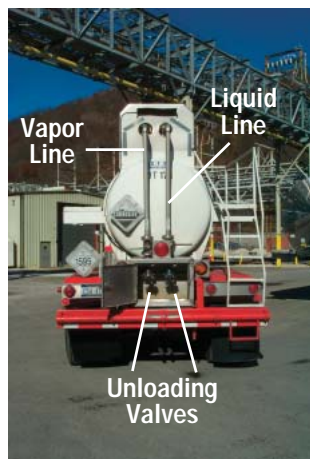
Figure 8. DMS Tank Truck Equipment Arrangement



tank is being filled, rather than venting to the atmosphere or a scrubber. The trailer is equipped with a compressor to purge lines with dry air when unloading is completed.

To receive such a truck, the consignee needs:

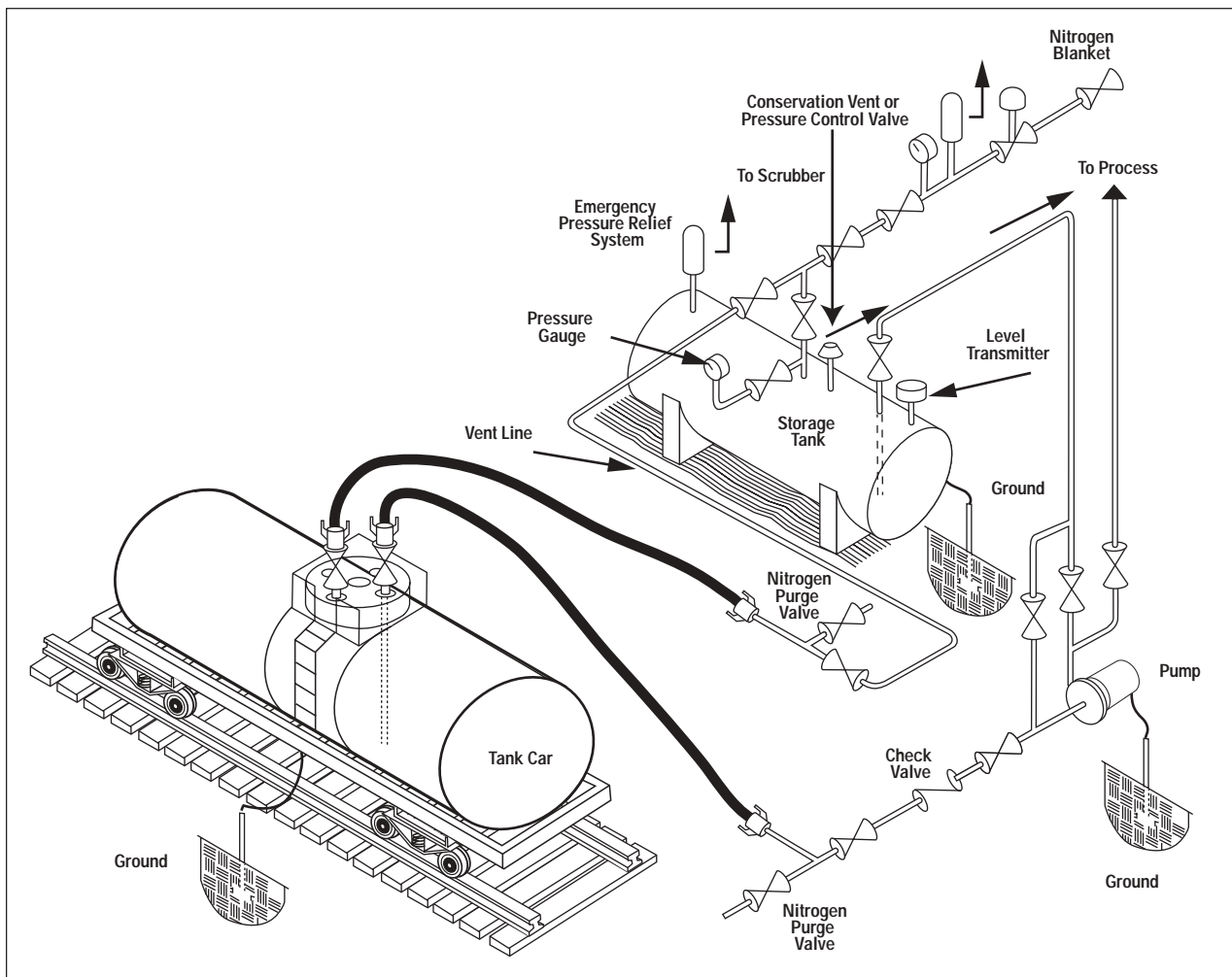
- An all-weather, serviceable roadway to the unloading station. Railroad sidings with open ties and full height rails are not suitable for tank truck movements.
- Vertical clearances of at least 13 ft.
- An open area at the unloading station that permits normal maneuverability of the tractor and trailer.



