BASF INTERMEDIATES

# Tetrahydrofuran (THF) Storage and Handling

# *Table of Contents*

# Chemical and Physical Properties

Tetrahydrofuran (THF) is a general purpose, highly volatile organic solvent. It is a colorless, water-miscible, mobile liquid. It offers very good solvent power for numerous organic substances and is used as a starting material for various syntheses.

THF can be recovered easily, without decomposition, from off-gas streams and contaminated solvents, making it suitable for closed-loop processes designed to avoid pollution.

The peroxide fraction in fresh THF produced by BASF lies well below 1 mg/kg (< 1 ppm). However, due to the nature of the product, it may rise during transport, filling, refilling, storage and sampling.

### Properties

Tetrahydrofuran distilled pure (THF) is a clear, colorless, low-boiling, volatile, polar liquid. It is a cyclic, aliphatic ether with a characteristic odor reminiscent of acetone.

THF has excellent solvent power for numerous organic substances. It is miscible with water and all common organic solvents.

THF reacts readily with oxygen, e.g., on contact with air, to form peroxides (predominantly hydroperoxides). The formation of peroxides can be largely inhibited by adding certain stabilizers. BASF offers THF stabilized with 250 – 400 ppm of BHT (3,5-di-tert-butyl-4-hydroxytoluene).

### A. Peroxides

Preliminary studies in BASF Solvent Laboratories indicate that THF peroxides are formed only in the liquid phase. In the vapor phase, under normal conditions, they appear to form very slowly, if at all. However, THF peroxides have not yet been detected by experiment. Light accelerates the reactions. Also, the nature of the peroxide formed depends on the energy of the incident light. In daylight, the hydroperoxide is preferentially formed (isolated by Criegee [1]). On exposure to ultraviolet radiation of greater energy, other peroxides of unidentified structures are formed.

Like other peroxides, THF peroxides are unstable. They decompose in stages to yield high-boiling organic acids. If contact with atmospheric oxygen is unimpeded, dynamic equilibrium is established between reformation and decomposition of the peroxides.
To the best of our knowledge, the equilibrium concentration is less than 2%.

In a closed system with a limited supply of oxygen, peroxides cannot be formed after the oxygen has been consumed. The peroxide that is formed during this period decomposes with time. Consequently, unstabilized THF may be almost peroxide-free after long storage periods despite peroxide formation in the initial stages.

To maintain the quality of fresh production, THF must not come in contact with oxygen. Deterioration of quality can be identified by an increase in the residue on evaporation, as determined in test method DIN 53 172. It may also be observed by an increase in color.

| Product Specification | Value | Test Method |
|---|---|---|
| Assay, % minimum | 99.9 | gas chromatography* |
| Water, % maximum | 0.03 | DIN 51 777, Part 1 |
| Platinum-cobalt color, maximum | 10 | ISO 6271 |

*See Page 8 for the GC conditions

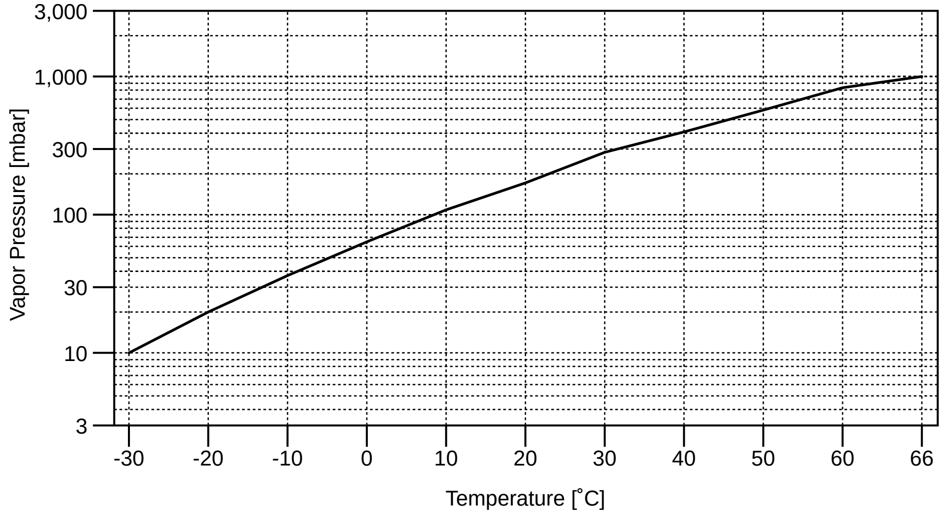
# Chemical and Physical Properties

**Physical Data**

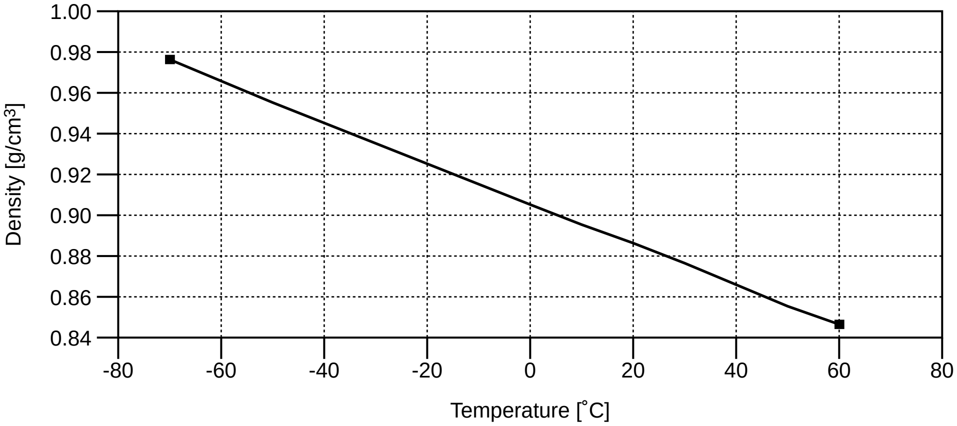
A large majority of the data provided below was compiled from the literature. Some data have been supplemented by mathematical methods.

