Chemical Safety Data Sheet SD-2

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

BENZENE

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Chemicals in any form can be safely stored, handled or used if the physical, chemical and hazardous properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment, are observed.

1960 (THIRD REVISION)

MCA MANUFACTURING CHEMISTS ASSOCIATION

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This Chemical Safety Data Sheet has been prepared as an activity of the General Safety Committee of the Manufacturing Chemists' Association. The medical information has been supplied by the Medical Advisory Committee of the Association.

TABLE OF CONTENTS

PREFACE

Benzene is a clear, colorless, flammable liquid with a characteristic odor. Acute poisoning results from inhalation of concentrations exceeding 3,000 parts per million in air. Chronic poisoning results from repeated exposures to concentrations exceeding 25 parts per million.

Benzene is classified by the Interstate Commerce Commission as a flammable liquid.

For details of the hazards of benzene and suggestions for their control, the full text of the safety data sheet should be consulted.

Chemical Safety Data Sheet

BENZENE

1960 (THIRD REVISION)

1. NAMES

Chemical name: Benzene
Common names: Benzene, benzol
Chemical formula: C_6H_6

2. PROPERTIES

2.1 GRADES AND STRENGTH (Nominal)

Industrial pure,	99% + benzene content
Thiophene free,	99% + benzene content
Nitration	99% + benzene content
Industrial 90%,	85% + benzene content
Reagent	99% + benzene content

2.2 CHARACTERISTICS

Physical state	Liquid above 5.4°C. (41.7°F.)
Explosive limits (by volume in air)	Lower 1.4%, Upper 8.0%
Flash point (Closed Cup)	−11.1°C. (12°F.)
Autoignition Temperature	580°C. (1076°F.)
Boiling Point	80.093-80.094°C. (176.2°F.)
Color	Water white
Corrosivity	Nil
Critical Pressure	47.9 atmospheres, 704 lbs./sq. in.
Critical Temperature	288.5°C. (519°F.)
Heat of Combustion. Liquid at 25°C. and constant pressure. All products of combustion as gas	9698.4 cal. per gram, 17457 Btu per lb.
Heat of evaporation at normal boiling point	94.14 cal. per gram, 169.4 Btu per lb.
Heat of fusion	30.14 cal. per gram, 54.25 Btu per lb.
Hygroscopicity	Maximum moisture absorbed, below 0.1%
Light sensitivity	Insensitive to light
Melting Point (Freezing Point)	5.4°-5.5°C. (41.7-41.9°F.)
Odor	Aromatic
Reactivity	Reactive to sulfuric and nitric acid, and the halogens in presence of catalyst.
Specific Gravity (20°C./4°C.)	0.8794
Specific Heat. Liquid at 6-60 C., 42.8-140 F.	0.419 cal. per gram, 0.754 Btu per lb.
Vapor concentration at saturation	9.9% by volume at 760 mm. and 20°C. (68°F.)
Vapor density, relative to air	2.70
Vapor pressure at 20°C. 69°F.	75.1 mm., 1.45 lbs. per sq. in.
Viscosity	0.647 centipoises at 20°C.
Threshold limit (toxicity)	25 ppm or 80 Mg/M³

3. HAZARDS

3.1 HEALTH HAZARDS

The principal hazard is from inhalation of the vapors of benzene. Acute poisoning results from inhalation of high concentrations of vapor (above 3,000 ppm. by volume in air) usually for short periods of time, often a matter of minutes. Chronic poisoning results from daily exposure to unsafe concentrations of benzene vapor over a prolonged period of time. Benzene is a mild skin irritant.

3.1.1 Warning Properties

Benzene does not have good warning properties.

3.2 FIRE AND EXPLOSION HAZARDS

Benzene is highly flammable and its vapors form explosive mixtures with air. (See 2.2.) (See 6.0 for methods of fire fighting.)

4. ENGINEERING CONTROL OF HAZARDS

4.1 BUILDING DESIGN

Equipment and vessels containing benzene should preferably be outdoors. Jacketed or heated tanks and equipment may be required to avoid freezing. If necessarily indoors, rooms should be separated from other areas by fire-resistive construction and should be provided with explosion venting.