DMS Tank Truck Rear

- A tractor-trailer spotting area with a surface capable of supporting 20,000 lb per axle.
- Securely anchored liquid and vapor return lines. Trucks do not carry hoses, so intake lines should include a 3- to 10-ft, flexible stainless steel “Resistoflex”⁴¹ chemical transfer hose. This hose should be equipped with a 2-in flanged plug valve on its trailer end to minimize dripping. A small support post should be provided when this hose is not in use to prevent kinking due to valve weight. A short spool piece located between the valve on the hose and the valve on the trailer allows for better hookups than direct valve-to-valve hookup. The hose ends should be capped when not in use.
- A safety shower and eye wash fountain within 25 ft in case of accident.
- Five gallons of 5–10% caustic solution to wash off tools and gloves.
- A 440–480 V, 4 wire, 4 pole, 30 amps, 3 phase, 60 Hz power source for the truck pump, including a Crouse Hinds receptacle (female), part number AR 348.

Figure 9. Unloading and Storage System



Tank Truck Placement and Unloading

Plant personnel should be:

- Properly trained and instructed for safe unloading of DMS
- Wear proper personal protective clothing (refer to the PPE section)
- Be sure the storage tank can take the entire delivery
- Barricade the unloading area
- Make certain the truck unloading hose is securely attached to the proper plant receiving line
- Be sure that all valves in the line to the storage tank are open
- Be sure that the storage tank vent is open
- Chock and ground the truck

Driver will:

- Wear proper protective clothing for safe unloading of DMS
- Observe DOT regulations spelled out for common carrier shipments
- Spot the trailer properly, and prepare it for unloading
- Connect the plant unloading and vapor return lines to the truck unloading valves
- Plug the pump extension cord to the plant's power receptacle, and operate the pump and other truck equipment
- Operate the truck compressor and fittings or the plant's nitrogen connections to purge DMS in lines and hoses to storage tanks
- Assist plant personnel with neutralizing any drippage at the unloading station

The driver has been instructed in proper procedures and carries detailed instructions (copies available on request). The tank truck carries all necessary tools and personal protective equipment for the driver.

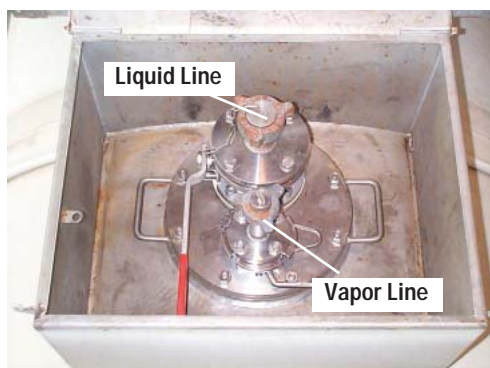
DMS ISO Tank



ISO Tanks

DuPont also supplies DMS in ISO tanks, DOT Class 51 (IMO 101 or Type 1). These containers hold approximately 39,000 lb of DMS. They are equipped with a 1-1/2 in liquid line, a 1-in vapor line, and a pressure relief valve set at 110 psig on the top of the tank. Huber Yale fittings are used for the connections. Delivery requirements are similar to those of tank truck receipts (see "Tank Trucks," page 20), because they are normally delivered to the using site on a flat bed truck chassis. Unloading is similar to that of tank cars (see "Tank Cars," page 18), because the ISO tanks are not equipped with an internal pump. Unloading is normally done by plant personnel. The drivers delivering the ISO tanks are not as highly trained to handle DMS the way the drivers for tank truck deliveries are.