| Tetrahydrofuran Properties | | |
|---|---|---|
| Synonym | tetramethylene oxide | |
| Abbreviation | THF | |
| Formula | $C_4H_8O$ | |
| CAS Registry No. | 109-99-9 | |
| Boiling range at 1,013 mbar, °C (95% vol.; 2-97 ml) | 65.5 – 66.5 | |
| Density (DIN 51 757), g/cm$^3$ | 0.886 – 0.888 | |
| Refractive index $n_D^{20}$ (DIN 53 491) | 1.406 – 1.408 | |
| Molar mass, g/mol | 72.107 | |
| Solidification point at 1,013 mbar, °C | -108 | |
| Vapor pressure at 1,013 mbar | T (°C) | P (mbar) |
| | -30 | 9.9 |
| | -20 | 19.5 |
| | -10 | 36.3 |
| | 0 | 63.9 |
| | 10 | 107 |
| | 20 | 173 |
| | 30 | 268 |
| | 40 | 402 |
| | 50 | 586 |
| | 60 | 831 |
| | 66 | 1013 |
| Antoine constants<br>$\ln P = A - B / (C + T)$,<br>with P in bar and T in °C | A = 9.49680<br>B = 2773.14<br>C = 226.44 | |
| Critical data | | |
| Critical temperature ($T_c$), °C | 267 | |
| Critical pressure ($P_c$), bar | 51.3 | |
| Critical density ($\rho_c$), g/cm$^3$ | 0.322 | |
| Critical volume ($V_c$), cm$^3$/g | 3.106 | |

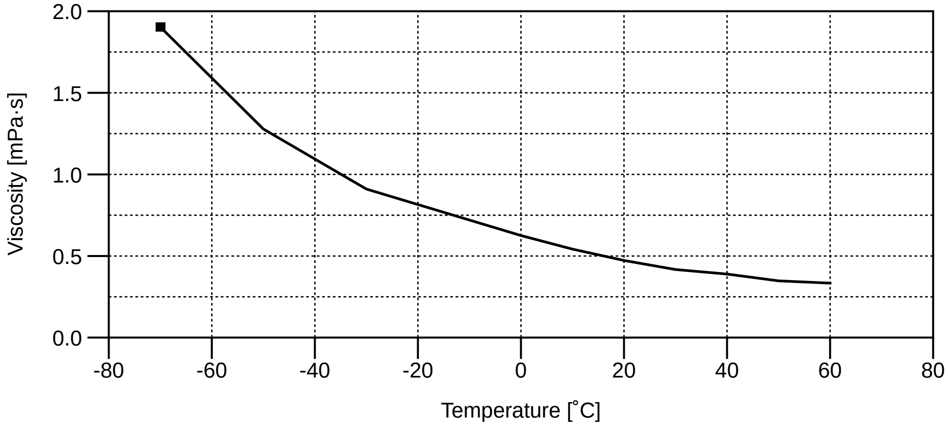
# *Chemical and Physical Properties*



**Vapor Pressure**



**Density**



**Viscosity**

# Chemical and Physical Properties

**Examples of solvents with which THF does not form azeotropes are:**

trans-1,2-Dichloroethylene

Ethylene glycol

2-Nitropropane

Isopropanol

Tetrahydrofurfuryl alcohol

Methyl borate

Methanol/ethylene glycol

Methanol/trimethyl borate

| T (°C) | Density $\rho$ (g/cm3) | Viscosity $\eta$ (mPa·s) | Surface tension $\sigma$ (mN/m) | Dielectric constant $\varepsilon$ |
|---|---|---|---|---|
| -70 | 0.9767 | 1.91 | — | 11.6 |
| -50 | 0.9560 | 1.28 | — | 10.4 |
| -30 | 0.9354 | 0.92 | — | 9.4 |
| 0 | 0.9052 | 0.61 | 30.8 | 8.2 |
| 10 | 0.8953 | 0.54 | 29.6 | 7.9 |
| 20 | 0.8855 | 0.48 | 28.4 | 7.6 |
| 30 | 0.8758 | 0.43 | 27.3 | 7.3 |
| 40 | 0.8661 | 0.39 | 26.1 | 7.0 |
| 50 | 0.8565 | 0.36 | 24.9 | 6.8 |
| 60 | 0.8470 | 0.33 | 23.7 | 6.6 |

| T (°C) | Specific Heat Cp [kJ/(kg K)] | Thermal Conductivity $\lambda$ [mW/(m K)] |
|---|---|---|
| 0 | 1.723 | 150.7 |
| 10 | 1.727 | 145.8 |
| 20 | 1.765 | 140.7 |
| 30 | 1.822 | 135.6 |
| 40 | 1.884 | 130.6 |
| 50 | 1.935 | 125.8 |
| 60 | 1.959 | 121.4 |

| | |
|---|---|
| Heat of formation ($\Delta H_f$) at 25°C, kJ/kg | -3,000 |
| Latent heat of vaporization ($\Delta H_v$) at 1,013 mbar, kJ/kg | 435 |
| Heat of combustion ($\Delta H_c$), kJ/kg | 35,141 |
| Latent heat of melting, kJ/kg | 118 |
| Net calorific value, kJ/kg | 32,270 |
| Dipole moment ($\mu$), D | 1.75 |
| Evaporation rate (DIN 53 170; ether = 1) | 2.3 |
| Solubility in water at room temperature | Freely miscible in water |

**Hansen solubility parameters at 25°C:**

$\delta_d = 16.8\ (\mathrm{mPa})^{1/2}$ Conversion Factor: $1(\mathrm{Cal/cm^3})^{1/2} = 2.0455\ (\mathrm{mPa})^{1/2}$
$\delta_p = 5.7\ (\mathrm{mPa})^{1/2}$
$\delta_h = 8.0\ (\mathrm{mPa})^{1/2}$
$\delta_t = 19.4\ (\mathrm{mPa})^{1/2}$

**Binary azeotropes:**

| THF (% wt) | Azeotrope with | (% wt) | b.p. (°C) (at 1,013 mbar) |
|---|---|---|---|
| 94.7 | Water | 5.3 | 64.0 |
| 34.5 | Chloroform | 65.5 | 72.5 |
| 69 | Methanol (984 mbar) | 31.0 | 60.7 |
| 55.5 | cis-1,2-Dichloroethylene | 44.5 | 69.8 |
| 46.5 | n-Hexane | 53.5 | 63.0 |

# *Solubility*

The bulk of the data submitted in the following table originates from single measurements at room temperature. For instance, a plastic is still listed as soluble in this table if the solution obtained is highly viscous or gel-like. The information is submitted solely as a guide and should be used only as a starting point for selecting materials to be tested in specific application trials.

