Tetrahydrofuran (THF)

Properties, Uses, Storage, and Handling

Product Information

Tetrahydrofuran (THF, tetramethylene oxide, diethylene oxide, 1,4-epoxybutane, tetrahydrofurane, oxolane) is an industrial solvent widely recognized for its unique combination of useful properties. INVISTA™ THF is > 99.9% pure with a small (75–150 ppm) amount of butylated hydroxytoluene (BHT, 4-methyl-2,6-di-tert-butyl phenol) added as an antioxidant.

Tetrahydrofuran is a cycloaliphatic ether and is not “photochemically reactive” as defined in Section k of Los Angeles County’s Rule 66 (equivalent to Rule 442 of the Southern California Air Pollution Control District). THF has an ethereal odor.

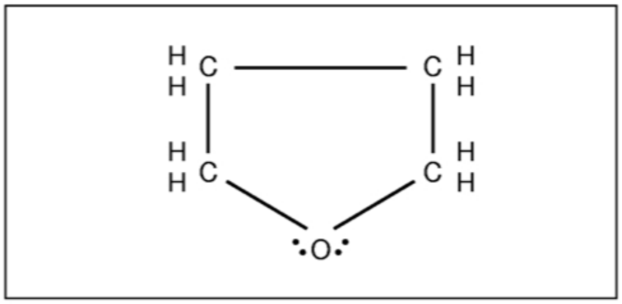
Specification

Purity (THF) , %	99.95max
Color, APHA	10 max.
Water, wt%	0.03 max.
Peroxide (calculated, as THF hydroperoxide), wt%	0.015 max.
Stabilizer (BHT), ppm	75-150

Tetrahydrofuran is miscible with water and common organic solvents. Thus, THF can be used alone or in mixtures with other less active solvents to inerease overall solvent power. Solvent mixtures of THF, MEK, and occasionally toluene are particularly useful in specific resin applications to realize the benefits of THF at optimum cost.

Tetrahydrofuran (THF) is a five-membered cyclic ether as shown in **Figure 1**. Its sterically unhindered oxygen atom carries two unshared pairs of electrons—a structure that favors the formation of coordination complexes and the solvation of cations. Both properties influence the rate and, therefore, the selectivity of chemical reactions.

Figure 1. Tetrahydrofuran Molecule



CAUTION: Tetrahydrofuran is extremely flammable. Forms organic peroxides. May cause eye burns. See “Personal Safety and First Aid Section.”

THF dissolves acetylene; carbon monoxide; and phosgene, thionyl chloride, and other inorganic oxychlorides. (Organic acid chlorides and anhydrides, however, tend to split the furan ring, particularly at reflux temperatures.) The major applications of THF as reaction solvent rely on its high solvent power for organo-magnesium chlorides, alkyl- and arylalkali metal compounds, lithium, aluminum and boron hydrides, and diborane; for steroids and other high-molecular weight organic compounds; and for cyclopentadienes and metal carbonyls.

A review of the literature leads to the conclusion that chemists select THF as the reaction medium most frequently when the reaction involves the use of a metal, an organic salt, or an organometallic compound. Grignard reactions, reactions of alkali metals, anionic polymerizations, metal hydride reactions, and hydroborations are classic examples. The broad solvent properties of THF also serve in countless reactions that do not involve metal compounds.

Product Stewardship

We encourage customers to thoroughly review their safety management practices in the handling of tetrahydrofuran. In support of product stewardship, INVISTA 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 THF users, INVISTA should be contacted before site selection has been made and/or facilities have been designed or built.

Table 1
Physical Properties of Tetrahydrofuran*

Specific Gravity, 20/4°C (68/39°F)	0.886–0.889
Molecular Weight	72.108
Boiling Point (760 mmHg), °C (°F)	66 (151)
Freezing Point, °C (°F)	–108.5 (–163)
Vapor Pressure, 20°C (68°F), mmHg (kPa)	143 (19.1)
Density, Liquid, 20°C (68°F), g/mL (mg/m^3)	0.888
lb/gal	7.41
Vapor (air = 1)	2.49
Evaporation Rate (n-butyl acetate = 1)	8.0
Viscosity, 20°C (68°F), cP (MPa·s)	0.48
Surface Tension in Air, 25°C (77°F), dyn/cm (mN/m)	26.4
Refractive Index, n_D^{20}	1.4073
Heat of Vaporization (at bp), cal/g	95
Btu/lb	171
kJ/kg	398
Heat of Combustion ($-\Delta h_C^0$) at 25°C (77°F) liq	
kcal/mol	598.4
Btu/lb	14938
kJ/g	34.72
Specific Heat, Liquid,	
20°C (68°F), cal/g·C (Btu/lb·F)	0.469
kJ/kg·K	1.97
50°C (122°F), cal/g·C (Btu/lb·F)	0.496
kJ/kg·K	2.090
Vapor, 66°C (151°F), cal/g·C (Btu/lb·F)	0.37
kJ/kg·K	1.55
Coefficient of Thermal Expansion,	
10–20°C, av/°C	0.00126
50–68°F, av/°F	0.00070
Flash Point (TCC), °C (°F)	–20 (–4)
Autoignition Temperature, °C (°F)	321 (610)
Flammability Limits in Air, 25°C (77°F), lower	2
upper	11.8
Critical Temperature, °C (°F)	268 (514)
Critical Pressure, atm (MPa)	51.2 (5.19)
Dielectric Constant, ε, 20°C (68°F)	7.54
30°C (86°F)	7.25
Conductivity, 25°C (77°F), μmhos/cm	0.015
μS/m	1.5
Dipole Moment, μ, 25–50°C (77–122°F), Debye Units	1.6
Solubility Parameter, δ	9.1
Hydrogen-Bonding Index, γ	5.3
Miscibility: water, esters, ketones, alcohols, diethyl ether; aliphatic, aromatic and chlorinated hydrocarbons	Infinite

* These properties are drawn from various INVISTA and other sources. INVISTA does not make any express or implied warranty that future production will demonstrate or continue to possess these typical properties.