The ISO tanks can be spotted for unloading at the plant, either on the flat bed truck chassis or removed from the chassis using a crane. If a crane is used, special care must be taken to avoid hitting any piping or other plant equipment containing DMS. The ISO tank must be spotted in an area that is diked or curbed to contain any spill during unloading.



DMS ISO Tank Fittings



DMS ISO Tank Relief Valve

Equipment

Storage Tanks

Dimethyl sulfate is not corrosive, unless contacted by moisture (including moisture in air). A carbon steel welded tank is satisfactory for bulk storage of DMS. If iron content is extremely important or the storage tank is located in an environment where it is exposed to external corrosion, 304 L or 316 L stainless steel may be used. Vessels should be code welded and fitted with ASME disked heads. Although not considered to be lethal service, 100% x-rays of all welds is recommended. The tank should not be insulated. Insulation can hide points of external corrosion caused by drips or spills that may lead to leaks.

The storage tank can be designed for atmospheric pressure rating. However, higher pressure ratings are frequently used to improve the mechanical integrity of the tank, enable pressurizing the contents (such as for filling the line to the suction of an external transfer pump), and to minimize vapor venting in an emergency.

The design of a storage system should be at least 1-1/2 times the maximum quantity normally ordered. This will allow flexibility in delivery scheduling to avoid overfilling the tank and to minimize freight costs. Storage tanks should be installed above ground and outside in an open area.

Tank supports should be installed on firm foundations, both of which should be competently designed. Floor loading and soil bearing must be considered to ensure an adequate design, taking into account the high density of DMS in the filled storage tank. Tank supports above the foundation should be made of concrete, masonry, or protected steel with a fire resistance rating of not less than 2 hr. In some locations, water spray protection for steel supports, such as automatic sprinkler systems, may be acceptable. Consult OSHA Standard 1910.106, "Flammable and Combustible Liquids," for applicable requirements.

All nozzles should be installed on the top of the tank. The storage tank will require one 22-in minimum diameter manhole with cover, one manhole for a submerged pump if used, and openings for the fill line, transfer line (if separate from the fill line), vent line, level measuring device, and emergency pressure relief device. The fill line should extend to within 6 in of the bottom of the tank to avoid generating static electricity during tank filling. It should have a siphon-break hole

provided in the vapor space of the tank if the fill line is not also used as the transfer line. A sump should be provided if the tank has a submerged pump. A clean-out valve at the bottom of the tank that is capped with a blind flange should be considered.

Use of centrifugal canned seal-less or mag-drive pump is the preferred means of transferring dimethyl sulfate from the storage tank to the point of use. The pump can be submerged or external to the tank. An external pump is usually easier to decontaminate if maintenance is required. The use of pressure in the storage tank to supply dimethyl sulfate to the consumption point is NOT recommended. Pumping makes it possible to stop a leak on the transfer line more readily without the need to vent off large quantities of DMS-laden air from the storage tank. The large reservoir of compressed gas also represents a considerable amount of motive force should the tank develop a leak.

A dry nitrogen blanket is required to prevent moisture pickup and hydrolysis of the dimethyl sulfate. The nitrogen blanket pressure is usually only several inches of water and can be tied into the tank's vent line. Higher pressure nitrogen should be available and tied into pipe lines to enable purging the lines back to the storage tank.

Newly installed storage and weigh tank systems should be hydrostatically tested and thoroughly dried before being put in service. All equipment should be electrically grounded with a maximum overall resistance of 10 ohms.

Vent

All storage tanks require some means of preventing pressure or vacuum buildup as liquid is added or withdrawn. Use of closed loop unloading with vapor return back to the shipping container will minimize vent losses. The tank should be equipped with a combination pressure-vacuum conservation-type vent or a pressure control valve and a pressure relief valve.

Vapors vented from storage tanks or processes and emergency venting services should be conducted to a scrubber or a flare.

Level

A reliable level indicator must be a part of the storage tank auxiliaries. Suitable level devices include bubbler-type manometers, float type level gauges, and magnetic type level gauges. Overflowing the tank is a maximum hazard because of possible spraying of DMS over the whole area. High level interlocks should be installed to shut-down the loading pump or close the tank's fill valve.

Level on head tanks can be measured by armored sight glasses, either built into or external to the head tank. These gauges should be equipped with shutoff valves.