**Legend**

**+** = soluble
**+o** = sparingly soluble (swollen)
**o** = insoluble/resistant

| | | |
|---|---|---|
| Poly(vinyl chloride) | | |
| Vinoflex® products | | **+** |
| Vinyl chloride copolymers | | |
| Laroflex® MP | | |
| Lutofan® products | | **+** |
| Poly(vinylidene chloride) (PVDC) | | **+** |
| Poly(vinyl acetate) | | **+** |
| Poly(vinyl propionate) | | **+** |
| Propiofan® products | | **+** |
| Poly(vinyl ethers) | | |
| Lutonal® M 40, A 25 & A 50 | | **+** |
| Polyethylene | | |
| Low-density Lupolen® | | |
| (0.918 - 0.930 g/$cm^3$) | @ 20 °C | **+** |
| | @ 60 °C | **+** |
| High-density Lupolen | | |
| (0.9 - 0.960 g/$cm^3$) | @ 20 °C | **+o** |
| | @ 60 °C | **+** |
| Lupolen V 3510 K | | |
| (ethylene/vinyl acetate copolymer) | | |
| | @ 20 °C | **+** |
| | @ 60 °C | **+** |
| Polyisobutylene | | |
| Oppanol® B products | | **+** |
| Polyacrylates | | |
| Acronal® 4F, 4L, & 700L | | **+** |
| Larodur® resins | | **+** |
| Lumitol® resins | | **+** |
| Polymethacrylates | | **+** |
| Polyamides | | |
| Ultramid® A | | **o** |
| Ultramid B | | **o** |
| Ultramid S | | **o** |
| Chlorinated paraffins | | **+** |
| Fluorinated hydrocarbons (PTFE) | | **o** |
| Styrene polymers | | |
| Suprapal® LG | | **+** |
| Suprapal AP products | | **+** |
| Polyurethanes | | |
| Solubility depends on raw materials and the production method. Details should be obtained from the individual manufacturers' literature. | | |

| | |
|---|---|
| Polyester resins | |
| Palatal® resins | **+** |
| Unmodified alkyd (phthalate) resins | |
| Phtalopal® PP & SEB | **+** |
| Cyclohexanone resins | |
| Laropal® K 80 | **+** |
| Urea-formaldehyde resins | |
| Plastopal® resins | **+** |
| Melamine-formaldehyde resins | |
| Luwipal® resins | **+** |
| Phenol-formaldehyde resins | **+** |
| Epoxy resins | |
| Aromatic | **+** |
| Aliphatic | **+** |
| Alkyd resins modified by oils or fatty acids | **+** |
| Natural resins | |
| Rosin | **+** |
| Ester gums | **+** |
| Dammar | **+** |
| Manila copal | **+** |
| Shellac | **+** |
| Drying oils | **+** |
| Plasticizers | |
| Palatinol® products (phthalates) | **+** |
| Plastomoll® DOA & DNA (adipates) | **+** |
| Palamoll® 646, 644 & 632 (polyadipates) | **+** |
| Plastigen® G (plasticizing urea resin) | **+** |
| Castor oil | **+** |
| Tritolyl phosphate | **+** |
| Cellulose derivatives | **+** |
| Natural rubber, unvulcanized | **+** |
| Chlorinated rubber | **+** |
| Cyclized rubber | **+** |

# Methods of Analysis

## 1. Gas Chromatography (GC)

Reliable results for the gas chromatographic assay can be obtained in practice under the following conditions:

| | |
|---|---|
| Column: | WCOT (fused silica) coated with DB 1; 1µm thickness; 30 meters in length; inner diameter 0.25 mm |
| Temperatures: | Injector: 200˚C |
| | Column heater: Initially heat for 5 minutes at 70˚C; then heat up at 20˚C/min. to 180˚C. |
| | Detector: 250˚C |
| Detector: | FID |
| Carrier gas: | Helium |
| Evaluation: | Percentage weight (n-octane as internal standard) |

## 2. Other Methods

The other properties listed under the heading “Product Specification” on Page 3 were determined by the methods indicated in that table.

## 3. Determination of the Peroxide Content of THF

### Method I: Semiquantitative

The sticks for the Merkoquant Ether Peroxide Test (Catalog No. 10011) produced by E. Merk, Darmstadt, Germany, allow a rapid, semi-quantitative identification of peroxide with the aid of a color scale. The gradations on the color scale are 0, 5, 60, 250 and 500 ppm of ether peroxide. The sensitivity can be increased somewhat by immersing the stick more than once in the THF.

### Method II: Titration with Potassium Iodide

This method is used frequently because it accounts for all active oxygen, i.e., hydroperoxides and other peroxides. If certain precautions are taken (see below), the limit of detectability is on the order of 1 ppm active oxygen. The determination is comparatively simple: the active oxygen released by a peroxide in an acid medium oxidizes iodide to iodine, which is then titrated against a sodium thiosulphate solution using a starch indicator.

The following labware and reagents are required for this method of determination:

- Two Erlenmeyer flasks (250 ml) with two-neck ground glass stoppers and gas inlet tube.
- Two burettes (50 and 10 ml) with 0.1 ml scale divisions.
- Glacial acetic acid, analytical grade.
- Potassium iodide, purest.
- $CO_2$ in cylinder (purified).
- .1N and .02N sodium thiosulphate solutions.

Since peroxides may reform or decompose, the samples should be examined as soon as possible and must be maintained under an inert gas.

The procedure for the determination of the peroxide content is as follows:

- Place 30 ml glacial acetic acid into each Erlenmeyer flask.
- Purge the flasks for five minutes with $CO_2$.
- Add approximately 0.5 – 1.0 g potassium iodide to each flask.
- Add the THF sample (up to 50 g) to one of the two flasks.
- Both flasks are stoppered, swirled to mix the contents and set aside in the dark for two hours.
- After the reaction has been completed, 50 ml water is run into each flask and the contents are titrated against a .1N or .02N sodium thiosulfate solution with a starch indicator. The titer of the blank should not exceed 0.1 ml of the .02N solution.
- If more than 20 ml of the .1N solution are used, the determination should be repeated with a smaller THF sample.
- The amount of peroxide present is determined by:

  1 ml .1N solution = 0.80 mg peroxide oxygen

  1 ml .02N solution = 0.16 mg peroxide oxygen

# *Methods of Analysis*

Normally, the iodide is in the form of the potassium salt, but some prefer the sodium salt. In the method described above, sodium iodide can be used in place of the potassium iodide in glacial acetic acid, with the result that a solution with a higher iodide concentration is obtained. However, this is not required for THF because the hydroperoxide is very reactive.

High concentrations of acid must be avoided in the determination of the peroxide. Oxygen must be excluded by working in an atmosphere of very pure carbon dioxide or nitrogen.