Figure 2. Vapor Pressure of Tetrahydrofuran

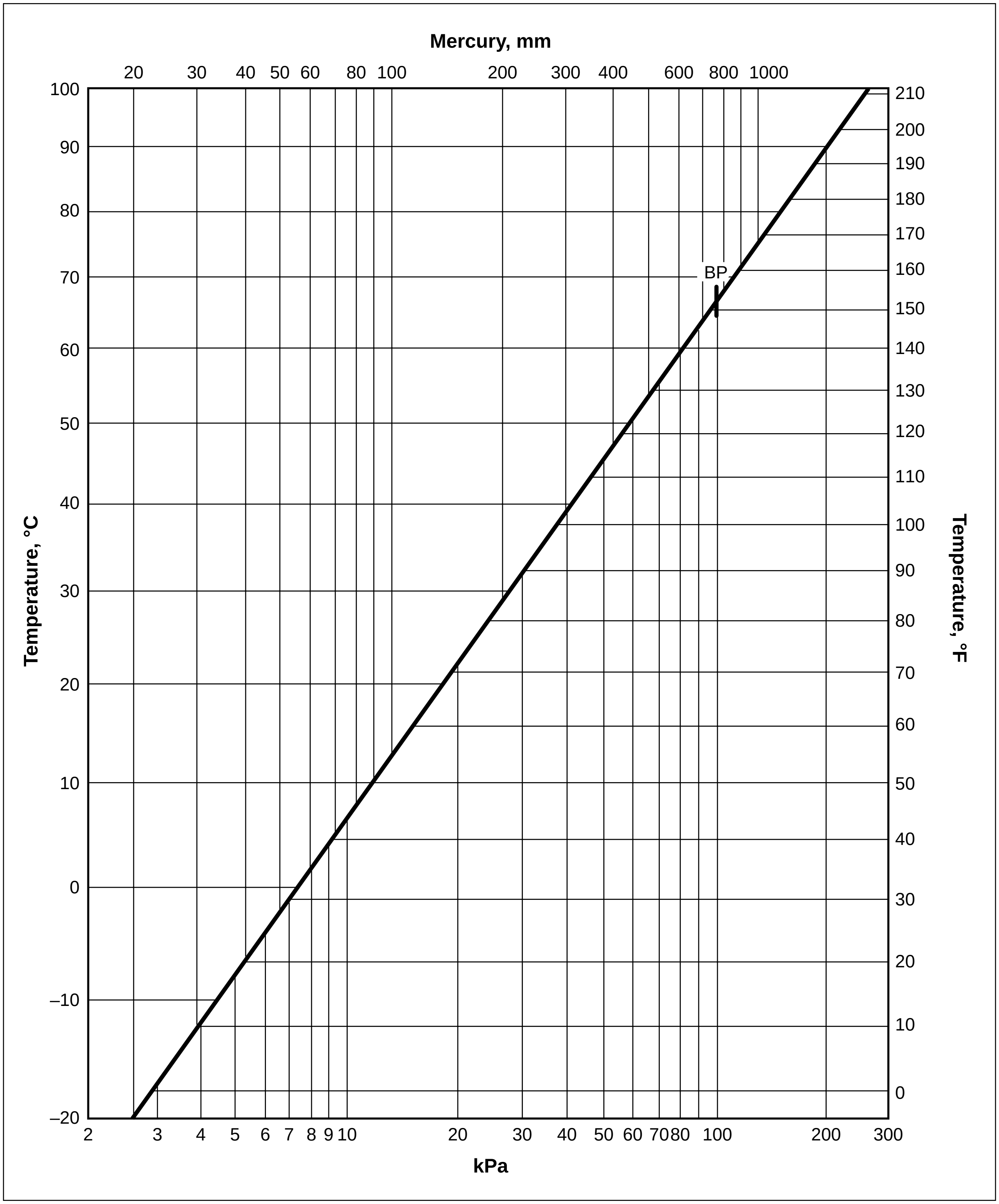


Figure 3. Density of Tetrahydrofuran

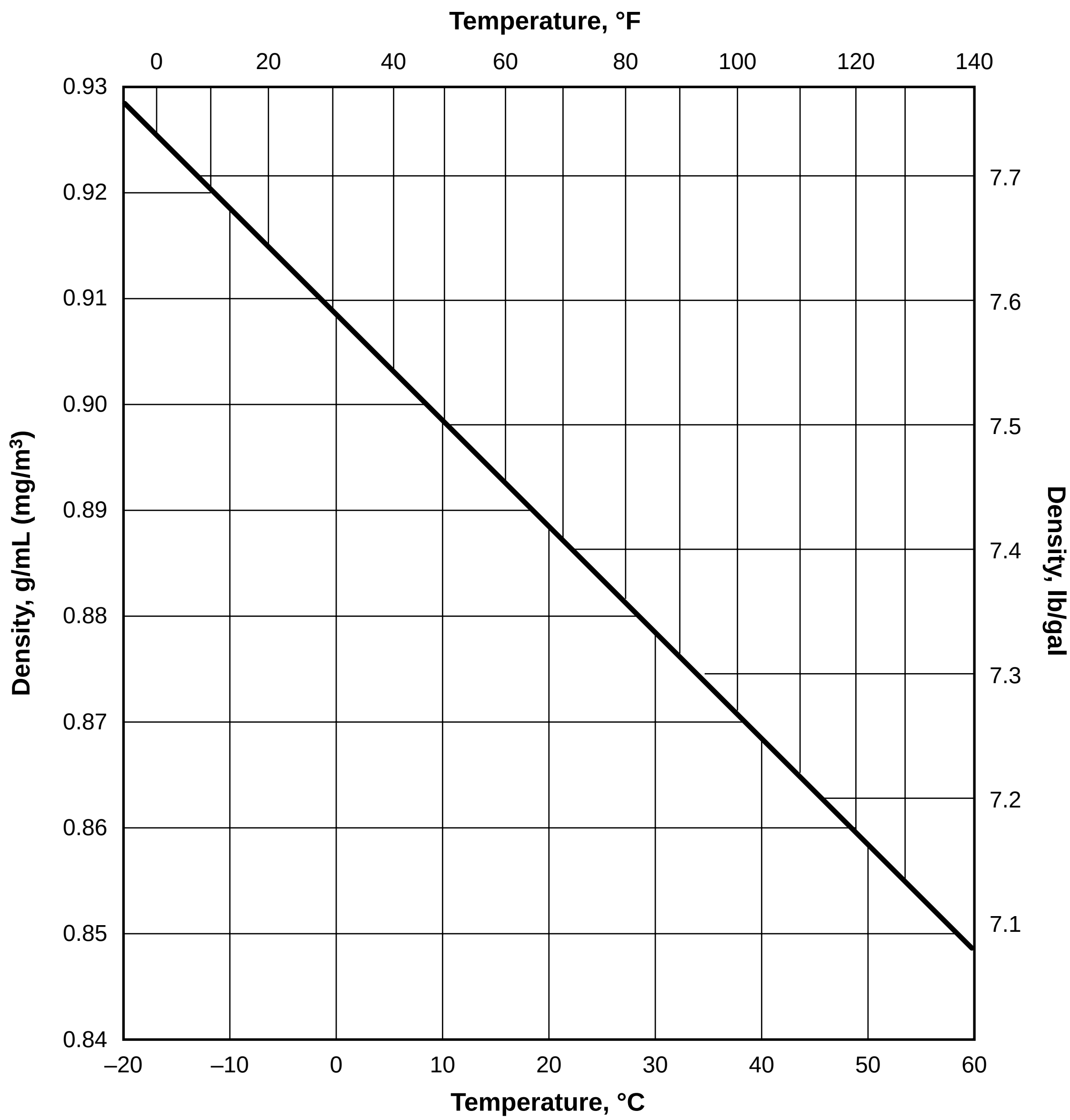
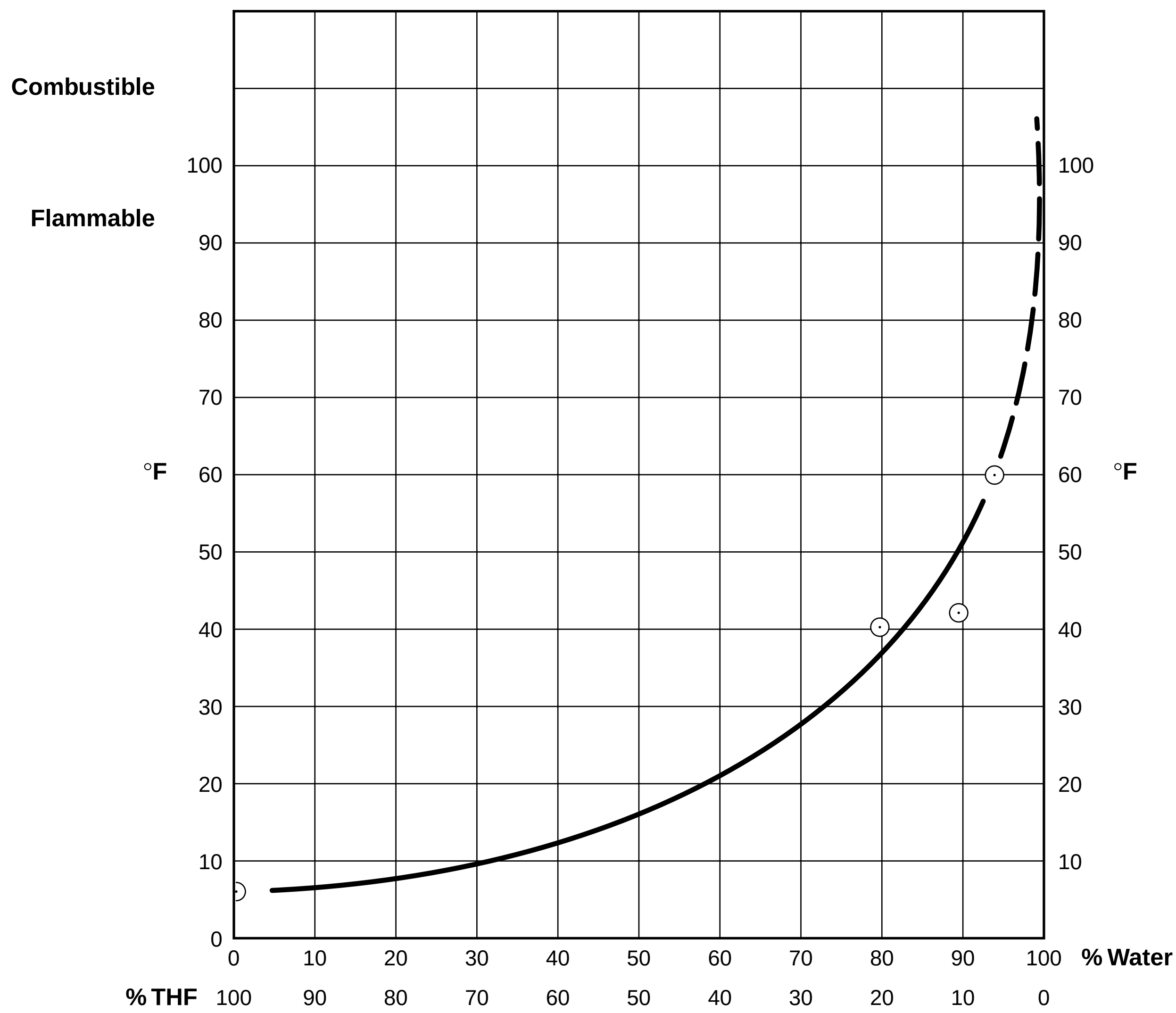


Figure 4. Flash Points of Tetrahydrofuran-Water Solutions (by Setaflash Closed Tester)



Ref.: Culver, L. J., "Modern Paint and Coatings," Vol. 71 (1981), No. 10, pp. 145–149. (C. A. 96(10) 70460F)

Personal Safety and First Aid

All persons handling THF should be thoroughly familiar with the INVISTA MSDS. This can be obtained from the Customer Service Center (see back cover).

Health Hazards

Contact with liquid THF may cause eye burns, corneal ulcerations, and defatting of the skin leading to skin irritation. By inhalation, THF may cause irritation of the upper respiratory passages and anesthetic-like effects such as nausea, dizziness, and headache.

THF is an organic solvent of relatively low toxicity. The 3-hr inhalation LC_{50} in rats is 21,000 ppm and the oral LD_{50} in rats is 2880 mg/kg. In some animal inhalation studies, slight liver effects, indicated by changes in clinical chemistry measurements, and respiratory damage have been observed. However, in other inhalation studies conducted at similar or higher vapor concentrations, no evidence of toxicity was observed in the liver, kidneys, or other organs.

The U.S. Department of Labor (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) recommend an employee exposure limit to THF in any 8-hr work shift of a 40-hr work week of 200 ppm (590 mg/m^3), 8-hr time weighted average (TWA). The OSHA short-term exposure limit (STEL) is 250 ppm (735 mg/m^3) and the ACGIH STEL is 250 ppm (737 mg/m^3). Excess tumors were found in lifetime studies in laboratory animals. For this reason, INVISTA has set the recommended acceptable exposure limit to the chemical at 50 ppm for 8- and 12-hr shifts and 75 ppm for a 15-min short-term exposure limit (STEL). The odor of THF is readily detectable by most people at concentrations of 25 to 50 ppm, near the threshold limit.

Safety Precautions

Do not get in eyes. Avoid contact with skin. Wash thoroughly after handling. Avoid prolonged breathing of vapor. Use THF with sufficient ventilation to keep employees' exposures below established exposure limits.

First Aid

In case of eye contact, immediately flush with plenty of water for at least 15 minutes. Call a physician.

For skin contact, immediately flush with plenty of water. Call a physician.

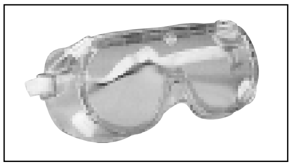
If swallowed, do not induce vomiting. This is to avoid the possibility of aspirating the solvent into the lungs where it could produce severe lung irritation. Immediately give two glasses of water or activated charcoal slurry. Never give anything by mouth to an unconscious person. Call a physician immediately.

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

Personal Protective Equipment

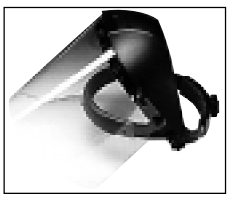
Personal protective equipment should be worn whenever there is the possibility of exposure to or repeated contact with THF.

The following personal protective equipment should be available and worn as appropriate to avoid exposure.

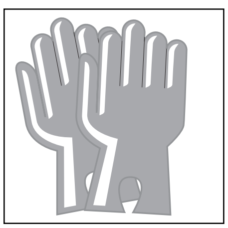


Chemical Splash Goggles

Hard Hat with Brim



Full Length Face Shield (Always with Chemical Splash Goggles)



Chemical-Resistant Gloves

Rubber Safety Shoes or Rubber Overshoes

Rubber Apron

NIOSH-Approved Respiratory Protection

Operator wearing proper personal protective equipment.

Precautions in Use

Fire Hazards

The chief hazard associated with THF is its flammability. The flammability characteristics of THF are similar to those of acetone and n-hexane. Like these, THF is a Class IB flammable liquid as defined by the National Fire Protection Association (NFPA). Every precaution should be taken to prevent exposure of THF to heat, open flames, sparks, or other sources of ignition. Electrically ground all equipment.

THF-water solutions are also flammable and should be treated with care. For example, a 5% THF solution has a flash point of 16°C (61°F) that is only slightly above the flash point of pure methanol. Consequently, water may not be effective as an extinguishing medium (see below).

The proper design and operation of facilities and equipment used for handling THF minimize the probability of fire; nevertheless, fire fighting equipment designed to combat Class B (flammable liquids and gasses) fires must be readily available for emergencies. Two extinguishers that have been found effective in combating fires involving THF and its water solutions are:

- Ansul "Purple-K" potassium bicarbonate-base dry chemical
- National "Universal" Polar-solvent, aqueous film forming foam (AFFF)

Buildings in which THF is stored or used should be of fire-resistant construction. Although water is not usually effective as an extinguisher of THF fires, sprinklers do help protect equipment in the event of fire.

Inert gas blanketing of the THF tanks is advisable and is strongly recommended for tanks located inside buildings and in process areas. All the THF tank vents should contain flame arresters. Indoor areas where THF is stored or handled should be adequately ventilated.

The U.S. Government (OSHA) regulations on handling flammable materials such as THF are contained in Title 29 CFR 1910.106. Many states and municipalities have regulations governing storage, handling, and sale of flammable liquids. Insurance underwriters have similar requirements. Fire inspectors from these organizations offer valuable safety inspections and provide excellent suggestions for fire prevention.

Additional information is available in NFPA No. 30, "Flammable and Combustible Liquids Code."[3]

Peroxide Formation

Under certain conditions, small amounts of THF-peroxide may form in THF, just as peroxides form in other commonly used ethers such as diethyl ether. However, INVISTA(TM) THF is stabilized with butylated hydroxytoluene (BHT) to prevent formation and/or accumulation of THF-peroxide; an accumulation of more than a few hundredths of one percent should not occur under normal storage or use conditions. THF-peroxide is of concern when it is permitted to concentrate in significant quantities by distilling or evaporating in a vessel. Also, because BHT stabilizer is a sacrificial antioxidant, prolonged exposure to air, especially from extended storage time, can deplete BHT and rapidly accelerate THF-peroxide formation. Unlike other ether peroxides, THF-peroxide tends to decompose quietly when heated; nevertheless, solutions and mixtures containing THF should never be distilled to dryness.

Do not store distilled THF unless it is immediately refortified with 75 to 150 ppm BHT or excluded from contact with air. Laboratory tests of unstabilized THF exposed to fresh air once daily indicate peroxide accumulation of greater than 0.30 wt% per day after seven days of storage.