Meters

Dimethyl sulfate can be batched to the process by weigh tanks or head tanks. If a weigh tank is set up on a load cell, the cells should be mounted so as to be easily removed for servicing without moving the weigh tanks and calibrated without breaking weigh tank lines.

Care must be exercised on overhead tanks to prevent overflow onto personnel and equipment beneath and to collect any leakage in an appropriate dam or drip pan for proper wash down and neutralization.

Badger oscillating piston meters with Teflon® gaskets have been reported as giving good service. Sonic, mass flow, and turbine meters can also be employed for continuous flow. It is best to employ meters that can be readily decontaminated for repairs. Magnetic flow meters are not suitable, because of the low electrical conductivity of DMS.

Hoses

High pressure (1,700 psig) hoses of 316 stainless steel convoluted core and overbraid are used for flexible connections.

Hoses should be inspected for evidence of wear prior to each use and pressure-tested for leaks on a fixed schedule. Hoses should be installed or stored with no tight bends. Unloading hoses should be capped to keep moist air out when not in use.

Valves

Non-lubricated plug cocks or non-lubricated ball valves are recommended for dimethyl sulfate service. Stainless steel valves (304 SS) with non-rising stems and packings of Teflon® may also be used. Flanged valves are preferred to socket welded valves, because valve replacement does not involve burning (which is not recommended for piping in DMS service).

Flanges

Weld neck raised face 150 lb flanges should be used to make up to valves and equipment. Flange finishes should be 125AA to 250AA with circular lay (spiral or concentric). The flanged connections should be protected with flange guards to prevent a

leak spray. Litmus paper impregnated in a Teflon® wrap will give a visual color change warning if a flange leak develops.

Piping

Stainless steel seamless schedule 40 pipe is preferred in order to minimize external corrosion or if iron contamination is a concern. Schedule 80 or extra heavy seamless mild steel piping can also be used. Threaded fittings should be avoided, and flanged connections should be held to a minimum. Minimize the number of pipe joints by bending (long radius bends) and/or welding pipes; pressure test hydrostatically prior to installation. All pipes should be thoroughly dried before installation by blowing with nitrogen. Welds should be 100% x-rayed.

Thin gauge piping is not recommended for dimethyl sulfate because of possible leakage due to physical damage, line setting, etc. Do not insulate lines which would conceal any corrosion. Cap or plug all drain valves. Provide a means to drain or blow out lines, especially unloading lines, with dry nitrogen.

Bolts

Use Standard A193 GRB7 hexagon headed bolts of ANSI B18.2.1 or equivalent. Studs need to be threaded their full length.

Gaskets

Gaskets of Blue Gylon or solid Teflon® are preferred. Full face gaskets are normally used.

O-rings

Buna N or Kalrez®. If Buna N O-rings are used on cargo tank and unloading hose fittings, they should be replaced for each delivery.

Pumps

A pump should be used to transfer DMS from the storage tank to the process. It can be submerged or external to the tank. Seal-less canned or mag-drive pumps are preferred to avoid seal leaks. These pumps require a low flow, low amperage, or low power interlock to avoid operating them dry. External pumps are usually easier to decontaminate and remove for maintenance than submerged pumps. However, pressure may be required initially to feed the pump if the tank outlet is on the top of the tank.

Filters

A cartridge-type filter may be installed in the process to remove rust or foreign solids. The filter should contain fiberglass or ceramic elements and have a removal capability of 5 µm or less. Filters should be decontaminated before cartridges are changed (see “Equipment Repairs”).

Ventilation

Process areas where dimethyl sulfate is used should be adequately ventilated. Ventilating equipment should be designed to handle the heavy DMS vapor and should have a vapor pick-up velocity of 2000 ft/min minimum around the entire area perimeter. The number of air changes should be no less than six per hour. Air exhausted from the process area should not be recirculated, as once-through ventilation is preferred.

Because dilution ventilation is not satisfactory for the control of a hazardous substance such as DMS, local exhaust at potential concern points, such as agitators and charging points, is also recommended if they are not totally sealed.

Diking

Because of dimethyl sulfate’s toxic nature, it is recommended that all tanks be diked to contain any spillage. Cargo tank unloading spots should also be curbed or diked to prevent runoff.