As a general rule, the more acidic the specimen to be titrated, the more inaccurate is the iodometric method. In acidic solutions, the equilibrium between the iodide and the hydrogen iodide is displaced in the direction of the hydrogen iodide with increasing hydrogen ion concentration. Hydrogen iodide can be oxidized comparatively easily to iodine. The concentration of acid in the specimen and in the blank should be kept as low as possible. Otherwise, the active peroxide content obtained for the solution of the specimen (expressed in milliliters of thiosulphate) represents the difference between two high numbers. Although the error may be negligible, if the amounts of peroxide are large and the analysis is intended only as a guide, its gravity increases as the peroxide content decreases.

**Method III: Colorimetric Determination With Titanyl Sulphate Solution**

Hydroperoxides react with titanyl sulphate solution to form yellow titanyl peroxyions. The coloration is determined photometrically.

The following reagents and labware are required for this method of determination:

- Reagent solution: 1% solution of titanium as titanyl sulfate in 10% aqueous sulphuric acid.
- Solvent blend: acetone dist. and methanol dist., 1:1.
- Photometer suitable for measurements at 436 mm.
- 4 cm coulette.
- Two 100 ml measuring flasks.
- 25 ml and 50 ml pipettes.

The procedure for determination of the peroxide content is as follows:

- THF is pipetted under nitrogen into the two 100 ml measuring flasks filled with nitrogen – 25 ml into one flask and 50 ml into the other.
- The contents of both flasks are then made up to approximately 98 ml with the solvent blend.
- Two ml of the reagent solution are added to each flask, bringing the volume in each flask to 100 ml.
- The contents of each flask are thoroughly mixed and allowed to stand in the dark for one hour.
- The absorbance of the yellowed solution is measured at 436 mm in the coulette against that of a blank.
- The colorimeter reading is recorded and used to determine the amount of oxygen from the calibration curve.
- The amount of peroxide oxygen is calculated from the following:

peroxide oxygen, ppm = (Amount of oxygen from Calibration curve, mg)

(0.888) (Volume of sample, ml)

# Applications

Tetrahydrofuran distilled pure has many applications as a solvent, reaction medium or starting product for syntheses. Only a few of the many examples of its usefulness are presented below.

### Coatings

Artificial leather: PVC or polyurethane spread-coating systems contain THF alone or in blends with other solvents.

Magnetic tapes: The abrasion resistance of video, computer or audio tapes can be improved by applying coatings derived from polyurethane or PVC in which the solvent phase is a blend of THF and toluene.

Cellophane: The mechanical strength, impermeability to water vapor, heat-sealability and printability of cellophane can be improved by applying coatings formulated from poly(vinylidene chloride) (PVDC), in which the solvent phase is a blend of THF and toluene.

### Adhesives

Tetrahydrofuran is suitable for the production of PVC adhesives for rigid PVC. It is used as a swelling agent for bonding plasticized PVC film and for fabricating PVC pipe systems. In both cases, the evaporation rate can be regulated by blending the THF with another solvent, such as cyclohexanone.

### Specialty Coating Systems

By virtue of its excellent solvent power, THF allows the preparation of highly concentrated solutions of various polymers. These solutions can be diluted to the appropriate final concentration by adding thinners. Although THF evaporates rapidly, films formed from its solutions have very minimal tendency toward blushing during drying.

### Reaction Medium

Tetrahydrofuran is a reaction medium, used primarily by the pharmaceutical industry, e.g., in Grignard syntheses or lithium aluminum hydride reductions. In fact, it is the only medium in which many Grignard compounds can be obtained. By virtue of its good solvent power for alkali metals, THF is a useful reaction medium for the production of organometallic compounds.

Anionic polymerization reactions can be carried out in THF as well.

### Extractant

Some drugs, e.g., alkaloids, can be obtained in the pure form from their natural or synthetic precursors by extraction with THF. Also, impurities such as fat, wax or substances with a high molecular mass can be removed from compounds that are insoluble in THF.

### Starting Material for Syntheses

Tetrahydrofuran is the starting material for a number of syntheses. For instance, ethers with a high molecular mass and chains of various lengths can be obtained by polymerization. The oxygen in the pentagonal ring can be replaced by nitrogen or sulfur to yield other five-membered heterocycles such as tetrahydrothiophene or pyrrolidine. The ring can be cleaved with halocarbons, e.g., 1,4-dihalobutane, or by oxidation (succinaldehyde and butyrolactone).

# Transportation, Storage and Handling Precautions

## A. Fire

THF is a highly flammable material and has been designated as a Class 1B flammable liquid by the National Fire Protection Association (NFPA). See NFPA diamond for THF on Page 15. The flash point and other safety data are as follows:

| | |
|---|---|
| Flash point, ˚C (ASTM Test Method D56) | -21.5 |
| Flammability limits (volume %) | 2.3 – 11.8 |
| Autoignition temperature, ˚C (closed cup) | 215 |
| Electrical conductivity, ohm/cm | |
| (20˚C) | $0.15 \times 10^{-10}$ |
| (23˚C) | $9 \times 10^{-10}$ |
| (25˚C) | $1.5 \times 10^{-8}$ |
| Temperature category for use in electrical equipment (DIN VDE 0165) | T3 |
| Density of vapor (air = 1) | 2.5 |
| Saturation concentration at 20˚C (calculated), $g/m^3$ | 511.5 |

Operational procedures should be designed to exclude atmospheric oxygen whenever possible. All handling facilities and equipment for THF should be designed to minimize the probability of fire and must be equipped with proper firefighting equipment designed to combat Class 1B fires. Buildings for the storage and use of THF should be fire-resistant. Although water is not effective in extinguishing THF fires, all areas should be equipped with water sprinklers to protect equipment. Only non-sparking tools should be used for opening and closing equipment and for making and breaking equipment connections. The accumulation of electrostatic charges must be avoided by thoroughly grounding all conductive parts in production units, storage facilities and drum filling plants.

Fires can be extinguished with water fog, alcohol foam or dry chemical extinguishing media. Dry chemical is the recommended portable extinguisher for extinguishing small THF fires. Alcohol-based foam is recommended for larger fires. $CO_2$ can be effective when used by a skilled firefighter. Use caution when applying water, as very low concentrations of THF are still flammable. For instance, a solution of THF in water is flammable down to a concentration of only 0.3%. Process equipment exposed to flames should be cooled with water until well after any fire has been extinguished. If there is any sound from a venting safety device or any discoloration of the storage tank due to fire, leave the area immediately. All nonessential personnel should be cleared of the area during a fire. Personnel need to stay upwind of the fire and out of low areas (such as runoff to sewer and drainage). Self-contained breathing apparatus (SCBA) and structural firefighter's protective clothing will provide limited protection in the case of fire emergency.