If it is desirable to test for THF-peroxide in the solvent, the peroxide test described in the "Test Methods" section can be used. If test results show more than 0.05% THF-peroxide present, the peroxide should be destroyed prior to distillation of the solvent. Tetrahydrofuran that has been recovered and stored for reuse should be restabilized or stored under a blanket of dry nitrogen gas.

Destruction of the peroxide is easily effected by agitating the THF with flake caustic soda, using 5 kg of caustic for each 100 kg of solvent. Alternatively, the THF can be agitated with a 73% solution of caustic, using about 15 kg of the solution for each 100 kg of solvent. Decanting the treated THF leaves 0.2 to 0.6% water in the solvent.

[3] Available from National Fire Protection Association, Batterymarch Park, Quincy, MA 02269

If analysis shows the THF-peroxide content to be 0.05 to 0.5%, the destructive treatment can be safely accelerated by raising the temperature of the caustic/solvent mixture. Refluxing the mixture to destroy THF-peroxide can precede recovery-distillation of the solvent, for example.

If analysis shows the THF-peroxide content to be over 0.5%, add the flake caustic or 73% caustic solution in small increments to the solvent. This will avoid the danger of a “runaway” reaction and sharp increase in temperature.

THF-hydroperoxide will form when THF is exposed to air, especially when the BHT stabilizer has been removed. Explosions and fires have been reported in instances where THF containing peroxide was reacted with caustic soda or caustic potash in single, excessive treatments.

A spontaneous explosion of borane-tetrahydrofuran reagent has been reported. See *Chemical & Engineering News*, 10/14/74, page 3; also *Chemical & Engineering News*, 11/25/74, page 3.

Safe Handling Precautions

THF should be stored in a cool location away from heat, sparks, and open flames. Electrically ground all equipment and shipping containers to prevent static discharge. Keep containers closed. Avoid breathing the vapors. Use sufficient ventilation to keep vapor concentrations below exposure limits. Wear eye protection and prevent contact with eyes. Avoid contact with the skin. Wash thoroughly after handling. Do not store together with oxidizing compounds or strong acids. Use drums on first in, first out basis.

Nonsparking tools should be used when opening or closing drums, tanks, or other equipment containing THF and for making or breaking connections to such equipment.

Waste THF should be kept in approved safety-type disposal cans for flammable liquids, properly labeled as to content and hazard. For additional information, see “Waste Disposal” section.

Shipping Containers

Tetrahydrofuran is classified as a FLAMMABLE LIQUID under DOT regulations. Drums carry a FLAMMABLE LIQUID label.

Tetrahydrofuran is available from INVISTA in nonreturnable, 55-gal steel drums (443 lb gross, 400 lb net), tank trucks, tank cars, and ISO containers.

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 for the up-to-date requirements for tetrahydrofuran.

Uses

- **Resin Solvent**
  - Coatings for magnetic tape
  - PVC top coating
  - PVC reactor cleaning
  - PVC film casting
  - Cellophane coating
  - Printing inks for plastics
  - Thermoplastic polyurethane coating
- **Reaction Solvent**
  - Grignard reagents
  - Alkali metals, alkyl- and arylalkali metal compounds
  - Alkali metal aluminum hydrides and borohydrides
  - Steroids and high-molecular-weight organic polymers
- **Chemical Intermediate**
  - Polytetramethylene ether glycols
  - Natural gas odorants
- **Chromatographic Solvent**
  - Gel permeation chromatography

Solvent Properties

The best-known characteristic of tetrahydrofuran is its high solvent power for a wide variety of synthetic and natural materials. This characteristic is evident in the case as a solvent for uncured polyurethanes and epoxies and for many other plastics, resins, and elastomers. Solutions with high solids content have practical working viscosities.

Rapid evaporation and high rates of diffusion of THF through vinyl and vinylidene chloride films are attractive properties for topcoating, printing, and adhesive joining. These properties plus high solvency power allow higher production rates and low solvent retention.

Resin Solvent Applications

The unique solvency of tetrahydrofuran for polymers is used to improve product quality and operating efficiency by upgrading mixtures of less active solvents. Specific advantages of THF are illustrated in the following applications:

Coating for Magnetic Tape

Tetrahydrofuran has been used in polyurethane, polyester, or polyvinylidene magnetic tape binder systems contributing uniform coating thickness, rapid drying, and high production rates.

Table 2
Tetrahydrofuran-Soluble Plastics, Resins, and Elastomers

Acrylic Resins	**Elastomers**
Methyl methacrylate polymers	Butadiene-acrylonitrile copolymers (some)
Ethyl, butyl, and other methacrylate polymers	Chlorinated rubbers
Acrylic polymers and copolymers	Chlorosulfonated polyethylenes
Alkyd and Amino Resins	Polysulfides
Alkyd resins	Polyurethanes (uncured)
Urea formaldehyde resins (uncured)	Rubber (natural, unvulcanized)
Phenol formaldehyde resins (uncured)	Chloroprene elastomers
Cellulosics	**Vinyl Resins**
Cellulose acetate	Polyvinyl acetate
Cellulose acetate butyrate	Polyvinyl butyrate
Cellulose acetate stearate	Polyvinyl butyrals
Ethyl cellulose	Polyvinyl chloride
Nitrocellulose	Vinyl chloride copolymers
Miscellaneous Resins	Vinylidene chloride copolymers
Acrylonitrile-butadiene-styrene copolymers	Vinyl acetate/ethylene (some)
Styrene-acrylonitrile copolymers	**Natural Resins**
Chlorinated polyethylene	Congo ester
Polycarbonates	Coumarone-indene
Polysulfones	Raw dammar
Epoxy (uncured)	Ester gum
Silicones (uncured)	Manila copal
Polyesters (low molecular weight)	Pentaerythritol ester gum
Polyamides (low molecular weight)	Rosin
Polystyrene	Shellac (many)
Styrene-butadiene copolymers (some)	

THF-soluble resin solutions are similarly used as prime coats for cellulose acetate and polyester film before deposition of the magnetic compositions.

Topcoating

High molecular weight polyvinyl chloride and acrylic resins have been used in THF base formulations to top coat supported vinyl fabric and sheeting. These are exceptionally durable, resisting abrasion, staining, and chemical degradation. The high molecular weight resin top coats are dielectric heat-sealable and possess a higher resistance to plasticizer migration and blocking than do those made with lower molecular weight resin. The THF-based formulations are easily coated at higher rates without tackiness or solvent-retention problems such as blushing. The rapid solvent action of THF provides quick uniform bite into substrates, ensuring good coating adherence.

PVC Reactor Cleaning

The solvent properties of THF for vinyl polymers, polystyrene, ABS resins, uncured polyurethanes, uncured epoxy resins, and other polymers serve to advantage in cleanup operations. THF does the job quickly and thoroughly.

Reaction Solvent

Tetrahydrofuran has a molecular structure that favors the formation of coordination complexes and the solvation of cations, properties that influence reaction rate and selectivity of chemical reactions. Tetrahydrofuran is most frequently used for reactions involving metals, inorganic salts, or organometallics. Grignard reactions, reactions of alkali metals, anionic polymerizations, metal hydride reactions, and hydrobrominations are classic examples. The broad solvent properties of THF also serve in countless reactions that do not involve metal reactions.

Grignard Reaction Solvent

Tetrahydrofuran is an important solvent for commercial applications of Grignard reactions. It is more basic than diethyl ether toward Lewis acids and has an ideal boiling point for these reactions. The 40°C (72°F) spread between the boiling point and average cooling-water temperature compared to 10°C (18°F) for diethyl ether facilitates good vapor control. The higher reaction temperature allowed by use of THF improves rates of sluggish reactions. Strongly exothermic reactions requiring refrigeration and slow addition of reactants to control turbulence in ether proceed smoothly in THF and require less reaction time to complete.

The scope of various Grignard reactions in THF is considerably broader than diethyl ether. Grignard reagents form readily in THF with vinyl and aromatic halides. Typical Grignard reactions are shown in **Table 3**.

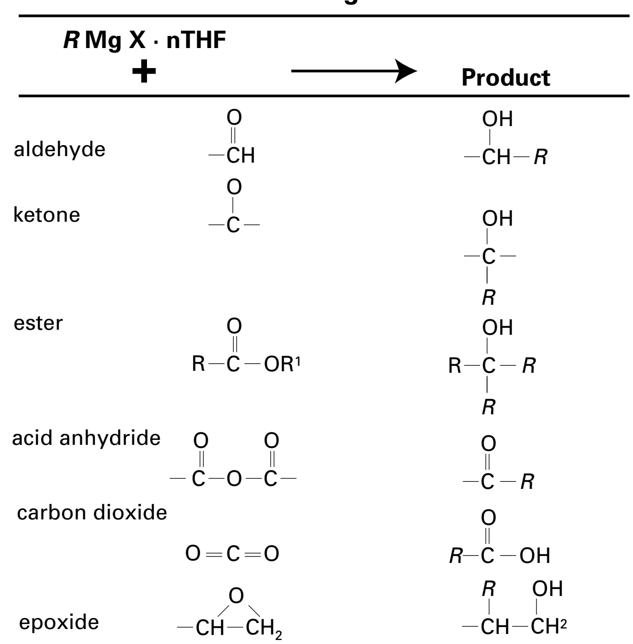
Alkali Metals

Syntheses based on organometallics often proceed more readily in THF than in ether due to the electron-donor characteristics of tetrahydrofuran. Typical organo alkali metal reactions are shown in **Table 4**.

Anionic Polymerization Reactions

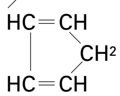
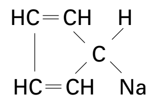
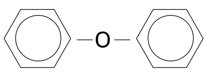
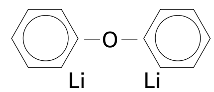
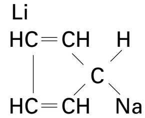
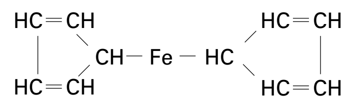
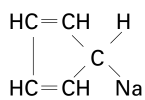
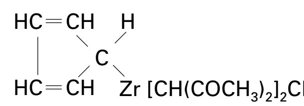
Nonterminating anionic polymerizations are one means of tailor-making polymers for a given application. Tetrahydrofuran is a good reaction medium to synthesize uniform polymers of specified molecular weight, blocks of polymers in a predetermined sequence, or polymers with a functional group on one or both ends.

Table 3
Some Common Grignard Reactions



Code: *R* = an alkyl or alkenyl radical (acrylic, cyclic, or heterocyclic) or an aryl radical
X = a halogen atom, usually Cl, Br, or I
n = 1, 2, or 3

Table 4
Typical Organo-Alkali Metal Reactions

Substrate		Reactant	Product
1-alkyne	$-C\equiv CH$	$C_{10}H_8 \cdot Na$	$-C\equiv CNa$
nitrile	$>CH-C\equiv N$	$C_{10}H_8 \cdot Na$	$>CNa-C\equiv N$
cyclopentadiene		Na	
diphenyl ether		n-BuLi	
vinyl chloride	$CH_2 = CHCl$	*A*	$CH_2 = CHA$
alkyl or aryl halide	RX	Li	RLi
aromatic chlorosilanes	$ArSiH_2Cl$	Li	$ArSiH_2Li$
chlorophosphines	$ArPH_2Cl$	Li	$ArPH_2Li$
triphenylmetal halide	$(C_6H_5)_3$ MX	Li	$(C_6H_5)_3$ MLi
ferrous chloride	$FeCl_2$		
zirconium diacetylacetonate dichloride	$Zr\,[CH(COCH_3)_2]_2Cl_2$		
1,1-diphenylethylene	$C_6H_5-C(C_6H_5) = CH_2$	RLi	$C_6H_5-C(Li)(C_6H_5)-CH_2R$

Code: *A* = alkali metal

Alkali Metal Aluminum Hydrides and Borohydrides

The selective action of complex metal hydrides in reducing organic functional groups is well known. Using THF as a solvent medium for such reductions often enhances this selectivity and/or increases yields, especially where the substrate is a high-molecular-weight compound that dissolves in conventional ether solvents.