Dikes may be of either the impounding type or the diversion type, as space permits. Due to the toxicity of DMS, impoundment is usually preferred. Dikes may be of earth, steel, concrete, or solid masonry designed to be liquid-tight and to withstand a full hydrostatic head. Consult NFPA Standard No. 30, “Flammable and Combustible Liquid Code” and OSHA Title 29 CFR 1910.106 for detailed recommendations.

Equipment Repairs

Caution

Wear proper personal protective equipment (see “Personal Protective Equipment,” page 10).

Valves and Piping

When a valve contaminated with dimethyl sulfate requires repair, the valve should be removed from the line, thoroughly washed with water, and totally

dismantled (including removal of any packing around the stem). These parts should be immersed in a 10% caustic solution for 16–24 hr, washed with water, repaired, and reassembled. A valve should never be repaired without decontamination. Small and inexpensive valves, and all piping, should be decontaminated and discarded rather than repaired.

Tanks and Equipment

A dilute caustic solution (less than 10%) or dilute ammonia solution (less than 5%) may be used to decontaminate tanks and equipment.

Use of ammonia will allow vapors to reach unwetted areas for better decontamination. However, emission of the vapors to the atmosphere must be controlled to avoid employee exposure or nuisance odors.

Caution

Do not use concentrated caustic or ammonia solutions. Violent exothermic reactions can result.

Thoroughly flush the vessel with water to remove any dimethyl sulfate and sludge and then fill it to the brim with caustic solution.

Allow this solution to remain in the vessel for several days (if dilute ammonia is used, allow it to sit in the vessel for 3–4 hr). Even this procedure will not ensure complete neutralization and removal of DMS from the metal pores.

Drain contents to empty the vessel. Wash out sludge with water. If dilute ammonia was used, purge to rid tank of ammonia vapors.

Check for DMS with a Dräger test kit. Because DMS is heavier than air, the bottom of the tank must be sampled.

Repeat the decontamination procedure if the sample tests positive for DMS.

Normally, welding of any metal that has been in dimethyl sulfate service should be avoided. When contaminated equipment must be repaired by welding, it should be thoroughly cleaned and decontaminated, and the welding should be planned and performed carefully in a well ventilated area.

If welding is necessary within a confined space, welders and other personnel must wear full protective equipment, including fresh air supplied by either air pack or cylinder. Personnel should not risk breathing any vapors within a confined area. Check the area for DMS vapors with a Dräger tube.

Waste Disposal

Disposal of waste liquid streams containing dimethyl sulfate must be accomplished within the regulations and guidelines applicable at the specific location involved. Users should check with the appropriate local, state, or federal authorities as to rules in force and possible changes under consideration. These regulations generally control the type of salt permitted in a waste stream as well as the total dissolved solids.

Wastes containing dimethyl sulfate are preferably diluted with water to low concentration (below 1%) and neutralized. Caustic soda, soda ash, or lime may be used. Similarly, ammonia may be used for neutralization, although it adds nitrogen as a nutrient to the waste stream. Because neutralization is an exothermic reaction (gives off heat), reaction with high concentrations or a hot solution can be violent and explosive and should be avoided. Cooling or further dilution may be necessary to remove liberated heat.

Small quantities of waste dimethyl sulfate may also be disposed of by pouring onto sodium bicarbonate or a sand-soda ash mixture (90–10). The mixture may be shovelled into boxes for burning in an open incinerator with scrap wood and paper.

Dimethyl sulfate may also be safely destroyed by burning in well-designed facilities. It should be mixed with other combustibles, such as No. 2 fuel oil, or air-atomized into a combustion chamber fueled by natural gas, to ensure that sufficient heat is present for complete combustion. Complete combustion must be ensured to avoid discharge of unburned DMS to the atmosphere. Products of complete combustion are carbon dioxide, water vapor, and sulfur dioxide.

Care must be exercised in any waste disposal procedure to prevent personnel exposure to concentrations of DMS above 0.01 ppm, time-weighted average.