For further information on precautionary measures, please refer to your supplier's Material Safety Data Sheet (MSDS).

**Suggested precautions to minimize the hazard of fire or explosion:**

- Locate handling and safety equipment in an area designated for flammable liquids.
- Specify proper electrical equipment and adequate grounding for static electricity.
- Inspect equipment and storage facilities regularly.
- Correct any leaks or potential leaks in equipment immediately.
- Maintain adequate ventilation and air change in the working area. Regularly or continuously test any area where THF vapors may accumulate with a flammable gas monitor.
- Design proper facilities to handle any accidental spill or fire.
- Use non-sparking tools in the work area.
- Provide adequate fire extinguisher and firefighting equipment, including automatic sprinklers in storage and work areas.

# *Transportation, Storage and Handling Precautions*

### B. Peroxide Formation

As with many other organic solvents, small amounts of peroxide may form in THF following prolonged contact with oxygen or air. The peroxide formulation is accelerated by exposure to light. However, this reaction can be inhibited by stabilizers. The storage tank should be padded with a nitrogen blanket, at a pressure of 30 mbar. This will exclude oxygen from the vapor space and prevent the formation of peroxides. The THF peroxides that do form will decompose when heated; but under no circumstances should THF solutions be distilled to dryness. If there is more than 0.05% peroxide present, the peroxide must be destroyed prior to distillation. If the peroxide concentration is 1% or more, the THF may no longer be used and must be destroyed by incineration.

The THF peroxide can be destroyed by agitating the THF with caustic soda. If flake caustic is used, one should use 5 lbs caustic per 100 lbs THF. If a 73% caustic solution is used, one should use 15 lbs caustic per 100 lbs THF. However, if the peroxide content is greater than 0.5%, the caustic (flake or solution) should be added slowly to prevent a runaway reaction and the accompanying sharp temperature increase. Once the peroxide is destroyed, the THF can be decanted and dried.

Once a drum has been opened and some portion of the contents removed, the shelf-life becomes limited, even if the nitrogen blanket is restored. For this reason, the remaining contents in the drum should be used as soon as possible. Eliminating peroxides with alkali has proved successful in practice. Smaller amounts of tetrahydrofuran for laboratory tests can be freed from peroxides before distillation by means of copper(I) chloride, iron(II) sulfate or another reducing agent and subsequently distilled over lithium aluminum hydride ($LiAlH_4$).

Examples of products on the market for the elimination of peroxides in general and THF peroxides in particular are Perex-Kit® (E. Merck)* and basic $Al_2O_3$ (ICN Biomedicals)**. They are preferably used in the laboratory.

### Hazards caused by THF peroxide

The only acute hazard in handling THF containing peroxide arises if the THF evaporates rapidly thereby concentrating the peroxides. This situation is most likely to arise during distillation. However, laboratory experiments have shown that, despite substantial peroxide content in the THF, heavy blows and vigorous shaking do not give rise to explosive decomposition if the product is stored under normal conditions, i.e., at room temperature with exclusion of light.

A check must be made to determine if any peroxide is present before any distillation process is performed with THF or preparations containing it. And any peroxide thus detected must be eliminated before distillation commences. Distillation should never be allowed to proceed to dryness; a high boiler should be added, if necessary, to prevent such.

### Stabilizers

Examples of stabilizers for inhibiting peroxide formation are hydroquinone, 3,5-di-tert-butyl-4-hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). Usually, proportions on the order of 250 mg/kg suffice to ensure stability during normal circumstances. However, although stabilizers slow down peroxide formation in THF, they do not prevent it completely. And once a peroxide has been formed, the initiation of radical reactions may proceed.

These stabilizers have high boiling points, and thus remain in the bottoms residue following any distillation. Consequently, the distillate must be restabilized if required. (Note that these stabilizers have an unpleasant odor that may persist after the tetrahydrofuran has evaporated.)

### C. General / U.S. DOT

The storage, handling and use areas for THF should be well ventilated. Spark-proof motors and tools are required. All equipment, tank cars, tank trucks and hose connections not permanently set must be grounded separately to “drain off” static electricity. The following publications are excellent references on safe practices for the storage and handling of flammable and combustible liquids:

- NFPA No. 30: Flammable and Combustible Liquid Code as adopted by the National Fire Protection Association (NFPA).
- NFPA No. 7: National Electric Code.
- API RP 521: Guide for Pressure Relief and Depressuring System by the American Petroleum Institute (API).
- API RP 2000: Venting Atmospheric and Low-Pressure Storage Tanks (Non-Refrigerated and Refrigerated) by the API.
- API RP 500A: Recommended Practice for Classification of Areas for Electric Installation in Petroleum Refineries by the API.
- API RP 540: Recommended Practice for Electrical Installations in Petroleum Processing Plants by API.
- API RP 620: Recommended Practice for Design and Construction of Large, Welded Low-Pressure Storage Tanks by the API.
- Underwriters Laboratories Standard No. 142 for steel aboveground tanks for flammable and combustible liquids.
- Underwriters Laboratories Standard No. 58 for steel underground tanks for flammable and combustible liquids.
- OSHA 1910.106: Flammable and Combustible Liquids, U.S. Dept. of Labor Occupational Safety and Health Administration (OSHA).

# Transportation, Storage and Handling Precautions

- 49 Code of Regulations on Tariff No. BOE-6000.
- Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazard Data by the International Technical Information Institute.
- "Chemical Hazards of the Workplace," Proctor & Highes, J.B. Lippincott Company.
- "Fire Prevention Handbook," NFPA.

### U.S. DOT HM-181 Rules

The United States Department of Transportation has established rules for packaging, labeling, marking and placarding of chemicals. These rules (HM-181) meet the United Nations guidelines and are in use worldwide. The DOT information provided in this brochure reflects the requirements of HM-181. For the most up-to-date information refer to your supplier's bill of lading.

### DOT Information

| | |
|---|---|
| DOT Proper Shipping Name | Tetrahydrofuran |
| Primary Hazard Class | 3 (Flammable) |
| Secondary Hazard Class | None |
| DOT Placard Required | Flammable Liquid |
| UN Number | 2056 |
| Packaging Group | II |
| E/R Guide | 26 |

In addition to the above, all applicable federal, state and local ordinances, the requirements of underwriters and insurance companies, and the rules of good safety practices should be followed carefully.

## D. Spills and Waste Disposal

In case of spills or leaks, all possible sources of ignition should be eliminated immediately. Only protected and trained personnel should remain in the area.