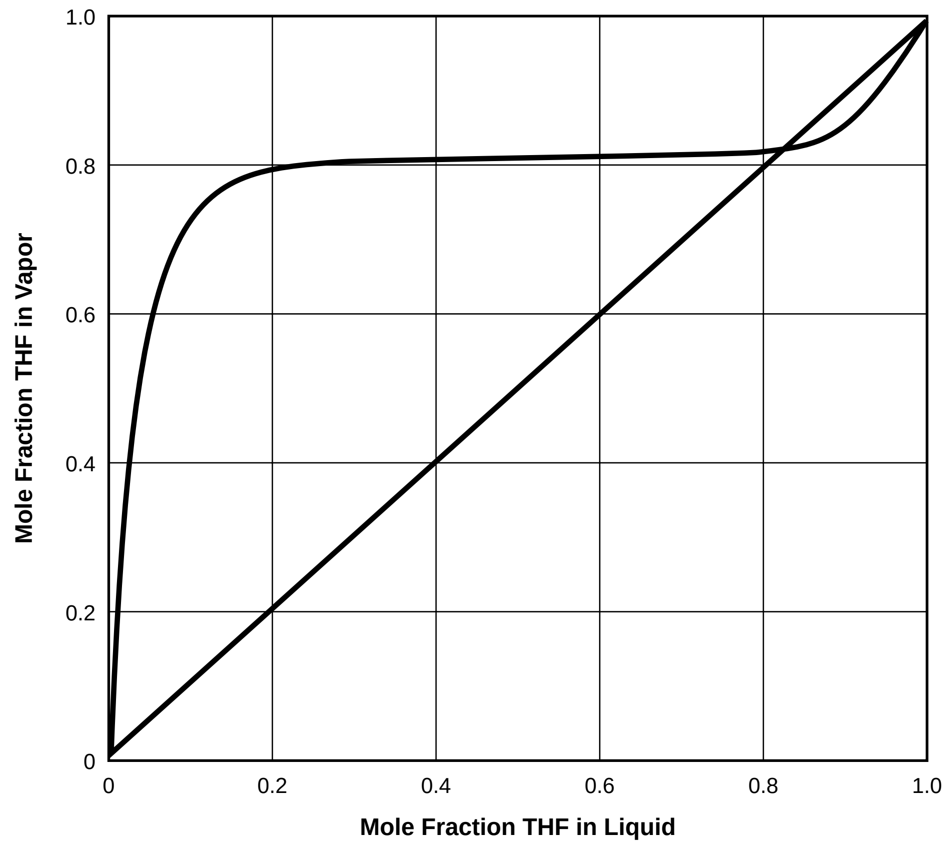
Lithium aluminum hydride (LAH) reductions of organic compounds usually proceed smoothly in THF and give good yields. Cleavage of THF has occurred, however, during the reaction of excess LAH on benzylchloride and on benzylphosphonium halides in THF. The ordinary active hydrogens in hydroxyl, amino, and similar groups consume LAH wastefully. The difference in reaction rates between these and other functional groups may result in the formation of insoluble complexes that interfere with the desired reduction reaction. The excellent solvent characteristics and moderate boiling temperature of THF tend to reduce the problem. Lithium aluminum hydride has been used in THF, for example, to reduce optically active amino acids to optically active amino alcohols in yields of 70–90%.

Finely powdered LAH and tert-butanol, stirred together in THF, form lithium tri (t-butoxy) aluminum hydride. Milder than LAH, this agent reduces aldehydes, ketones, and acid chlorides, but does not react with esters and nitriles.

Sodium aluminum hydride (SAH) reacts with substrates similarly to LAH, but somewhat less readily as a rule. This may be due to its lower solubility characteristics.

Lithium borohydride (LBH) is a less active reducing agent than LAH, but more active than sodium borohydride. Some nitrile and halide functions may resist the action of either borohydride, while some amide functions resist only that of SBH. Sodium borohydride hydrolyzes in water, but is soluble in ether and THF.

Figure 5. Vapor-Liquid Equilibria of Tetrahydrofuran + Water (760 mmHg)



The simple hydrides of lithium, sodium, and calcium are available commercially as are LAH, LBH, SBH, and potassium borohydrides.

Carbonylations

THF is a good solvent for carbon monoxide and exhibits a good coordinating action toward heavy metals. THF is one of the preferred solvents for the preparation and reaction of metal carbonyl compounds such as the bis (phosphine) metal tetracarbonyls of chromium, molybdenum, and tungsten.

Other Reactions Run in THF

The advantages of THF in organometallic reactions apply in many more reactions where coordination complexes, solvated cations, bulky substrates, and/or isometric products are controlling factors.

- **Inorganic Oxychloride Reactions**
  THF is used in a classical Reppe synthesis of acrylic acid from acetylene, carbon monoxide, and water. Tetrahydrofuran is a good solvent for acetylene and serves as reaction medium for making acetylene tetramer and for the preparation and reaction of sodium and other alkali metal acetylides.

- **Amine Reactions**
  Tetrahydrofuran is a preferred reaction medium for the condensation of amines with aldehydes to form Schiff bases. It also has been found useful in diazotization reactions when the amine forms salts that are sparingly soluble in dilute mineral acid or acetic acid, or the subsequent diazonium salt reaction is fast compared to deamination.

- **Hydrogenations**
  THF is useful as a reaction medium for catalytic hydrogenations of double bonds. Polymers containing double bonds can be hydrogenated to modify resin properties. Hydrogenations involving nascent hydrogen from aluminum amalgam in aqueous THF proceed nicely.

- **Oxidations**
  Although THF oxidizes under relatively mild conditions, it is useful as a solvent for oxidations of higher molecular weight amines and steroids.

Recovery of THF from Reaction Mixtures

The complete miscibility of THF with water is one factor that distinguishes THF from the other ethers commonly used for organic reactions. By adding an inert, water-immiscible cosolvent to the reaction mixture before separating the organic and water phases, the organic phase that separates contains the reaction product THF and about 1% water.

The organic phase is preferably dried before product separation. Common drying agents (e.g., magnesium and calcium sulfates) are used, but tend to absorb substantial amounts of THF. Molecular sieves avoid this solvent loss.

THF Recovery Procedures[4]

THF vapor from coating operations has been recovered from air, either by conventional fixed-bed carbon absorption with steam stripping or by fluidized-bed carbon absorption with nitrogen stripping (The Purasiv® HR System, Union Carbide). In both cases, the THF is recovered by condensation with some water present.

If the aqueous solution contains more than 5 wt% water, it can be readily concentrated by distillation to the low-boiling azeotropic composition, which is 94.7 wt% THF at atmospheric pressure. The THF can be further dried in several ways, of which the most common are pressure distillation or liquid-liquid extraction with either strong salt solutions or organics.

The THF-water azeotropic composition shifts with pressure such that at 100 psig, the azeotrope contains 12% water. Completely dry THF can be obtained from an aqueous stream by distilling at atmospheric pressure and about 100 psig in series. The atmospheric still produces water as a bottoms stream and the (atmospheric) azeotrope overhead for feed to pressure still. The pressure still produces dry THF as a bottoms stream and the (pressure) azeotrope overhead for recycle to the atmospheric still.

Drying from about 5% water has also been accomplished by contact with solid, or concentrated aqueous, caustic or calcium chloride. Drying with caustic can lower water to 0.2 to 0.6%. There have been episodes of forceful eruption of THF from drying columns containing solid caustic flake, possibly because of excessive heat of reaction between water and caustic and/or fused bridging of caustic particles. Using caustic briquettes instead of flake and making sure that incoming THF contains no more than about 5% water should minimize this kind of hazard if column drying is used. An advantage to drying with 50% aqueous caustic is that the original strength of caustic solution can be reconstituted by evaporative removal of water. Caustic-dried THF can be further dried by atmospheric distillation to remove lower-boiling 95:5 azeotrope. Molecular sieves (Union Carbide Corporation) can be used to remove small concentrations of water.

Extraction with pentane or toluene, followed by distillation, has been used to make dry THF from THF-water solutions.

Of course, any recovery scheme can result in the accumulation of organic impurities not present in virgin THF. Over time, these could build to objectionable levels for some THF applications if not adequately purged. Furthermore, the user should determine whether these impurities introduce additional hazards beyond those normally associated with THF and, if they do, take protective measures.

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[4] "Liquid Vapor Equilibrium of the System Water Tetrahydrofuran at Atmospheric Pressure" by R. Cigna and E. Sebastiani, Annali du Chimica *54,* 1048–1059 (1964) in Italian

"Activity of Water in Solution with Tetrahydrofuran" by K. L. Pinder, J. Chem. and Eng. Data *18,* 275–277 (1973)

"Vapor-Liquid Equilibrium Data Collection" by J. Ginchling and U. Onken, Vol. 1, Part 1, Aqueous-Organic Systems, Dechema (Germany), 367–372 (1977) in English (has several sets of correlated data)

Test Methods

Color

Determine the color of THF by comparing with APHA standards. Make the comparison in matched 100-mL, tall-form Nessler tubes with the aid of a Fisher Nesslerimeter, or, alternatively, place the tubes together in a Nessler tube holder with a white porcelain plate background, and compare the colors in direct daylight.

Water

Titrate about 50 mL of diluent for stabilized Karl Fischer reagent to the first permanent light-brown color with Karl Fischer single solution stabilized reagent.[5] Add a 25-mL sample of THF and titrate immediately to the same endpoint with Karl Fischer reagent, using an “Aquameter” titrating moisture analyzer[6] or the visual endpoint.

For the most sensitive determination, dilute the Karl Fischer reagent with diluent for stabilized Karl Fischer reagent to titer of about 0.001 g/mL.

NOTE: Diluent for stabilized Karl Fischer reagent (combination of pyridine and 2-methyoxyethanol) must be used as the solvent. Use of methyl alcohol gives inaccurate results due to interferences caused by reactions with THF impurities.

Calculation

$$\frac{(\text{mL reagent})(\text{water equivalent})(100)}{(\text{specific gravity})(25)} = \%\ \text{water}$$

Peroxide

The following is a simple and accurate method for the determination of THF-peroxide levels at concentrations ≥15 ppm. For lower levels, the procedure described in ASTM E-299 is recommended.

1. Prepare duplicate solutions in two 500-mL flasks. To each flask, transfer 200 mL of distilled water. Add 25 mL of a sulfuric acid solution (prepared by adding 1 part concentrated sulfuric acid to 4 parts distilled water), followed by 3 drops of 5% ammonium molybdate.
2. Transfer 10.00 mL of sample to one of the flasks. The second flask is used as a blank.
3. Sparge the blank with nitrogen (2 min at 300 mL/min). Excessive sparging may result in sample loss, while insufficient sparging will produce negative peroxide assays. The sparge tube should be placed in a beaker of distilled water with positive nitrogen flow between tests.
4. Add 25 mL of a 40% potassium iodide to the sparging blank. Continue the sparge for an additional 2 min.
5. Stop the sparging and immediately seal the flask. Store in the dark for 5 min.
6. Resume sparging with magnetic stirring. Add 2 mL of 0.5% starch solution.
7. Titrate with 0.005N sodium thiosulfate to the starch end point (violet → yellow). Do not titrate beyond the end point (yellow → colorless).
8. Repeat steps 3–8 for the sample flask.

Calculation

$$\text{THF Hydroperoxide, ppm} = \frac{(S - B) \times N \times 52{,}000}{8.8}$$

Where S = Volume of thiosulfate titrant for sample
B = Volume of thiosulfate titrant for blank
N = Normality of thiosulfate solution

Organic Impurities

The trace amounts of acetone, lower alcohols, aldehydes, and other organic impurities present in THF are determined by gas chromatography. An accurate measurement of the impurities in a product as pure as INVISTA THF requires the use of the most sensitive equipment and techniques available. The recommendations that follow are therefore subject to revision as significant improvements become available.