Standard fire walls are recommended for the isolation of larger equipment and storage tanks, while partitions of 2" plaster on expanded metal lath may be used to isolate smaller equipment from other combustible materials.

Not less than two means of exit, each remote from the other, should be provided from each separate room or building in which benzene is stored, handled or used. No portion of such a room or building should be farther than 75 ft. from the nearest exit. Additional exits should be provided, depending upon the number of persons in the building (see NFPA "Building Exits Code").

All exit doors should open out in the direction of travel and should be provided with panic hardware. Fire doors should open out in the direction of travel and be of an approved type.

Operations where large quantities of benzene are used should preferably be housed in one story buildings. Provision of automatic sprinklers is recommended.

4.1.1 Explosion Venting

Explosion vents are a safeguard to reduce destructive damage to buildings, ducts, mixers, blenders, driers, and similar equipment in which flammable vapors are liable to concentrate. Approved explosion venting windows, roof and wall panels, skylights, light windows, diaphragms, etc., are available to relieve pressures caused by burning vapors. Since the required area of explosion vents depend upon such factors as the intensity of an explosion, vapor temperature, type of structure, the type of vent closure, etc., the determination of vent ratios should be made by experienced engineers and safety and fire protection specialists. (See NFPA #68, A Guide To Explosive Venting.)

4.2 EQUIPMENT DESIGN

4.2.1 Special Equipment and Design

The design of benzene piping and equipment is specialized because of the flammable properties of the material. The technical problems of designing equipment, providing adequate ventilation, and formulating operating procedures which ensure maximum security and economy can be handled best by experienced engineers and safety and fire protection specialists.

4.2.2 System Types

4.2.2.1 *Totally Enclosed Systems*

Totally enclosed systems are recommended for processes using benzene as a raw material. Opening equipment during the operation for addition or removal of materials should be avoided. A commercial combustible gas indicator is useful for periodic inspections, or to locate sources of small leaks.

4.2.2.2 *Partially Enclosed Systems*

Processes where solid materials are extracted or treated with benzene are usually totally enclosed, but part of the equipment is opened periodically to remove solids. A method of completely removing benzene vapors from residual materials before the equipment is opened should be installed. Heat or vacuum may be used for this purpose. Equipment that is periodically filled with benzene should be vented to the outside atmosphere and the vents

should be protected with flame arresters approved for this material. Flame arresters and connecting pipe exposed to temperatures at or below the freezing point require special installation to prevent plugging.

4.2.2.3 *Open Containers*

High concentrations of hazardous vapors may be discharged from open or partially closed containers. Open equipment should be avoided, but if such equipment is necessary, the working area should be protected with local mechanical ventilation to prevent hazardous vapors from escaping.

4.3 VENTILATION

Good ventilation is essential in rooms or areas where benzene is handled to prevent the accumulation of toxic or explosive mixtures. The type of ventilation needed will depend upon such factors as vapor density, dead air spaces, temperature, convection currents, wind direction, etc., which must be considered by the engineer when determining equipment location, type and capacity. If mechanical ventilation is used, sparkproof fans are desirable and electrical equipment should meet Article 500 of the National Electrical Code requirements.

4.4 AIR ANALYSIS

Analysis of the air for benzene in the work area will give a measure of the effectiveness of engineering control of the vapors. It may be performed to detect leakage of benzene vapors from equipment and also to ascertain the order of magnitude of the health and fire hazard existing in work areas. It should be kept firmly in mind that the use of the following instruments and test procedures for the detection of benzene in the air requires specially trained personnel.

Benzene vapor concentrations in air about the explosive range are most easily determined by the use of a standard combustible gas indicator. The concentration of benzene vapor may be read directly on the meter which is usually graduated in per cent of the lower explosive limit.

NOTE: Most combustible gas indicators are not sufficiently sensitive to detect a concentration of benzene which may be hazardous to health.

A specially calibrated indicator is commercially available for benzene determinations within the toxic range. Ampules which change color on exposure to benzene vapors are also commercially available and may also be employed for the detection of toxic concentrations of benzene.

4.5 ELECTRICAL EQUIPMENT

All wiring should be installed as given in Article 500 of the National Electrical Code. Motors, controls, switches, relays, lights, etc., should be explosion-proof, or as otherwise stated in this code. No heating apparatus capable of reaching 80% of the autoignition temperature of benzene should be used in connection with it. Flashlights approved for the exposure should be used.