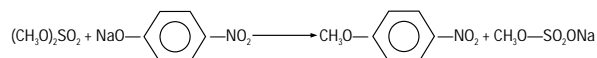
Analytical Method to Determine Dimethyl Sulfate in Air

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a TLV of 0.1 ppm for dimethyl sulfate, time-weighted average. DuPont recommends an Acceptable Exposure Limit of 0.01 ppm for dimethyl sulfate, time-weighted average. The Dräger Multi-Gas Detector can detect DMS vapors and is valuable for determining immediate hazards such as in a spill, but it is not sensitive enough for determining long-term exposure during normal working conditions.

DuPont has developed a monitoring method for detecting low levels of dimethyl sulfate vapor in air.

Principle

A measured volume of air is pulled through a sorbent tube. The samples are desorbed with a saturated solution of sodium p-nitrophenoxide in acetone and analyzed by gas chromatography using an Electron Capture Detector. The sodium p-nitrophenoxide converts DMS to p-nitroanisole according to the following reaction:



Applicability

The method has been demonstrated to be applicable from 0.70 to 3.98 μg DMS in the air sample and gives a linear response to concentrations within this range. For a sampling volume of 35 L air, it is applicable for the determination of 4–23 ppb DMS.

Limitations

None identified

Sensitivity, Precision, and Accuracy

Sensitivity

The detection limit of the analytical procedure was 0.2 µg DMS per injection. This was the amount of analyte that gave a peak whose height was sufficiently large to permit its visual detection in a sample chromatogram when it was compared to a blank sample chromatogram.

Precision

It was not measured due to the difficulties in the preparation of an air sample with known DMS content.

Accuracy

Recovery of spiked samples was 100 ±5%. The studied range: from 0.66 µg to 2.46 µg DMS/sample. Under 0.66 µg DMS/sample, the deviation was more than ±10%.

Special Apparatus (Equivalent apparatus may be substituted)

- Low Flow Pump, Gilian LFS 113—Gilian Instrument Corporation, Wayne, NJ
- Poropak Q Sorbent Tube 39/78 mg, Cat. No. 226-59-03—SKC, Inc.
- Tube Scorer/Breaker—SKC, Inc. Cat. No. 800-00010
- Gas Chromatograph with ECD-HP 5890
- Automatic Sampler—HP 7673 A
- Glass Column (8 ft x 2 mm ID) packed with 2% OV-101 on Ultra-bond 100/120 mesh
- Integrator, Hewlett-Packard

Reagents (Reagent grade except as noted)

- Dimethyl sulfate, 99%, DuPont or Aldrich
- Sodium-4-nitrophenoxide, Aldrich
- 4-nitroanisole, 97%, Aldrich
- Acetone, HPLC grade, Fisher Scientific
- Magnesium sulfate, Fisher Scientific (for preparing dried acetone)

Special Safety Considerations

Refer to the latest vendor MSDS for safety precautions in handling each of the reagents.

Procedure

Operating Conditions

Install the packed column into the gas chromatograph and set the following conditions:

Column Temperature:	165°C (329°F) (isothermal)
Column Flow:	20 cc/min
Injection Temperature:	250°C (482°F)
Detector Temperature:	250°C (482°F)
Injection Volume:	1 µL

Integrator parameters

Zero:	10	THRSH:	0
Attn:	4	PKWD:	0.16
Chrsp:	0.5	ARREJ:	0

Calibration

1. Prepare stock standard by weight 0.6300 ± 0.0100 g p-nitroanisole to 50 mL volumetric flasks, and bring the volume up to the mark with dried acetone.
2. Prepare working standard by diluting 100 µL of stock standard to 25 mL with dried acetone.
3. Add 0, 5, 10, 20, and 50 µL of working standard to 3 mL dried acetone saturated with sodium-4-nitrophenoxide. Shake them well.
4. Inject the standards in order three times.
5. Prepare calibration graph.

Comment

Prepare new calibration graph every time when the check standard value deviates more than ±10% of the expected value (see "Quality Control," p. 30).

Sampling

1. Break ends of sorbent tube with a tube scorer/breaker to allow openings at least 1 mm diameter.
2. Attach the tube to the sampling pump with flexible plastic tubing, such that the large front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler. The sampler should be attached vertically in the worker's breathing zone in such a manner that it does not impede work performance or safety.
3. Measure and record the atmospheric pressure (mmHg), temperature (°C), flow (L/min), and time (hr) as accurately as possible. Recommended sample rates would be 0.05–0.2 L/min
Sample volume max. 35 L.