Gas Chromatograph (GC)—Any high-quality, flame ionization detecting gas chromatograph suitable for use with ⅛-in columns and a 1-mV recorder.

[5] Available from the Fisher Scientific Company

[6] Beckman Instruments, Inc.

Column[7]—For complete analysis, each of the following columns must be used for analyzing organic impurities in THF.

A = Capillary gas chromatographic column, DB1301, 60 m × 0.32 mm, 1 µm film thickness, catalog no. 123-1363, J&W Scientific, Folsom, CA 95630

B = Capillary gas chromatographic column, DB1, 60 m × 0.32 mm, 3 µm film thickness, catalog no. 123-1064, J&W Scientific, Folsom, CA 95630

	Column	
Operating Conditions	**A**	**B**
Helium carrier gas flow (mL/min)	2.8	3.3
Injection temperature, °C (°F)	220 (503)	220 (503)
Detector temperature, °C (°F)	280 (641)	280 (641)
Column initial temperature,[7] °C (°F)	55 (126)	45 (103)
Sample size, µL	1	1

Calibrations

Prepare calibrating samples I, II, and III by adding, respectively, 10, 20, and 40 ppm of one or more impurities to freshly distilled THF (see box). Suggested impurity samples[8] are:

acetone	isobutyraldehyde
isopropanol	2,5-dihydrofuran
n-propanol	3-methylfuran
n-butyraldehyde	tetrahydro-2 methylfuran
methyl ethyl ketone	tetrahydro-3 methylfuran
	propionaldehyde
	methacrolein

Inject 1 µL (0.001 mL) of calibrating sample I into instrument. For each impurity, note deflection on recorder and elution time. Repeat this procedure using samples II and III. Make 3-point calibration curve by plotting instrumental response versus known quantity with three samples. The slope of the line is the response factor.

Test Procedure

Inject 1 µL of THF sample into the instrument. For each impurity, note deflection on recorder and elution time.

Calculation

(deflection)(“response factor” at elution time)(10^{-4})
= % impurity

Stabilizer

The amount of butylated hydroxytoluene (BHT) present in THF is determined spectrophotometrically at a wavelength of 2775 Å. Any spectrophotometer capable of accurately measuring absorbance at the specified wavelength is suitable.

Calibration

Prepare calibrating samples containing, respectively, 50, 100, 150, 200, 300, and 500 ppm BHT[9] in freshly distilled THF. Measure the absorbance at 2775 Å of each sample, and plot the value against BHT concentration to obtain a calibration curve.

Test Procedure

Measure absorbance of a sample of INVISTA(TM) THF under the same conditions as those used with the calibrating samples. Read directly from calibration curve the concentration of BHT in the sample.

[7] Column temperature program can be obtained by contacting the INVISTA(TM) Customer Service Center listed on the the back.

[8] Those listed are available from Aldrich Chemical Co., Inc.; Chemical Samples Co.; Eastman Kodak Co., Eastman Organic Chemicals; and/or Fisher Scientific Company.

[9] 2,6-Di-tert-butyl-p-cresol (BHT) is available from J. T. Baker Chemical Co.

Storage and Handling

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. Tetrahydrofuran is very flammable and should be stored and used in areas protected from flames, sparks, and excessive heat. Plants handling THF 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, explosion, or release of THF 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 THF leaks while they are still small through the use of chemical detectors.
- Lines, tanks, and equipment that have been opened to the air must be purged with nitrogen before use in THF service.
- Storage tanks and equipment must be electrically grounded.
- Tank vents must be equipped with suitable flame arrestors. Fill pipes must extend to within 6 in of tank bottoms.
- Electrical equipment, wiring, and fixtures must meet the requirements of National Electrical Code, Article 500.[10] The hazard classification for THF is Class I, Division 1 or 2, Group C.
- 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 THF equipment/storage to other vessels in the event of leaks.
- The number of nozzles on the storage tank should be minimized. The outlet nozzle should be of heavy-duty construction with a remotely actuated valve mounted directly to the nozzle.
- Appropriate, remote operated actuated valves should be installed to allow isolation of equipment in the event of a THF 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.
- To warrant adequate sealing wherever needed, gaskets made of Teflon® PTFE resin are recommended, as most other synthetic or natural resins will be attacked by THF (see **Table 2**). Spiral-wound stainless steel and flexible graphite gaskets may also be used.
- 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.
- Means of isolating tank car or tank truck with remote-controlled block valves in the event of a hose failure.
- 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 THF in an emergency situation.

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[10] Available as NFPA No. 70 from National Fire Protection Association, Batterymarch Park, Quincy, MA 02269

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 THF 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 THF 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. Test methods that can be used include wet fluorescent magnetic particle weld inspections and P-scan shear wave inspections. Acoustic emission (AE) testing of storage tanks can be used to pinpoint potential problem areas that can be examined closer in an internal inspection.
- 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 ohm.
- 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 reviews, 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 THF.
- Thorough training and regular retraining of personnel in the important aspects of handling THF. These include:
  - use of personal protective equipment
  - hazards resulting from improper handling of THF
  - 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 INVISTA THF is involved in an accident or emergency anywhere in the continental United States, make a toll-free telephone call to the American Chemistry Council`s 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 as well as what happened, 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 INVISTA(TM) of the emergency, and one of our specialists will get in touch with the caller promptly.

In Canada, call:

(613) 348-3616
24 hours a day, 7 days a week

Drums

Drums of THF should be unloaded carefully to prevent damage. Do not drop or bump drums. INVISTA takes special precautions when packing and shipping to provide a leak-tight drum. However, occasionally a leak may develop in transit. Handle any leaking drum carefully, and move it to a well-ventilated location away from people and traffic, where the leak can be stopped or the contents transferred to a sound container.

Store drums bung-up in a cool place. Keep bungs tightly closed. Limit drum storage to no longer than 6 to 12 months (see “Peroxide Formation” section).

The transfer of THF (or any other flammable liquid) from one container to another is a hazardous operation, and both containers should have bonding and ground connections unless their capacities are 1 gal or less. **Figure 6** illustrates one recommended technique. Transfer by pump is the preferred method. Compressed air or gas should never be used for transfer purposes. Transfer should always be to approved safety cans with flame arresters, painted red, and clearly labeled “TETRAHYDROFURAN—Extremely Flammable—Volatile Liquid.”

Hand pumps used to dispense petroleum solvents are satisfactory for use with THF, if they contain no brass or bronze parts and are properly packed (see “Pump and Valve Packings” section). The pump should have a built-in pressure-vacuum relief vent and protecting fire baffles.

Ground clamps and copper conductors should bond and ground the two containers. Only conductive hose should be used for the transfer, if the receiving container is not grounded.

Where a hand pump is not available, the drum can be placed horizontally on a rack and a self-closing faucet (¾-in Briggs straight threads) inserted in the ¾-in bung hole. The 2-in bung hole serves as vent and will require a flame arrester.

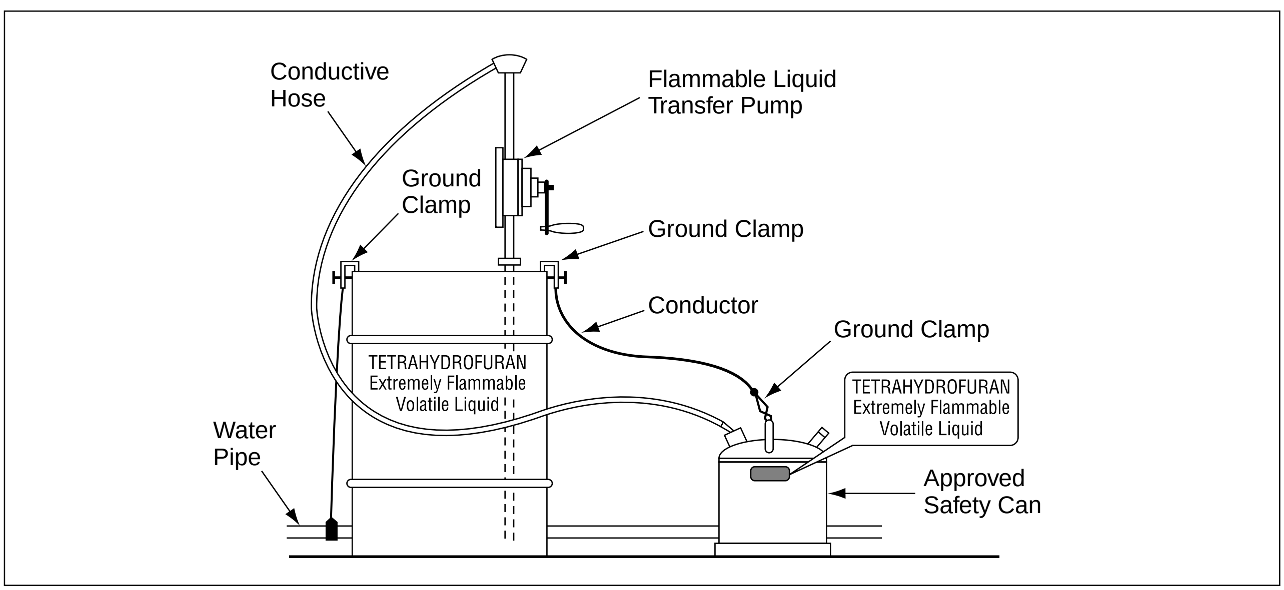
If the drum rack is of metal, it should be grounded; if of wood, a copper bus should be attached to the front of the rack and connected by a copper wire to a water line. A ground clamp and welding cable with neoprene jacket or equivalent should bond each container to the copper bus for grounding.

Unloading and Transfer

Federal, State, and local laws specify appropriate provisions and procedures for the bulk unloading of flammable solvents from tank cars and tank trucks. Receivers of bulk shipments of INVISTA(TM) THF must comply with all such regulations.

Open flames, sparking devices, or other sources of fire should be kept away from an unloading operation. “No Smoking” signs should be prominently displayed at the unloading station. Chemical fire extinguishers, fire blankets, a safety shower, and an eyewash fountain should be easily accessible and well-marked at the unloading station.

Figure 6. Dispensing Tetrahydrofuran with Hand Pump



AIR PRESSURE MUST NEVER BE USED TO UNLOAD THF OR OTHER FLAMMABLE LIQUIDS. Nitrogen pressure for priming unloading pumps and for pressure unloading is sometimes used, but is not recommended because of the difficulty in controlling leaks.

Only approved electrical fixtures should be permitted at the unloading station, and all electrical facilities in the vicinity should be explosion-proof and conform in design and installation with the provisions in Article 500, and supplements, pertinent to "Hazardous Locations: Class I Installations" in the National Electrical Code.[11]

A supply of dry nitrogen at 2–3 psig is recommended for padding the carrier tank during unloading, if a closed loop system with vapor return is not used.

Unloading operations should be performed only by reliable persons wearing appropriate safety equipment, who are properly instructed and made responsible for careful compliance with applicable regulations.

Avoid striking steel against steel. Use nonsparking tools.

Operator wearing proper personal protective equipment during transfer operation.

Unloading Tank Cars

Tank car brakes must be set and wheels chocked and blue[12] caution signs placed during the unloading operation. Derails should be placed at least one car length away from the tank car toward the open end(s) of the siding, unless the unloading location is protected by a closed and locked switch.

[11] Available as NFPA No. 70 from National Fire Protection Association, Batterymarch Park, Quincy, MA 02269

[12] Federal Regulation 49 CFR 174.67

When a tank car of INVISTA THF is received, each outlet should be inspected to ensure that its shipping seal is intact. If one of the seals is broken or missing, this fact should be reported immediately by telephone to our Customer Service Center, which will advise on the proper procedure for accepting or returning the shipment.

Be sure the storage tank can accommodate an entire car load. Check the nearest safety shower and eyewash fountain to be sure they are operational. Wear the proper personal protective equipment during the unloading operation.