**A recommended procedure for handling spillage would be:**

- Assign trained personnel with proper protective equipment to clean up. Notify all appropriate authorities. Consult the OSHA Standard for hazardous waste operations and emergency response (29 CFR 1910.120). THF is a CERCLA regulated material. The Reportable Quantity (RQ) is 1000 lbs.
- Provide proper protective equipment: neoprene or nitrile rubber gloves, chemical goggles, chemical splash suit and boots. A respirator or self-contained breathing apparatus (SCBA) may be required based on the size and nature of the spill.
- Provide maximum ventilation until area is cleaned up.
- For small spills, cover with sand, sawdust and/or other absorbent material. This material should be placed in a container; the container closed, labeled and isolated for later disposal as per federal, state and local regulations.
- Larger spills should be contained and vacuumed into a vacuum truck for disposal or reprocessing. If water is used on a spill to reduce the chance of fire, the water-THF mixture can be incinerated if it is greater than 7% by weight THF in a RCRA licensed facility.

Strict attention to federal, state and local laws regarding the disposal of flammable substances should be observed.

## E. THF Recovery

THF can be recovered undecomposed from mixtures of its vapor with air or from contaminated solutions. The following remarks are intended as a brief overview.

### Recovery from Vapor Streams

The THF fraction of the vapor stream is adsorbed on activated charcoal, which is subsequently desorbed with steam or a hot inert gas. Then multi-stage distillation is run as THF forms an azeotrope with water. Therefore, the first stage, azeotropic distillation, is followed by dehydration with solid or aqueous sodium or potassium hydroxide and a final distillation stage to obtain pure THF.

Recovery by condensation or extraction is technically possible, but generally not economically feasible.

### Recovery from Contaminated Solutions

First inorganic or high-boiling organic impurities must be removed from THF solutions to avoid their deposition on column plates, heat exchangers, etc. This is achieved by distilling off all fractions with boiling points up to about 100 ˚C. The THF can then be recovered from the distillate as described above.

## F. Health Hazards

### Toxicity — General

Solvents can only be handled safely if physical and toxicological properties are understood and suitable precautions are observed. Refer to your supplier's Material Safety Data Sheet (MSDS) for the most accurate and up-to-date information.

THF is considered moderately toxic based on acute animal studies. The LD50 Oral is 3 g/kg.

# Transportation, Storage and Handling Precautions

### Acute Effects

THF is irritating to the eyes, skin and mucous membranes. It has a severe local irritating effect when allowed to evaporate on human skin, due to the defatting action exerted by the solvent.

Overexposure by inhalation, ingestion or skin contact may produce nausea, dizziness, headaches, respiratory irritation and possible skin burns. Severe over-exposure to the vapors may produce central nervous system effects such as dizziness and narcosis. THF can be detected by most people in concentrations as low as 25 – 50 ppm.

### Chronic Effects

In an animal study, rats exposed to concentrations of 1000 ppm for 4 hours/day for 12 weeks exhibited adverse liver function. White blood cell count, blood sugar level and liver function were affected at 5000 ppm.

THF was tested for carcinogenicity where the material was applied to the skin of mice twice per week over an observation period of 17.5 months. No carcinogenic effect was observed.

### G. Personal Protection and First Aid

Since THF is an eye irritant, side shield safety glasses are the minimum eye protection for handling small (laboratory) quantities. Chemical splash goggles are recommended for handling larger amounts. If THF enters the eye, flush eyes with running water for a minimum of 15 minutes and seek medical attention.

Skin contact with THF can lead to irritation. Protective clothing including gloves and aprons should be worn to prevent THF from coming in contact with the skin. Recommended types of gloves include either nitrile or neoprene. Gloves should be rinsed following use and discarded according to all applicable state and federal regulations. If skin contact does occur, wash affected areas with soap and water. Remove and launder contaminated clothing before reuse. If irritation develops, consult a physician.

If THF is ingested, do not induce vomiting as solvent aspiration could produce lung irritation. Get immediate medical attention.

THF irritates the mucous membranes of the nose and throat. Overexposure to THF vapor may produce nausea, dizziness, headache or unconsciousness. If overexposure occurs, the victim should be moved to fresh air. Aid in breathing, if necessary, and get immediate medical attention.

### H. THF Exposure Limits

The OSHA permissible exposure limit (PEL) for THF is 200 parts per million (ppm) per 8-hour time weighted average (TWA). The American Conference of Governmental Industrial Hygienists (ACGIH) also recommends a Threshold Limit Value (TLV) of 200 ppm per 8-hour time weighted average. The ACGIH Short Term Exposure Limit (STEL) is 250 ppm. A STEL is defined as a 15-minute exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the PEL or TWA.

OSHA PELs are subject to change. Consult 29 CFR 1910.1000.

# *Transportation, Storage and Handling Precautions*

**Flammability**

4. Danger: Flammable gas or extremely flammable liquid.
3. Warning: Flammable liquid Flash point below 100° F.
2. Caution: Combustible liquid Flash point of 100° to 200° F.
1. Combustible if heated.
0. Not combustible.

**Health**

4. Danger: May be fatal on short exposure. Specialized protective equipment required.
3. Warning: Corrosive or toxic. Avoid skin contact.
2. Warning: May be harmful if inhaled or absorbed.
1. Caution: May cause irritation.
0. No unusual hazard.

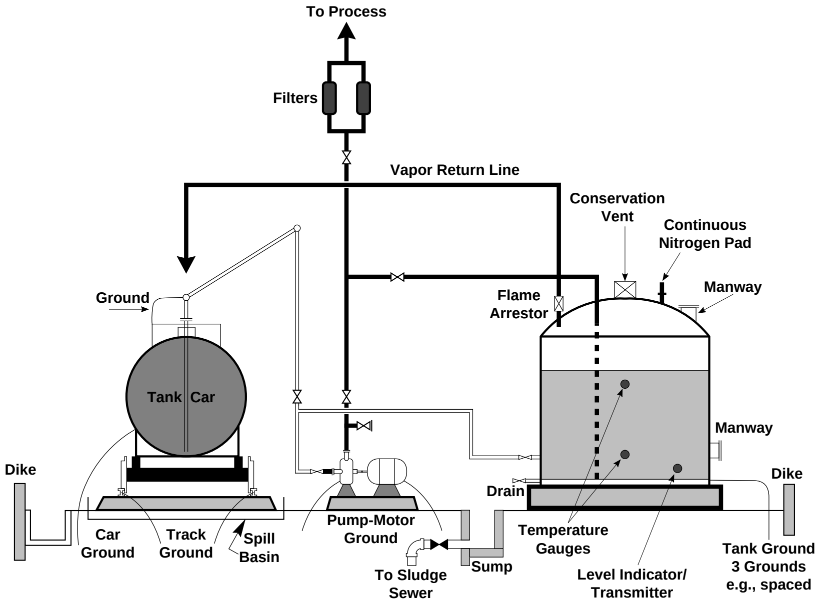
**Reactivity**

4. Danger: Explosive material at room temperature.
3. Danger: May be explosive if shocked, heated under confinement or mixed with water.
2. Warning: Unstable or may react if mixed with water.
1. Caution: May react if heated or mixed with water.
0. Stable: Not reactive when mixed with water.