4.5.1 **Overheating**

Automatic temperature controls are recommended for processes where benzene is heated, but even with these, close supervision is necessary because the control system may become inoperative. Low pressure steam or hot water is recommended for heating benzene or mixtures in which it is used.

4.5.2 **Static Electricity** (See National Fire Protection Association pamphlet, "Static Electricity")

Sparks from static electricity will ignite benzene vapor or air mixtures.

Benzene flowing through or being discharged from a line generates static electricity and effective grounding of the line is necessary to prevent possible ignition.

Before benzene is poured or discharged from one metal container to another, the two vessels should be grounded and electrically interconnected. All metal surfaces with which benzene comes in contact should be grounded and bonded so that the resistance to ground is not greater than five (5) Ohms. This applies to all metal equipment and piping such as tanks, mixers, stills, and pipe lines. Where drive belts are necessary, conductive "v" belts are recommended. Pulley and drive shafts should be grounded. Nonconductive drive belts are liable to accumulate an electric charge and their use should be avoided.

5. EMPLOYEE SAFETY

5.1 EMPLOYEE EDUCATION AND TRAINING

Safety in handling benzene depends, to a great extent, upon the effectiveness of employee education, proper safety instructions, intelligent supervision and the use of safe equipment.

The education and training of employees to work safely and to use the personal protective equipment or other safeguards provided for them is the responsibility of supervision. Training classes for both new and old employees should be conducted periodically to maintain a high degree of safety in handling procedures. Workers should be thoroughly informed of the hazards that may result from improper handling

of benzene. They should be cautioned to prevent spills and thoroughly instructed regarding proper action to take in case they occur. Each employee should know what to do in an emergency and should be fully informed as to first aid measures.

In addition to the above, employee education and training should include the following:

(a) Instruction and periodic drill or quiz regarding the locations, purpose, and use of emergency fire fighting equipment, fire alarms and emergency shutdown equipment such as valves and switches.

(b) Instruction and periodic drill or quiz regarding the locations, purpose and use of personal protective equipment.

(c) Instruction and periodic drill or quiz regarding the locations of safety showers, eye baths, and bubbler drinking fountains, or of the closest source of water for use in emergencies.

(d) Instructions to avoid all unnecessary inhalation of vapors of benzene and all direct contact with the liquid.

(e) Instructions to report to the proper authority all equipment failures and/or signs of illness of employees exposed to benzene.

5.2 PERSONAL PROTECTIVE EQUIPMENT

5.2.1 Availability and Use

While personal protective equipment is not an adequate substitute for good, safe working conditions, adequate ventilation, and intelligent conduct on the part of employees working with benzene, it is, in many instances, the only practical means of protecting the worker, particularly in emergency situations. One should keep firmly in mind that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area may be exposed to danger.

The correct usage of personal protective equipment requires the education of the worker in proper employment of the equipment available to him. Under conditions which are sufficiently hazardous to require personal protective equipment, its use should be supervised and the type of protective equipment selected should be capable of control over any potential hazard.

The following personal protective equipment should be used when indicated.

5.2.2 Eye Protection

5.2.2.1 *Chemical Safety Goggles*

Cup-type or rubber framed goggles, equipped with the approved impact resistant glass or plastic lenses, should be worn whenever there is danger of benzene coming in contact with the eyes. Goggles and head band to ensure maximum protection and comfort.

5.2.2.2 *Spectacle-Type Safety Goggles*

Metal or plastic rim safety spectacles with unperforated side shields which can be obtained with prescription safety lenses or suitable all plastic safety goggles may be used where continuous eye protection is desirable, as in laboratories. These types, however, should not be used where complete eye protection against benzene is needed.

5.2.2.3 *Face Shields*

Plastic shields (full length, eight inch minimum) with forehead protection may be worn in addition to chemical safety goggles where complete face protection is desirable. Chemical safety goggles should always be worn as added protection where there is danger of material striking the eyes from underneath or around the sides of the face shield.