The tank car must be electrically grounded before any connection or contact is made between the car and the unloading line. The tank car must be attended throughout the entire unloading period and whenever it is connected to the plant unloading line. The unloading connections should be detached as soon as unloading is completed. If it becomes necessary to discontinue unloading for any reason, all connections should be severed, and all valves and other openings must be securely closed.

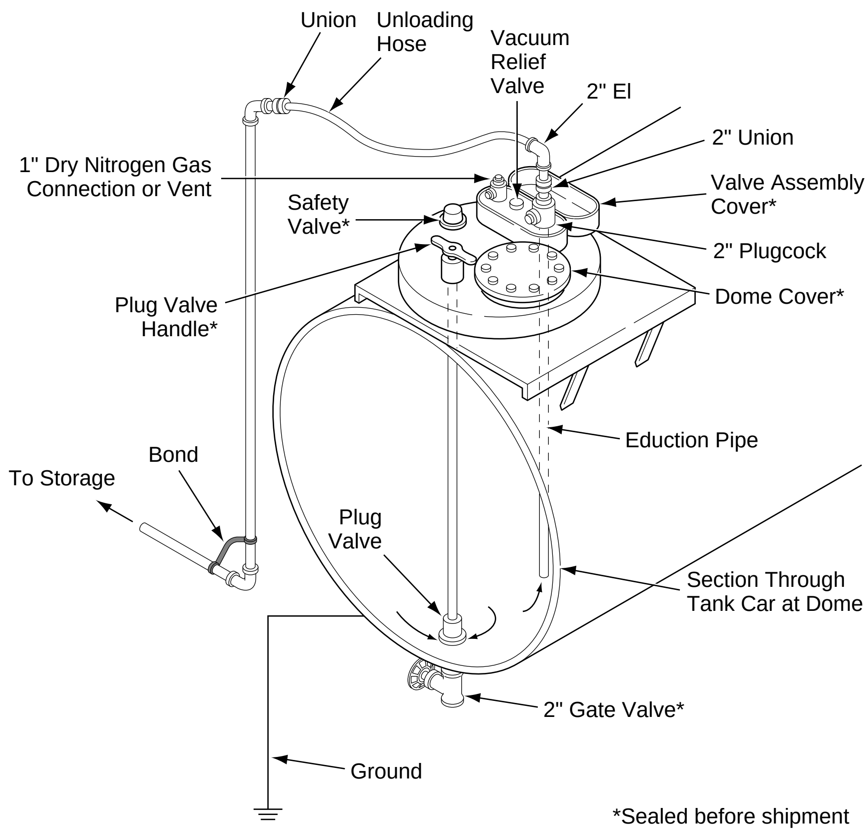
Most INVISTA THF tank cars have connections that permit either top or bottom unloading by pump or by gravity. Unloading through the top by a self-priming pump is a safer procedure than bottom unloading, which is prohibited in some localities because of the dangerous spillage that could result from a valve or line failure. **Figure 7** illustrates the dome connections for top unloading. Piping attached for unloading purposes should contain several feet of corrugated stainless steel hose or conductive hose lined with Teflon® to allow for alignment inaccuracies.

The first step in unloading is to raise the valve-assembly cover, and CAREFULLY open the vent valve in the valve-assembly housing to relieve the internal pressure. The vent valve is then closed, and, if a sample is desired, the dome cover opened and a clean nonmetallic thief lowered. The dome cover should be closed and secured as soon as the sample is removed.

CAUTION
Avoid "dropping" the cover. It might generate a static spark. Use nonsparking tools.

If dry nitrogen is used to displace the THF, the nitrogen gas line is attached to the vent valve in the valve-assembly housing on the car dome. Next, the unloading hose is coupled with the plugcock on the eduction pipe. Unloading can then proceed. A slight

Figure 7. Connections for Top Unloading Tank Cars



positive nitrogen pressure must be maintained to prevent collapse of the tank car.

If the THF will be unloaded using a pump, low-pressure nitrogen or the vapor return line from the storage tank is attached to the vent valve in the car dome. The pump unloading hose is attached to the eduction valve. Open the vent and eduction valves, then start the pump.

When the self-priming pump has unloaded the tank car and cleared the THF line, the pump should be stopped, the plugcock closed, and the unloading line detached from the plugcock. If regulations permit bottom unloading, the unloading line can then be attached to the gate valve underneath the tank car; care is needed to ensure that all joints are tight. After first opening the internal plug valve and then the gate valve, the pump can be restarted to unload the “heel” of THF remaining in the tank car.

When unloading is complete, and the pump has been stopped, the unloading and gas valves are closed, the respective lines are disconnected, the valve assembly cover is closed, and the UN 2056 placards are still in place and in good condition.

Unloading Tank Trucks

Tank truck brakes must be set and wheels chocked during the unloading operation. The tractor engine must be shut off, unless needed to operate the tractor mounted pump.

Always check the identity of the tank truck contents by reading the bill of lading and/or sampling before unloading. Drivers of bulk liquid tank trucks should not unload without supervision by the receiving location.

Carefully inspect the tank truck, especially for leaks, before unloading. Tank trucks used to transport INVISTA THF normally carry four 15-ft (4.6-m) lengths of 2-in (5.1-cm) Chemsolv® hose.

Under no circumstances use air to unload. If closed loop venting is used, the customer must supply fittings and hose to return vapors to the tank truck. See **Figure 9**.

Tank trucks carrying THF must be promptly grounded with a suitable grounding cable upon arrival. The ground cable will remain connected to the truck cargo tank until operations are complete and the truck is ready to depart.

Figure 8. Typical Tank Car Unloading and Storage System for Tetrahydrofuran

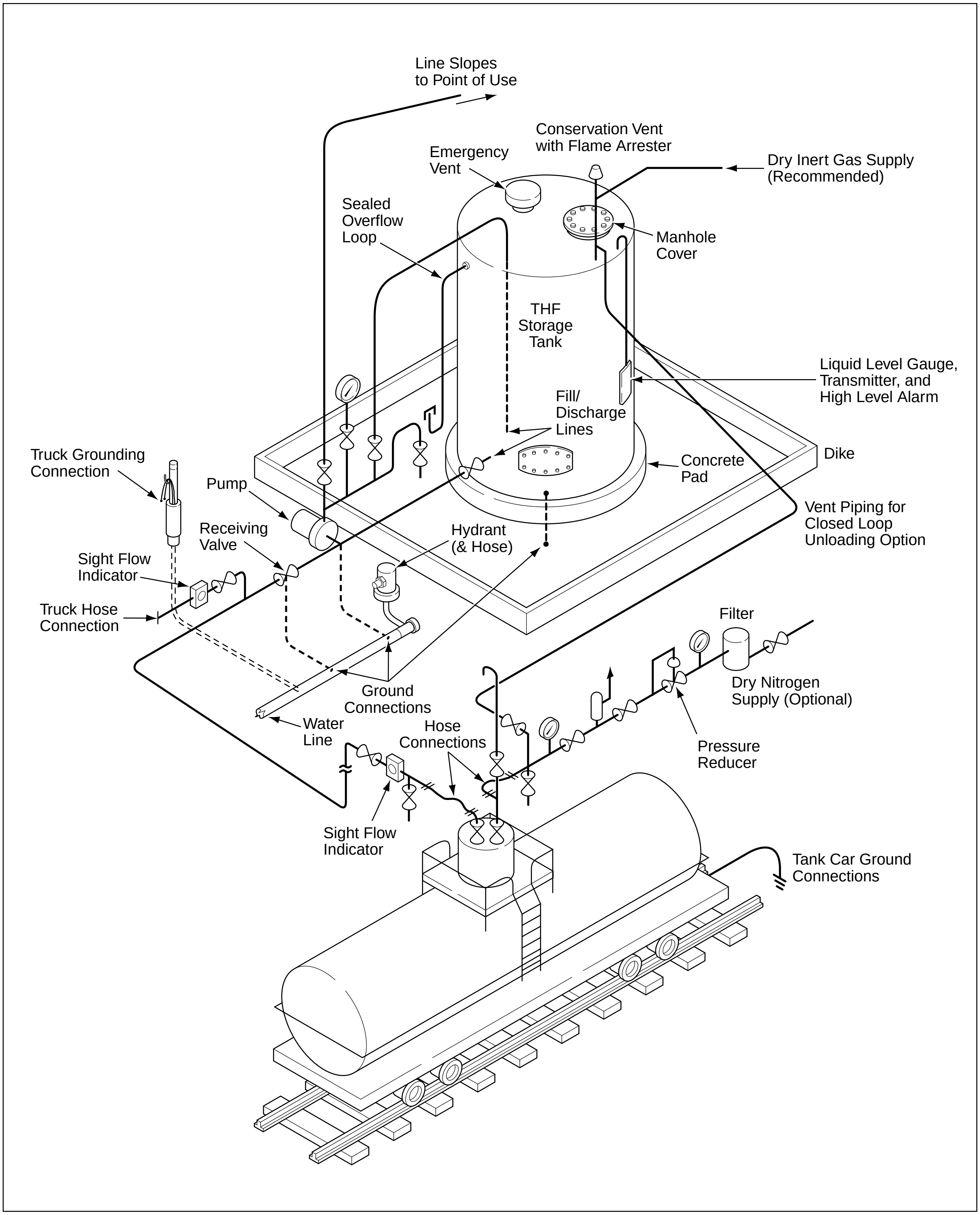
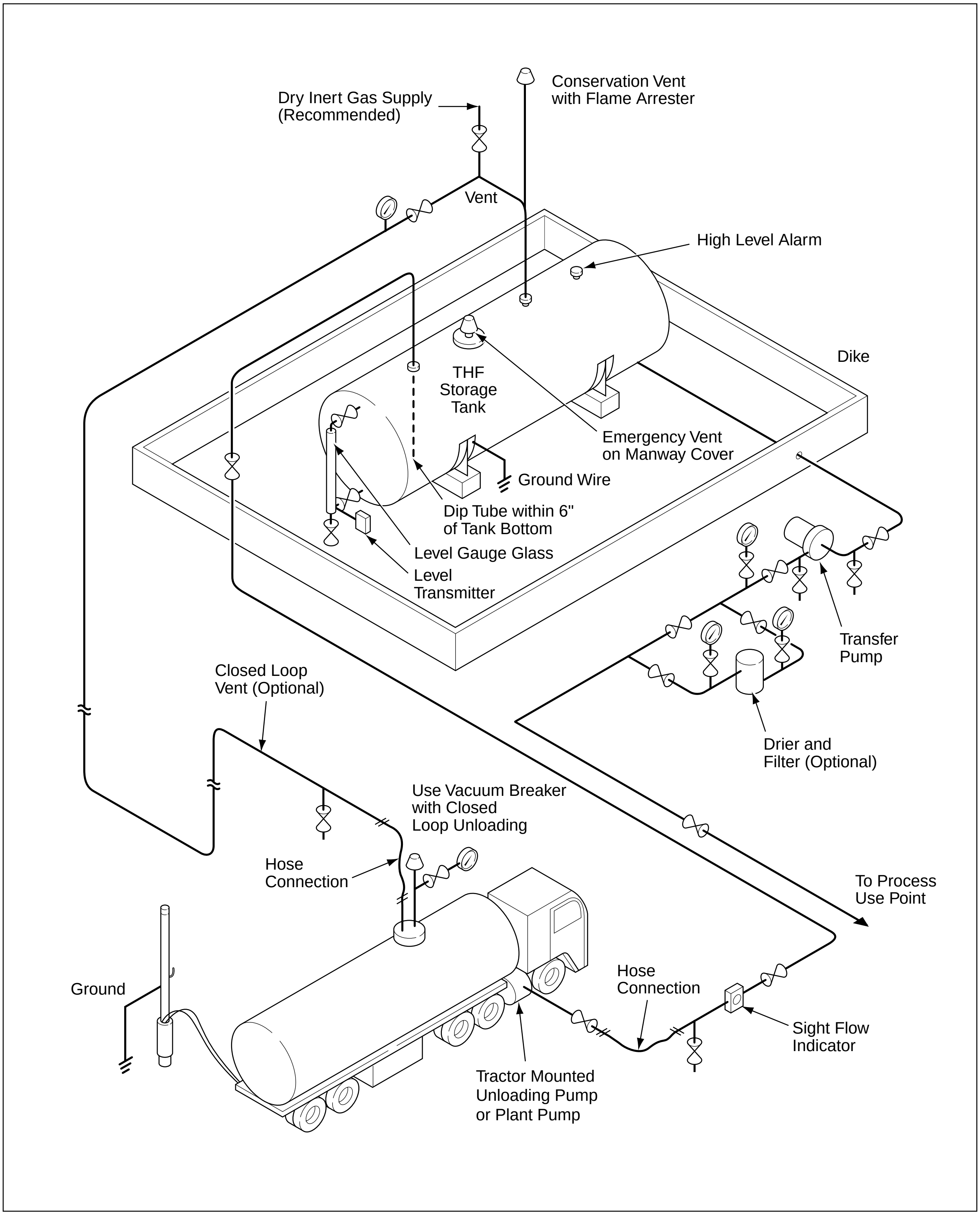


Figure 9. Typical Tank Truck Unloading and Storage System for Tetrahydrofuran



In order to ensure the safe unloading of tank trucks and tank cars, plant personnel should:

- be sure to wear appropriate personal protective equipment;
- be sure the storage tank can take the entire delivery;
- be certain the tank truck or tank car is properly grounded;
- make certain the unloading hose is securely attached to the proper plant receiving line;
- check safety shower and eyewash fountain;
- be sure that all valves in the line to the storage tank are open;
- be sure that the storage tank is adequately vented to accommodate displaced gas from the tank and any gas blown from the truck when the transfer is completed;
- operate or supervise the operation of all plant equipment involved in the unloading.