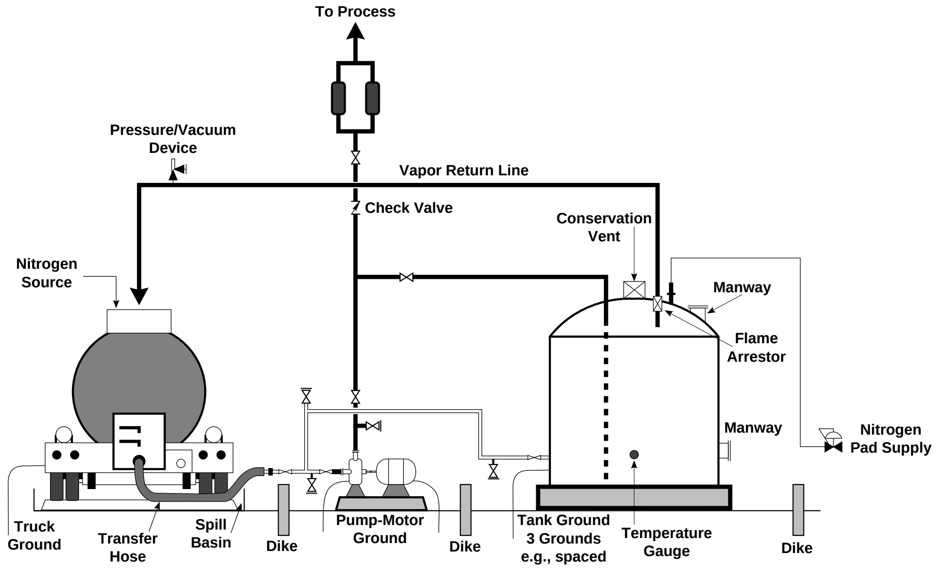
**Warning:**
Acute exposure to tetrahydrofuran may be irritating to the eyes, skin and mucous membranes. Overexposure by inhalation, ingestion or skin contact may produce nausea, dizziness, headaches, respiratory irritation and possible skin burns. Severe overexposure to the vapors may produce central nervous system effects, such as dizziness and narcosis.

# *Transportation, Storage and Handling Precautions*

**Bulk Handling Facility for THF**
**Tank Car Unloading**



**Bulk Handling Facility for**
**Truck Unloading**



# *Bulk Storage Tanks*

## A. Tanks

THF can be handled in ordinary steel equipment. However, THF discoloration can occur from rust. Storage at ambient temperatures will not affect THF (BP 66˚C, MP -108˚C). Cool storage locations and light colored paint on above-ground tanks will decrease evaporation losses.

Either vertical or horizontal tanks are suitable for bulk storage and may be located indoors, outdoors or underground. Location of the tank should be in a protected area and in compliance with governmental regulations and engineering practice for the storage of flammable liquids. The storage tank should be sized 1.5 times larger than the maximum normal receipt to avoid running out of solvent.

Above-ground tanks should be equipped with top and side manholes. Provisions should also be made for a two-inch or larger flanged bottom outlet, as well as top connections for the fill pipe, level gauge, emergency vent and flame arresting conservation vent. The outside of the tank should be protected with a white, chemical-resistant finish. The white color is for heat reflection.

Underground tanks make it difficult to detect leaks and are more difficult to install. There are strict regulations concerning leak detection on these tanks. As such, underground storage tanks are not recommended.

Tank foundations should be designed in accordance with accepted engineering practice and applicable codes. Diking of the storage area is required to prevent uncontrolled spreading, due to potential overfilling, line breakage or rupture from fire or explosion. The containment basins must be large enough to accommodate a tank's entire contents. If one basin serves more than one tank, its capacity must be sufficient to contain 110% of the contents of the largest tank plus the maximum rainfall in a 24-hour period over the last 100 years. (Reference NFPA Guidelines on Storage Tanks, #30).

Materials for tanks and pipelines were investigated by immersing 50 mm x 20 mm x 3 mm coupons in THF at 50 ˚C and atmospheric pressure. The coupons were examined every week for a total of four weeks, and the THF was replenished continuously. The linear corrosion rate in mm/year was calculated from the losses in weight. The results obtained were as follows:

| Material | Linear corrosion rate (mm/year) |
|---|---|
| Boiler plate | 0.006 |
| Stainless steel | 0.003 |
| Aluminum | 0.004 |
| Tinplate* | 0.02 |

*The layer of tin was corroded, but no signs of attack could be seen on the underlying metal.

It can be seen from this table that unalloyed steels (e.g., boiler plate), austenitic chromium-nickel steels (e.g., AISI 316 Ti) and aluminum are resistant. Tinplate should not be used, because the tin is attacked by THF.

## B. Piping

The storage tank should be equipped with a fill pipe that extends to within four inches of the bottom to prevent static electricity charges from forming. It should be provided with a gas bleed hole near the top of the dip pipe to act as a siphon break.

ASTM A53 seamless pipe with gasketed flanges is preferred. Polytetrafluoroethylene (PTFE) machined or split type gaskets are suitable up to 500˚F. However, schedule 80 pipe with 3,000 lbs screwed, forged steel fittings, assembled without pipe dope and back welded is acceptable also. All screwed connections should be sealed with a PTFE thread sealant. For corrosion protection, underground piping should be welded and coated with asphalt or wrapped in plastic adhesive tape.

Flanged, 150 psi rating, carbon steel gate valves are strongly preferred. Carbon steel ball valves may also be used. Avoid brass or bronze valves. A wedge ring of PTFE is preferred for valve stem packing.

# Bulk Storage Tanks

### C. Pumps

To prevent leakage, a canned motor pump is preferred for THF transfer. Submerged pumps are frequently used in underground storage. Self-priming centrifugal or positive displacement pumps are needed if the storage system is located below the pump.