5.2.3 Respiratory Protection

Severe exposure to benzene may occur in tanks during equipment cleaning and repairs, when decontaminating areas following spills, or in case of failure of piping or equipment. Employees who may be subject to such exposures should be provided with proper respiratory protection and trained in its use and care. Available types are described below.

NOTE: Respiratory protective equipment must be carefully maintained, inspected, cleaned and sterilized at regular intervals, and always before and after use by another person.

(a) *Self-contained Breathing Apparatus* which permits the wearer to carry a supply of oxygen or air compressed in the cylinder, and the self-generating type which produces oxygen chemically, allow considerable mobility. The length of time a self-contained breathing apparatus provides protection varies according to the amount of air, oxygen or regenerating material carried. Compressed oxygen should not be used where there is danger of contact with flammable liquids, vapors, or sources of

ignition, especially in confined spaces such as tanks or pits.

(b) *Positive Pressure Hose Masks* which are supplied by blowers requiring no internal lubrication. The wearer must be able to use the same route for exit as for entrance and must take precautions to keep the hose line free of entanglement. The air blower must be placed in an area free of contaminants.

(c) *Air-line Masks* supplied with clean compressed air are suitable for use only where conditions will permit safe escape in case of failure of the compressed air supply. These masks are usually supplied with air piped to the area from a compressor. It is extremely important that the air supply is taken from a safe source, and that it is not contaminated by oil decomposition from inadequate cooling at the compressor. The safer method is to use a separate compressor of the type not requiring internal lubrication. Pressure reducing and relief valves, as well as suitable traps and filters, must be installed at all mask stations. An alternate arrangement frequently used is high pressure breathing air from standard (200 cu. ft.) cylinders, with a demand-type valve and face piece. This arrangement may also be used with 50-100 lb. clean piped plant air, and, as an additional precaution with the demand mask, a small cylinder of compressed air may be worn for use as an emergency escape from the area. Consult a reliable safety equipment dealer for details on the proper use of Bureau of Mines approved equipment.

(d) *Industrial Canister Type Gas Masks,* equipped with full face pieces and approved by the U. S. Bureau of Mines, fitted with the proper canister for absorbing benzene vapor, will afford protection against concentrations not exceeding 2 per cent by volume when used in accordance with the manufacturer's instructions. The oxygen content of the air must not be less than 16 per cent by volume. The masks should be used for relatively short exposure periods only. They may not be suitable for use in an emergency since, at that time, the actual vapor concentration is unknown and an oxygen deficiency may exist. The wearer must be warned to leave the contaminated area immediately on detecting the odor of a harmful vapor. This may indicate that the mask is not functioning properly, that the vapor concentration is too high, that the canister is exhausted or that the mask is not properly fitted.

NOTE: Where carbon monoxide or other gas having little or no odor may be encountered in addition to benzene, the mask should be equipped with an "all purpose canister" and a "timing device" as approved by the U. S. Bureau of Mines.

(e) *Chemical Cartridge Respirators may be used* to avoid inhaling disagreeable but relatively harmless concentrations of benzene. These respirators, however, are not recommended for protection where toxic quantities may be encountered.

Caution: Filter type respirators do not offer protection against gases and are unsuitable for use when working with benzene.

5.2.4 Head Protection

"Hard" hats should be worn where there is danger from falling objects. If hard hats are not considered necessary, soft-brimmed hats or caps may be worn to give protection against liquid leaks and splashes.

5.2.5 Foot Protection

Leather safety shoes with built-in steel toe caps are recommended for workers handling drums and cans of benzene. The leather can be coated with a shoe coating compound impervious to hydrocarbon aromatic solvents. Overshoes made of synthetic rubber or other materials impervious to hydrocarbon aromatic solvents may be worn over leather safety shoes. Overshoes and shoes should be thoroughly cleaned and ventilated after contamination.

NOTE: Benzene attacks natural rubber.

5.2.6 Body, Skin and Hand Protection

Sustained or intermittent skin contact with liquid benzene may produce dermatitis at the site of contact. It is imperative that contaminated clothing be removed promptly and laundered before re-use. Affected areas of the body should be washed thoroughly with soap and water to prevent possibility of absorption of benzene. Eyes should be flushed with copious amounts of water. As a general hygienic measure, facilities for personal cleanliness should be provided and washing before lunch and at the end of the work day should be encouraged.