Driver will:

- observe DOT regulations spelled out for common carrier shipments in 49 CFR 177.834, General Requirements, or in Tariff No. BOE-6000;
- spot the trailer properly and prepare it for unloading;
- connect the unloading hose to the plant receiving line;
- operate or supervise the operation of all truck equipment.

A typical tank truck unloading and storage system is shown in **Figure 9**.

When unloading is completed, the driver will close the valves on the truck while the plant personnel will close all valves to the storage tank. The driver will then disconnect the unloading line on the truck and blank or cap the unloading valve. He/she should also assist plant personnel in washing down any drippage at the unloading station before requesting the plant receiving department for release of the tank truck.

Repacking Bulk THF

Direct drumming from a tank car or tank truck is hazardous and may only be done in facilities inspected and approved by a INVISTA representative. Contact our Customer Service Center for details.

All THF drumming operations require a permanently installed grounded drumming station equipped with fixed piping and an accurate method of measuring drum contents.

A centrifugal pump with a delivery rate of about 25 gpm (95 Lpm) is recommended. Higher drum filling rates tend to increase vapor losses and can result in overfilling and spills. Nozzles that automatically close when containers are nearly filled help to control spills.

THF being repacked into drums should be filtered. A 10-µm nylon cartridge will help maintain the "as-manufactured" quality of the THF.

Draw-off station can be equipped to either weigh or meter THF.

Weighing System

Figure 10 illustrates equipment for weighing. A platform scale of 500 to 600 lb (227 to 272 kg) capacity is required. Sections of roller conveyor on the scale and adjacent to it will assist in handling the heavy filled drums. A suitable exhaust system and a source of dry nitrogen gas are also required. A grounded THF delivery pipe with a filter, short conductive hose, and a dip tube with suitable spring-release valve complete the assembly. The dip tube should be spark-resistant and long enough to reach within 6 in (15 cm) of the drum bottom. Electrically controlled valves complying with NEC Class 1 requirements[13] are available for automatically shutting off the liquid flow when the drum reaches the desired weight.

Metering System

Meters are available as an alternative method of measuring THF into drums. A metering system should include a grounded, wall-mounted displacement meter, filter, short conductive hose, and spark-resistant dip tube with a suitable spring release valve.

The conductive delivery hose can be lined with Teflon® with ground wire incorporated. The quality of the ground arrangement on drums in the fill position should be checked at frequent and regular intervals. A drip collection funnel should be installed and protected by a flash screen.

THF drumming facilities must be inspected and tested periodically to make sure all equipment items—including feed line, scale, drum platform and conveyors—are properly grounded and that line connections are tight and valves secure. All potential sources of sparks or flame and all non-operating personnel should be excluded from the

[13] Available as NFPA No. 70 from National Fire Protection Association, Batterymarch Park, Quincy, MA 02269

area when drumming. Exhaust ventilation must be operating. Observe OSHA standards.

Drums must conform to DOT requirements. Drums to be filled should be as cool as possible to minimize vapor losses. When drums are lined up and the bungs removed, the drum interior should be visually inspected for cleanliness with a drum light.

Purging empty drums with dry nitrogen is recommended to minimize moisture pickup by the THF and reduce the fire hazard during filling.

Drumming Operation

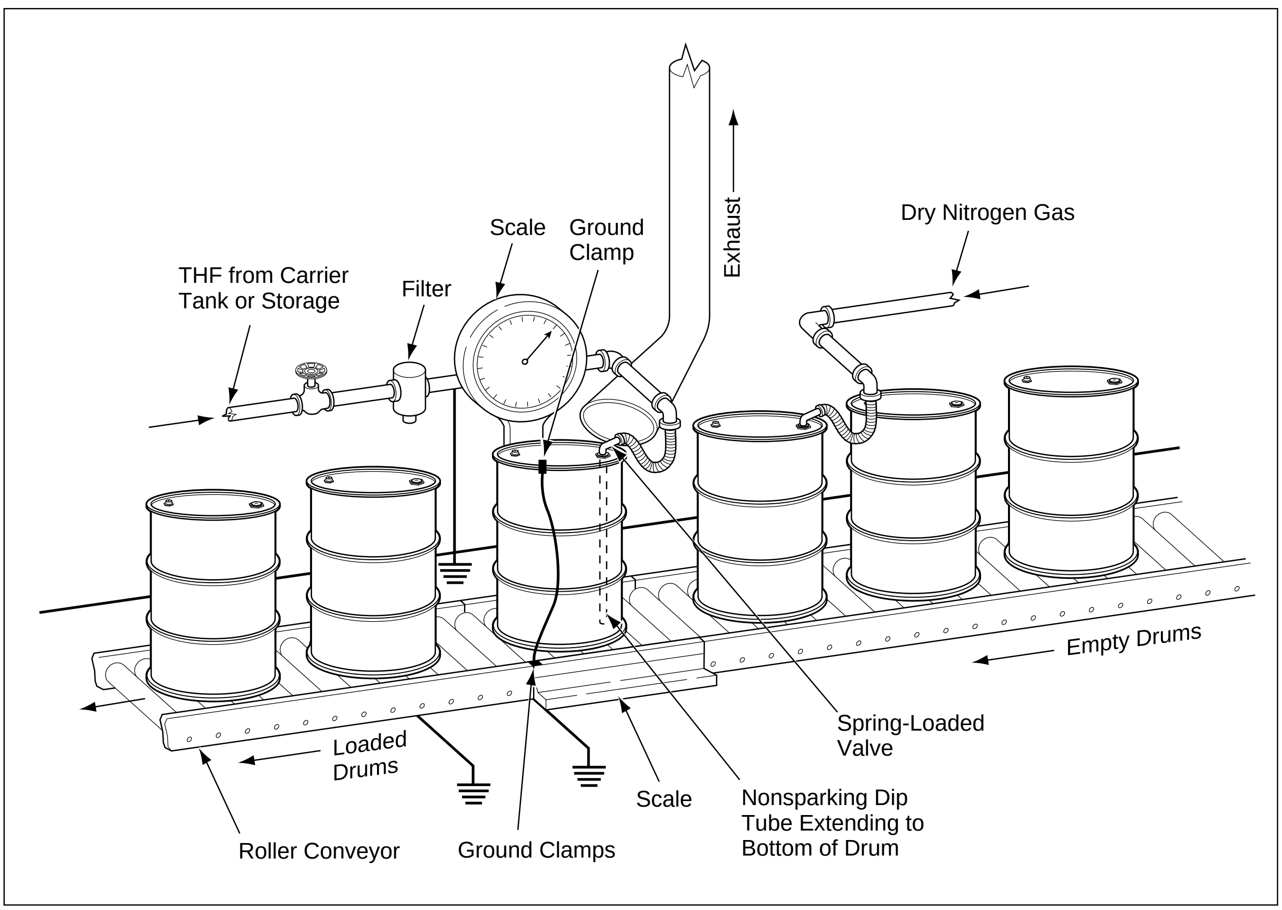
The drum is positioned for filling and a ground clamp attached to the drum as shown in **Figure 10**. The spark-resistant dip tube is inserted through the large bung hole, and the drum is filled to the desired weight. Both bungs are replaced in the drum head and tightened with a torque wrench set for 75 ft·lb. The drum ground wire is transferred to the next empty drum.

When all drums have been filled and removed from the packing station, the area should be inspected to make sure the system is properly shut down and all spills cleaned, prior to shutting off the exhaust ventilation.

Drums filled with THF should be tightly closed and stored in a cool place away from sources of ignition and heat. Leaking drums should be removed promptly to the outdoors or to an isolated, well-ventilated area, and the contents transferred to a sound drum. Flush the leaker with water, and steam it to remove all traces of THF vapor before scrapping (see “Waste Disposal” section).

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. Consult and follow the current governmental regulations, such as Hazard Classifications, Labeling, Food Use Clearances, Worker Exposure Limitations, and Waste Disposal Procedures for the up-to-date requirements in handling of THF.

Figure 10. Typical Weighing Station for Repacking Tetrahydrofuran



Equipment

Tetrahydrofuran can be handled in ordinary steel equipment, because it is noncorrosive and does not hydrolyze. If atmospheric moisture causes the steel to rust, however, the THF may pick up some color from the rust. Bearing bronze has caused discoloration in the solvent on occasion.

The outside of an aboveground storage tank and piping should be protected by a good chemical-resistant finish (white, for heat reflection) such as Corlar® Epoxy Chemical Resistant Finish. Storage tanks installed underground should have an outside protective coating of asphalt or pitch.

The capacity of the storage system should be about 1.5× the maximum quantity normally ordered to ensure against running out of solvent between receipt of shipments. Avoid installing too large a storage system, however, to restrict vapor losses. Vapor losses induced by "thermal pumping" are directly proportional to the vapor space in a tank. Keeping the tank full, therefore, minimizes vapor loss.

Storage Tank

Either horizontal or vertical tanks are suitable for bulk storage of THF, but vertical tanks are usually less expensive to install, require a smaller area per gallon of storage, and are less subject to inventory errors. The tank must be liquid- and vapor-tight and structurally capable of supporting various forces applied to it.

Whether located indoors, outdoors, or underground, the storage tank should be in a protected area and in compliance with any local ordinances covering storage of flammable materials.

A disadvantage of underground storage tanks is that leaks are difficult to detect. Also, installation is more difficult when a tank goes underground because of the measures needed to prevent the tank from "floating."

Temperatures usually encountered will not affect THF (freezing point, –108°C [–163°F]; boiling point, 66°C [151°F]). However, very warm storage locations and heavy dirt or dark paint on aboveground tanks increase solvent evaporation losses.

Aboveground storage tanks should have both top and bottom manholes. Other openings required are a 2-in or larger, flanged bottom outlet and three or four flanged top connections for fill/discharge dip pipe, liquid level gauge, emergency vent, and flame-arresting conservation vent/nitrogen padding connections. Where sight glasses are preferred to the manometer- or differential pressure-type level gauge, the level gauge connection will not be necessary. However, suitable openings in the side of the tank must be provided for the sight glasses. Sight glasses should be protected from accidental blows and fitted with self-closing valves. A pressure-type valve with ball shutoff is recommended. Ladders and a safety platform around the top openings are desirable.