Suitable pumps are the centrifugal types normally used in the chemical industry. Suitable materials of construction include cast iron or cast steel depending on the pressure rating, bronze or cast chromium steel (e.g., German steel Nos. 1.4312, 1.4410 and 1.4885). They should have a slip-ring seal (e.g., a combination of Europac 600 and material KATGG conforming to DIN 24 960). Canned motor pumps or canned magnetically coupled pumps are preferred to safeguard against leakage and peroxide formation.

### Seals

Examples of seals that have given good performance in practice are the chemical-resistant Klingerit® types. Polytetrafluoroethylene (PTFE) is resistant to chemicals as well. Other plastics should be tested for suitability before use.

### Lubricants

Moving parts can be lubricated with graphite or molybdenum disulfide. Since normal oil and grease are readily soluble in THF, they cannot be used.

### D. Pressure and Vacuum Relief

Storage tanks should have a pressure-vacuum relief system to prevent the buildup of pressure as THF is charged and withdrawn from the tank. A conservation type safety vent with flame arrestor is advisable. Dry nitrogen blanketing of storage tanks is required to provide moisture control. This will eliminate rusting of the interior which would cause discoloration of the THF. The nitrogen atmosphere also prevents the formation of a potentially explosive mixture in the tank vapor space and reduces the rate of THF peroxide formation.

The nitrogen blanket on the tank is maintained at a slightly positive pressure by pressure regulating valves. A regular maintenance schedule should be maintained on all vents to ensure proper operation.

### E. Testing

The bulk storage system, tanks and piping should be hydrostatically tested for leaks before introducing THF. Upon completion of the test, displace the water with nitrogen and dry thoroughly prior to charging the system with THF.

### F. Grounding Requirements

Each part of the THF bulk storage system—tank, pump, piping, platforms, tank car and tank truck—should be electrically grounded to a ground rod. This is to prevent static electricity buildup during solvent pumping operations. Jumpers should be installed at swing joints and other necessary locations to provide a low resistance ground circuit. Required ground resistances are shown below. Adequate grounding is required for drum loading stations and includes both the drum and conveyor. The minimum size for grounding cable should be AWG No. 4.

### G. Vapor Return Line

The vapor return line connects the vapor space in the tank to the vehicle being unloaded. It serves a double function, i.e., environmental protection—it prevents solvent vapor from escaping to the environment—and product quality assurance.

| Service | Maximum Allowable Resistance (OHMS) | Type of Grounding |
|---|---|---|
| Motors–Hazardous Areas | 3 | Grounding wire in conduit with circuit connectors |
| Tanks and Vessels | 2-5 | Cable to establish ground |
| Pipelines with Flammables | 2-5 | Driven rods, cable |
| Tank Cars and Rails | 2-5 | Driven rods, cable |

# *Bulk Storage Tanks*

### H. Level Indicators

A level indicator should be on each tank. Differential pressure type gauges or float type indicators with tape can be used for measuring the tank level. Level gauges can be calibrated to indicate depth, pounds or gallons in the tank. A transmitter can be connected to the level indicator and tied to one or more level gauges installed on the plant site. The installation of a high-level warning device may be advisable when the carrier unloading spot is at a distance from the tank.

Overflow prevention devices will automatically shut off the delivery of solvents into a tank whenever certain fixed levels are exceeded.

“No Load” protection ensures that the pump for discharging the contents of a tank is automatically switched off when the level in a tank falls to a certain minimum.

### I. Manhole Covers

Manholes should also be provided to allow entry into the tank for repair and maintenance. Inspection of all working parts (e.g., internal safety valves, relief vents, flame arrestors, etc.) should be made at regular intervals to detect any stoppage or plugging by corrosion or freezing.

### J. Drum Storage and Handling

Drums can be stored outside plant buildings in a cool place, protected from unauthorized access.

Recommendations of the NFPA as outlined in the National Board of Fire Underwriters Bulletin (NBFU) No. 30 should be followed.

### K. Cleaning Tanks

If it is necessary to clean or repair a THF storage tank, all traces of the solvent, both liquid and vapor, must be removed from the storage system, including the pumps, piping and associated equipment. First, the solvent is drained, then the entire system is rinsed thoroughly by filling with water and draining at least four times.

Caution: During the first water dump a flammable mixture may be present if solvent draining was poor. 0.3 vol% THF in water is sufficient to provide ignition and sustained combustion at 70˚C.

After the last water dump, the entire system is purged with air. Prior to any spark producing maintenance (welding, wire brushing, etc.), the atmosphere in the tank and in its immediate vicinity should be checked with an explosimeter to ensure the absence of explosive mixtures.

Cleaning the tank from the outside is preferred. However, if entry is required, the following additional precautions should be taken:

- All piping to the tank is to be disconnected and capped.
- A positive continuous flow of fresh air is to be provided.
- Tank oxygen content is to be tested and monitored while personnel are inside the tank.
- Tank atmosphere is to be rechecked with an explosimeter for explosive mixtures.
- Personnel entering the tank must have a safety rope and wrist straps attached. The other end of the rope is to be tended constantly by personnel outside the tank who will keep the person inside the tank under constant observation. Adequate additional help should be nearby if assistance is needed to withdraw individuals from the tank. It is mandatory that adequate personal protective equipment be worn.

The interior of the tank can be cleaned by brushing down the side walls from top to bottom and removing all debris. As an aid to cleaning, either trisodium phosphate or sodium carbonate can be used in concentrations of 0.5 lbs/gal of water. Chemical goggles, gloves and other protective clothing should be worn during this procedure. The cleaning solution can be flushed with water. Wastewater must be disposed of in accordance with appropriate regulations. Do not discharge into waterways or sewer systems without proper authorization.

Before bringing the system back on stream, it should be tested hydrostatically for leaks. Upon completion of the test, displace the water with nitrogen and dry thoroughly prior to charging with THF.

This bulletin is offered as a guide to the handling and storage of BASF THF. The information contained here is the best available to BASF Corporation and is supplied as a service to our customers.

## Call us!

| | |
|---|---|
| **U.S.** | (800) 526-1072 ext. 4753 |
| **Canada** | (416) 674-2888 |
| **Mexico** | (52) 5-325-2655 or 3656 |

## Fax us!

| | |
|---|---|
| **U.S.** | (973) 426-4752 |
| **Canada** | (416) 674-2839 |
| **Mexico** | (52) 5 661-1029 |

BASF Corporation
Chemicals Division
3000 Continental Drive–North
Mount Olive, NJ 07828-1234

www.basf.com

**We don’t make your products.
We help make them better.**

**BASF**