4. After sample has been taken, stop the sampling pump, immediately cap both ends of the tube, pack securely for shipment, and transport to the laboratory for analysis with the recorded data.

Sample Analysis

1. Score sample tube with a file, break, transfer the larger and smaller section into separate 4 mL glass vials. Prepare reagent blank using the front part of an unexposed tube.
2. Add by pipet 3 mL dried acetone and approximately 50 mg of sodium-4-nitrophenoxide to each vial.
3. Seal the vials with caps, and let stand for 2 hr with occasional shaking.
4. Run with the samples, blank and check standard.

Desorption Efficiency

1. Remove and discard back sorbent section of Poropak Q tubes.
2. Inject separate known amount of DMS (1, 2, 3 μ L of 3.9 mg DMS/10 μ L dried acetone) directly onto front sorbent section with a microliter syringe. For each concentration, use triplicates.
3. Cap the tubes and allow to stand overnight.
4. Transfer the sorbent into 4 mL glass vials.
5. Add approximately 50 mg of sodium p-nitrophenoxide and 3 mL of dried acetone saturated with sodium 4-nitrophenoxide to each vial.
6. Seal the vials with caps and let stand for 2 hr with occasional shaking.
7. Prepare check standard and three media blanks.
8. Run them on GC.
9. Calculate the DMS concentration according to "Calculations" section (below).
10. Determine desorption efficiency with the following formula:

$$DE \% = \frac{\text{measured DMS } \mu\text{g} \times 100}{\text{expected DMS } \mu\text{g}}$$

11. Take the average of the calculated results.

Calculations

1. Determine the sample volume in liters from the flow meter readings and time of sampling. Calculate the volume at 760 mmHg and 25°C (77°F) using the correction formula:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

Where:

V_s = volume of air, liters at standard conditions

V = volume of air, liters

P = barometric pressure, mmHg

T = temperature, °C

2. DMS, ppb = $\frac{Y \times 24.45}{\text{air volume (L)} \times 126.1 \times DE}$

Where:

Y = μ g DMS in the desorption solution
= (Slope of the 5 point calibration curve \times sample area – blank) + the intercept.

24.45 = molar volume at 25°C (77°F) and 760 mmHg

126.1 = DMS molecular weight

DE = desorption efficiency (the development work indicated 0.991)

Example

Flow rate: 0.1 L/min

Sampling time: 350 min

Barometric pressure: 750 mmHg

Temperature: 26°C (79°F)

Sample area: 211,500

Sample blank area: 42,500

Slope and intercept: From calibration graph

$$V = 350 \times 0.1 = 35 \text{ L}$$

$$V_s = 35 \times \frac{750}{760} \times \frac{298}{26 + 273} = 34.4 \text{ L}$$

$$Y = (211,500 - 42,500) \times 0.0016354 + 6 = 282.4 \text{ ng}$$

$$\text{DMS, ppb} = \frac{282.4 \times 24.45}{34.4 \times 126.1 \times 0.99} = 1.6$$

3. Add the areas reported in the front and back sections of the same sample tube to determine the concentration of the sample. If the acetone concentration in the back section is greater than 10% of the front, the absorbing capacity of the sorbent tube has likely been exceeded and sampling should be repeated.
4. Report results to the nearest 1 ppb. If the result is below 4 ppb, report as less than 4 ppb.

Quality Control

1. Determine desorption efficiency (DE) at least once for each lot of Poropak Q tubes used for sampling in the calibration range. Prepare three tubes with concentrations of DMS corresponding to the three middle points of the calibration curve, plus three media blanks.
2. Analyze check standard (10 μ L working standard to 3 mL dried acetone saturated with sodium 4-nitrophenoxide) with each batch of samples to ensure the measurement system is

within limits. The response for the check standard shall be within 10% of the value for the corresponding point of the calibration curve. If it exceeds 10%, corrective action shall be taken to eliminate the source of the error. If necessary, a new calibration curve shall be prepared.

3. Analyze a reagent blank for each batch of samples.

Comments

After every eight runs, the temperatures should be raised and the system cleaned (oven temperature from 165–200°C [329–392°F], detector temperature from 250–350°C [482–662°F]) while the signal is stabilized.

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