Underground storage tanks should have a top manhole and flanged top connections for fill/discharge dip pipe, liquid level gauge, and flame-arresting conservation vent/nitrogen padding connections. The emergency vent can be mounted on the manhole cover. If a submerged pump is to be used, the tank will also require a flanged top nozzle large enough to accommodate the pump. Special provision for complete drainage of the tank prior to cleanout is necessary in case of accidental contamination.

Follow EPA Underground Storage Tank Systems Regulations and any other state and local regulations that apply. Requirements may include leak detection, spill/overflow prevention, tightness testing, secondary containment, cathodic protection, etc.

Blanketing of THF storage tanks with dry nitrogen is recommended to minimize pickup of moisture from the air and to avoid the flammable THF vapor-air mixture that is otherwise present in the free space of tanks containing THF. Refer to **Figures 8** and **9**.

THF storage tanks should be grounded to dissipate static electricity. Smoking, flames, welding, and other possible sources of ignition should be restricted in the storage area. Lightning protection should be considered.

Tank Foundation

The normal load to be supported by a tank foundation is the tank weight plus 7.4 lb/gal for tetrahydrofuran (specific gravity at 20°C [68°F], 0.888; density, 55.4 lb/ft^3).[14] Connections to the tank must be sufficiently flexible to permit slight settling of the tank without breaking.

In designing the tank foundation, as in designing the tank itself, the local climate may make it necessary to include safety factors for snow and wind loads, floods, etc. The foundation of aboveground tanks should be surrounded by a dike to prevent uncontrolled spread of the contents in case of overfilling, line breakage, or rupture from fire or explosion.[15]

A vertical storage tank can be set on a concrete pad of appropriate size or on an oiled sand pad. Usually the concrete floors in existing buildings are not strong enough to support a solvent storage tank. Whether placed on a concrete or sand pad, the outside of the bottom of the tank should be coated with asphalt and the tank caulked around the edge to prevent rusting of the bottom of the tank.

Supports for tanks above their 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.

Underground tanks buried in flood areas are installed on concrete saddles or strapped to a concrete foundation; in other areas, they are usually embedded in sand.

An improperly supported tank is dangerous and subject to leaks. Competent advice should always be obtained on the design of the foundation and supports.

Pipes, Fittings, and Valves

Dip piping on the fill line should extend to within 6 in of the bottom of the storage tank. A gas bleed hole should be drilled in the line inside the tank, near the interior wall of the tank. The bleed hole acts as a siphon break in the event of line breakage.

[14] If the tank is to be hydrostatically tested before use, the foundation will need to support the tank weight plus 8.3 lb/gal for water (specific gravity at 20°C [68°F], 0.998; density, 62.3 lb/ft^3).

[15] See NFPA No. 30, "Flammable and Combustible Liquids Code."

Welded pipe connections or screwed connections sealed with a thread sealant tape of Teflon® TFE fluorocarbon resin are preferred for THF service, because ordinary pipe dopes quickly leach out and leaks develop at fittings. ASTM specification A53 pipe (seamless preferred), with gasketed flanges where necessary, is satisfactory. A suitable alternate is extra heavy (Schedule 80) pipe and 3,000-lb screwed, forged steel fittings assembled without pipe dope and backwelded as necessary to eliminate leaks. Care must be taken to remove all oil from fittings and pipe prior to assembly to permit backwelding.

All underground piping should be welded and heavily coated with asphalt or wrapped with adhesive plastic tape to prevent corrosion.

Gaskets made of Teflon® TFE fluorocarbon resin are suitable for pipe flange connections at temperatures to 204°C (400°F). Spiral wound stainless steel and flexible graphite gaskets can also be used.

Fittings for indoor piping in concealed areas must be welded. Noncombustible gaskets, such as "Graphonic"[16] flexible graphite and metal gaskets, should be used for other indoor piping fittings requiring gaskets.

Flanged gate valves of carbon steel with stainless steel trim and a 150-psi rating are recommended for THF service. Ball valves may also be used. Avoid brass or bronze valves.

If ASA standard color coding is used, piping for tetrahydrofuran should be indicated with yellow paint.

Pump

For reasons of safety, it is recommended that tank cars be unloaded from the top, using a self-priming pump. Tank trucks are unloaded from the bottom of the tank trailer. A centrifugal pump with ductile iron casing is economical and preferred for transfer of the solvent.

A self-priming pump, centrifugal or positive displacement, is needed if the storage system is located below the pump. Positive displacement pumps should be equipped with a spring-loaded bypass to prevent pipe or pump damage in case a discharge line valve is closed while the pump is operating. It is desirable to maintain a positive head on the pump suction line at all times.

[16] Marine and Petroleum Manufacturing, Houston, TX

Pump and Valve Packings

Mechanically sealed pumps employing bellows or chevron rings of Teflon® to seal against leakage along the pump shaft give the most satisfactory performance with tetrahydrofuran. Pumps with packing glands may be packed with Teflon® TFE fluorocarbon resin. Valve stem packing should also be made of Teflon®.

Pressure and Vacuum Relief

All storage tanks require some means of preventing pressure or vacuum buildup as solvent is withdrawn or added and as atmospheric conditions change.

A conservation-type safety vent with flame arrester is advisable on tanks containing THF. In addition, an emergency relief valve should be installed on the tank roof or top manhole cover.

Where the moisture content of the solvent is critical, a vent dryer containing silica gel may be connected in series with the safety vent to remove moisture from air entering the tank. The silica gel must be regenerated every 3 to 6 months.

It is recommended that the storage tank be padded if a source of dry nitrogen gas is available. Nitrogen padding provides positive control of moisture and thereby prevents rusting of the interior walls of the tank. Nitrogen padding also prevents the chance of an explosive air/THF-vapor atmosphere building up in the tank. Moreover, a nitrogen atmosphere reduces the rate of THF-peroxide formation. A nitrogen inlet line can normally be incorporated with the safety vent. A slight, positive pressure is employed in combination with one or more pressure-regulating valves, so the entire vapor space within the tank is filled with dry nitrogen and all air is excluded.

All vents should be inspected at least once a year to make sure they are functioning properly.

Liquid Level Gauge

The solvent level in storage tanks can be determined by using a manometer- or differential pressure-type level gauge, a totally enclosed float gauge, or a protected gauge glass. Unless constructed of wood, measuring rods should not be used to gauge a storage tank containing THF or other flammable liquid. Manometer- or differential pressure-type level gauges are recommended.

Mercury is the fluid most commonly used in manometer-type level gauges, but it is about 15× as heavy as THF, so the gauge level changes only 1 in for every 15-in change in solvent level. Where required, greater accuracy is obtainable using an inclined tube gauge or a lighter gauge fluid, such as acetylene tetrabromide (3.3× as heavy as THF). The latter, however, freezes at about 0°C (32°F), necessitating a heated enclosure or indoor location for the gauge.

Level gauges can be calibrated to indicate depth, pounds, or gallons of solvent in the tank. The scale desired, the solvent to be measured, the tank height, and the type of gauge fluid desired should be specified. If a scale reading in pounds or gallons is desired, the gauge manufacturer will need a calibration chart (from the tank manufacturer) showing gallons per inch of tank depth.

Testing

A bulk storage system, including tank and all piping, should be tested hydrostatically for leaks before any solvent is put into it. Care is necessary to dry the tested tank and piping thoroughly before charging with THF.

Cleaning Storage Tanks

When only clean dry solvent is stored in a THF storage tank, maintenance cleaning of the tank should be unnecessary. However, if cleaning or repair is necessary, all traces of THF liquid and vapor must first be removed from the storage system—the tank, pipelines, pump, and associated equipment. The entire system is then rinsed thoroughly by filling it with water and dumping, at least four times.

CAUTION
The first rinse may be flammable if solvent drainage was poor. Even a mixture containing 5 vol% of THF in water is capable of igniting at 16°C (61°F) and sustaining combustion.

Finally, the entire system is purged with inert gas or air. The atmosphere within the tank and in its vicinity should be checked with an explosimeter to ensure the absence of explosive mixtures wherever welding or other potential spark-producing operation (e.g., wire brushing) is necessary.

The tank should be cleaned from the outside whenever possible. If entry is required, the following additional precautions should be taken before anyone enters the tank:

1. Disconnect and cap all pipelines to or from the tank.
2. Provide a positive and continuous flow of fresh air through the tank.
3. Test oxygen content of air inside tank.
4. Recheck tank atmosphere with an explosimeter to make certain no flammable mixture is present.
5. Attach safety rope and wrist straps to anyone entering the tank. The other end of the rope should be constantly tended by a person outside the tank who should keep the person in the tank under constant observation. There should also be adequate help nearby to assist in drawing the person from the tank, if necessary.

The tank can be cleaned by brushing down the side walls and removing all foreign material from the tank bottom. Trisodium phosphate or sodium carbonate can be used to aid cleaning; concentrations of about 0.5 lb/gal of water usually suffice.

CAUTION
Wear chemical splash goggles and chemical-resistant gloves!

If design permits, the cleaning solution can be flushed with water. The entire system is then filled with water, drained, and retested as described above.

Waste Disposal

Spills and Leaks

Equipment layout and design should include facilities to contain THF leaks where possible. This can include dikes, curbed areas, sumps, and collection tanks. Collected THF can then be transferred for recovery or disposal.

Small spills can be absorbed with sand or other noncombustible absorbent material. The THF-wet material can be shoveled into drums for disposal by a licensed waste contractor. The area should then be flushed with water until all traces of THF are gone. Water containing small amounts of THF should be disposed of following Federal, State, and local regulations.

CAUTION
See "Personal Safety and First Aid" section for safety precautions while handling THF.

In the event of a leak or spill, immediately ensure that there are no open flames or other sources of ignition in the area. To safeguard personnel from exposure, rope off or barricade process areas promptly whenever a tank, piece of equipment, or piping develops a leak. If feasible, collect the leaking THF in a drum or container of noncombustible absorbent material for subsequent disposal. Take immediate steps to shut down, depressurize, and empty the leaking equipment. Clean up the contaminated area promptly. When indicated, water spray can be used to control or disperse THF vapors, flush away spills, raise the flash point, or protect personnel working to shut off a leak. Dilute water solutions of THF may still be flammable.

Disposal Methods

THF is specifically listed as a RCRA hazardous waste. Its hazardous waste number is U213. Comply with Federal, State, and local regulations for disposal.

EPA-approved disposal methods for non-waste water forms of THF are fuel substitution or incineration in a properly designed and permitted incinerator. Precautions and protective equipment required in the disposal of THF should be identical to those required for handling THF in plant operations.

EPA-recommended methods for disposal of wastewater forms of THF are: wet air oxidation or chemical oxidation, followed by carbon absorption; biodegradation, followed by carbon absorption or incineration by permitted facilities.

Based on five-day BOD studies, THF is highly resistant to biodegradation, a property shared by some other cyclic ethers. Studies indicate, however, that biodegradation may occur after extended periods (20 to 25 days) of exposure using acclimated microbial seed. Individual testing should be done to determine biodegradability of a particular waste stream. The Chemical Oxygen Demand (COD) of THF was determined experimentally to be 1.1 lb of oxygen per pound of THF. This equals 45% of the Theoretical Oxygen Demand (2.44 lb O_2 per pound THF). In an aerated treatment system, air stripping may result in partial removal of THF due to its volatility. Studies have also shown that THF does not interfere with the BOD_5 test or the performance of an activated sludge treatment system at concentrations of up to 2000 mg/L.

NOTICE

Tetrahydrofuran is extremely flammable, forms organic peroxides, and may cause eye burns. See "Personal Safety and First Aid" section on page 6.

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

INVISTA(TM) can assist qualified engineering/operations personnel in consultation regarding tetrahydrofuran safety with unloading/storage design, operation, first aid/medical treatment, and personal protective equipment issues.

The responsibility for tetrahydrofuran 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 tetrahydrofuran.

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P.R.China	86-21-6387-2702	86-21-6335-3609
Japan	81-3-5434-3441	81-3-5434-3413
Korea	82-2-550-5206	82-2-550-5288
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