Clothing made and coated with plastics or other impervious material may be worn to protect the body against benzene splashes. These garments must be cleaned inside and out each time they are used.

6. FIRE FIGHTING

6.1 Benzene is a flammable liquid and as such introduces a potential fire hazard (see 3.2). However, if reasonable precautions are taken, proper type and arrangement of equipment, care and handling of the material and adequate ventilation will minimize the fire hazard. (See NFPA # 30.)

6.2 Foam is considered most effective for extinguishment of fires involving benzene. Carbon dioxide and dry chemical are also recommended as extinguishing agents. Water spray can also be used but water in a straight hose stream should not be used, except under controlled situations. Automatic sprinklers and hose lines with spray nozzles are recommended for general fire control.

6.3 Firemen fighting fires of benzene should use necessary protective equipment and breathing apparatus as would be normally used when fighting fires where there may be danger of breathing hazardous products of combustion.

7. HANDLING AND STORAGE

7.1 SHIPPING CONTAINERS

7.1.1 ICC Classification and Regulations

Benzene is classified by Interstate Commerce Commission as a flammable liquid. When shipped by rail, water or highway it must be packaged in authorized containers and shippers must comply with all ICC regulations regarding loading, handling and labeling.

7.1.2 Usual Type and Size

NOTE: Other types authorized by Section 73.119(a) of ICC Regulations for the transportation of benzene may also be used.

(a) Tank cars, Class ICC 103, 104, and 105A as detailed in Section 73.119(a) (12) of ICC Regulations.

(b) Tank trucks[1], ICC Specifications MC 300, MC 301, MC 302, MC 303, MC 304 or MC 305.

(c) Metal barrels or drums, returnable, ICC Specifications 5, 5A, 5B, 5C, or 5M, 55 gallons maximum with openings not exceeding 2.3 inches in diameter.

(d) Metal drums, single-trip, ICC Specifications 17E (5 gallons maximum) and 17C (55 gallons maximum) with openings not exceeding 2.3 inches in diameter. ICC 17E drums not over 55 gallons capacity are also authorized until further order of the Commission under conditions set forth in Section 73.119(a) (16) of ICC Regulations.

(e) Glass bottles (1 quart maximum) or metal cans (1 gallon maximum), enclosed in ICC Specification 12B fiberboard boxes.

(f) Glass bottles (1 gallon maximum) or metal cans (10 gallon maximum), enclosed in ICC Specifications 15A, 15B, 15C, 16A, 19A or 19B wooden boxes.

7.1.3 Labeling and Identification

Tank cars and box cars must bear the ICC "Dangerous" placard as specified in ICC Regulations Section 74.552. Motor vehicles, other than tank trucks transporting 2,500 pounds gross weight or more of benzene or 5,000 pounds gross weight or more of benzene and other dangerous articles, must be marked or placarded on each side and rear with the word "DANGEROUS" as specified in ICC Regulations, Sections 77.823(a). Tank trucks must be marked as required by ICC Regulations, Section 77.823(c).

Packages containing inside containers of one quart capacity or larger must be packed with filling holes up and outside container must be plainly marked "This Side Up." Refer to ICC Regulations, Section 73.401(c).

Drums and each box containing inside containers must bear the ICC red label for flammable liquids as set forth in ICC Regulations, Section 73.405(a).

ICC Regulations require that the Red label for Flammable Liquids must be removed, defaced, destroyed or covered by the prescribed ICC white "Empty" labels, before empty containers are returned to the shipper. The ICC Dangerous placards on the side and ends of cars must be removed or reversed in a manner required by ICC Regulations, Section 74.562 after emptying.

[1] Note: The term "Tank Trucks" includes tank motor vehicles of all types such as single units, semi-trailers, full trailers, etc.

The empty car must be offered to the receiving carrier either without placards, or preferably with four (4) "Dangerous-Empty" placards.

The Manufacturing Chemists' Association recommends that all containers of benzene should bear the following label in addition to or in combination with any label, warning or other statement required by statutes, regulations or ordinances:

BENZENE (BENZOL)

DANGER! EXTREMELY FLAMMABLE
VAPOR HARMFUL

Keep away from heat, sparks, and open flame.
Keep container closed.
Use only with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.
Avoid prolonged or repeated contact with skin.

POISON

Call a Physician
First Aid

7.2 HANDLING—GENERAL

7.2.1 All precautions must be taken to guard against health and fire hazards whenever benzene is handled. Spark resistant tools are recommended when the work is not wet down and the area should be posted with NO SMOKING or other appropriate warning signs as required by the operation. If leaks or spills occur, only properly protected personnel should remain in the area. Leaking containers should be removed to the outdoors or to an isolated, well ventilated area, and the contents transferred to other suitable containers. All spills should be flushed away promptly with water. Excessive quantities of benzene should not be permitted to enter drains or sewers where there is danger of vapors becoming ignited.

7.2.2 The unloading dock and the surrounding area should be considered as a Class I hazardous location as defined by the National Electrical Code. Conformance of electrical installations in the area to Division 1 or Division 2 requirements of the National Electrical Code depends upon such local conditions as proximity to other hazardous locations, congested areas, etc.; therefore, a qualified fire protection engineer or the fire insurance carrier concerned should be consulted.

7.2.3 Railroad locomotives and automotive equipment, capable of causing ignition should be excluded from the dock or vapor areas during both unloading and loading operations.

7.3 SMALL CONTAINERS

(a) The storage and handling of benzene in glass containers is not recommended. Safety cans with pouring outlets, equipped with tight-fitting caps or valves normally closed by springs and with fire baffles in the outlets should be used.

(b) All indoor storage areas should be provided with automatic sprinklers or some other adequate extinguishing system.

(c) For waste disposal of small containers of benzene and of materials contaminated with it, see section 9.

7.4 DRUMS

7.4.1 Handling

When a carload or truckload of drums containing benzene is received, the truck doors or the doors on both sides of the car, as the case may be, should

be opened to allow thorough ventilation of the vehicle before it is entered. Each shipment should be examined for leaking drums.

7.4.2 Emptying

Before drums are opened they should be supported and grounded. The latter can be done by fastening a screw clamp to the rim of the drum, and connecting this clamp through No. 4 AWG extra flexible copper wire to a water pipe or to any permanent ground.

Drums should be opened preferably with spark resistant tools, and fittings should never be struck with tools or other hard objects which may cause sparking.

To remove the body plug from a drum of benzene, the operator should wear goggles and use a bung or plug wrench. He should place the bung up, stand to one side, and face away during the operation. After the plug starts to loosen, it should be given not more than one full turn. If internal pressure exists, it should be allowed to escape to the atmosphere. Then only should the operator loosen the plug further and remove it.

The preferable safe method for emptying drums is by hand pump, or electrical pumps with explosion-proof motors. If drums are emptied by gravity, the faucets should be self-closing. The use of pressure for emptying drums is not desirable.

7.4.3 Disposal

Metal drums to be returned to the supplier must be completely drained and all openings (for bungs, plugs, etc.) must be closed tightly. ICC Regulations, concerning return labeling must be observed. Before a metal drum is scrapped, it should be steamed to remove traces of benzene vapor and rendered impossible for re-use by crushing or piercing.

7.5 TANK TRUCKS

7.5.1 Unloading

The use of tank trucks is authorized by ICC Regulations. Sections 73.115 to 73.119 inclusive and Part 77 of those regulations must be followed where applicable. Local rules, regulations and ordinances must be observed.

Ordinarily all operations concerning the tank truck and its appurtenances (fittings, pumps, hose, etc.) are the responsibility of the operator. Therefore, unloading operations should be carried out by reliable and properly instructed employees in cooperation with the driver. The shipper should be consulted for details on proper unloading procedure.

Before unloading a truck, the engine should be stopped and not started again during the entire unloading operation unless it is necessary to operate the pump by power take-off. Truck brakes should be set and, if necessary, the wheels blocked.

Before any connection or contact is made between the tank truck and the unloading line or other unloading equipment, the tank truck should be electrically grounded. All containers filled from the truck should be bonded (electrically connected) and grounded to the truck before filling operations are started.

It is preferable that truck unloading facilities be level and paved and so located that the truck can be easily and safely maneuvered to the unloading spot.

Air pressure should never be used for unloading tank trucks of benzene.

7.6 TANK CARS

7.6.1 Unloading

Because of the flammable properties of benzene the unloading of tank cars containing it is a hazardous operation. Detailed instructions regarding unloading procedures set forth in the MCA Manual Sheet TC-4 are a complete and recommended guide to assist unloaders in performing this operation safely. Shippers' instructions should always be followed and all caution markings on both sides of tank and dome should be read and observed.

See that train or engine crew accurately spots the car at the unloading line. The unloading track should be level. Brakes must be set and wheels blocked on all cars being unloaded.

It is considered good practice that derails be placed at one or both ends of the unloading track approximately one carlength from the car being unloaded, unless the car is protected by a closed and locked switch or gate.

Caution signs, described in ICC Regulation 74.561(a) (3) must be so placed on the track or car as to give necessary warning to persons approaching car from open end or ends of siding and must be left up until after the car is unloaded and disconnected from discharge connection.

Car number should be compared with that on shipping papers or invoice to verify contents of car and avoid mixing of products.

All tools and implements used in unloading car should be spark resistant and should be kept free from oil, dirt and grit.

Before manhole cover or outlet valve cap is removed, tank car must be relieved of all internal pressure by cooling tank with water or venting tank by raising safety valve or opening vent on dome at short intervals. If venting to relieve pressure will cause a dangerous amount of vapor to collect outside the car, venting and unloading must be deferred until pressure is reduced by allowing the car to stand overnight or otherwise cooling the contents.

Before any connection or contact is made between the tank car and unloading line or other unloading equipment, the tank car must be grounded in an effective manner.

Tank cars should be unloaded through the dome connection rather than through the bottom outlet. *Air pressure must never be used for this purpose.* Use of a pump is the recommended method. If the car does not have an eduction pipe, one can be inserted through the dome and the contents removed by pumping. The car should be vented through an approved (U.L.) flame arrestor during unloading. If necessary to leave a tank car unattended after unloading has been started, all unloading connections must be disconnected. All valves must first be tightly closed, and the closures of all other openings securely applied.

7.6.2 Return Precautions

As soon as the tank car is completely unloaded all valves must be made tight, the unloading connections removed, and all other closures made tight, except the heater coil and steam connections. ICC Regulations concerning return placarding should be observed.

Empty tank cars should be returned as promptly as possible, in accordance with instructions received from the shipper. The shipper's routing instructions should always be strictly followed.

7.7 STORAGE

7.7.1 Indoor Storage

When filled drums or other containers are stored indoors, they should be stored in noncombustible, well ventilated structures. Consult your state and city Fire Codes and your insurance carriers.

When filled drums or other containers are stored in separate storage rooms, trapped floor drains should be provided. The floors should be pitched to the drains and the latter should lead to a safe location and be properly trapped. In case no drains are provided, 4" curbs or a drained gutter, covered with an appropriate grill, should be constructed at door openings. In either case, only those properly protected should attempt to clean up areas in which benzene has been spilled.

All storage areas should be provided with automatic sprinklers or some other adequate extinguishing system desirable on interior storage.

Other combustibles, acids, or oxidizing materials should not be stored nearby.

7.7.2 Bulk Storage

Bulk storage of benzene poses problems such as size of vents, diking and separation distances. It is recommended that tank storage requirements be determined through consultation with qualified fire protection engineers and the fire insurance carriers concerned. What is considered general good practice is discussed below, but local conditions and regulations should be the final determining factor.

Benzene storage tanks can be located either above or below ground level. If the tank is above ground, it should be surrounded by a dike. The size of the dike is governed by local regulations. The tank can be either horizontal or vertical. Carbon steel construction is satisfactory for the tank, pipes, and accessories.

The tank should be equipped with the following:

1. A flame arrestor breather vent with a manual flame snuffer.

2. A pressure-vacuum emergency vent that can be combined with either a gauge hatch or manhole depending on the size of the vent which is in turn dependent on the tank size. This vent is usually set at ± 2 oz. pressure.

3. A cleaning manhole on the side of the tank near the bottom.

4. A fixed foam installation for fire fighting.

5. A sump to the bottom of the tank to catch water that gravitates to the bottom.

6. A tank outlet line to the pump with a dip leg into the sump.

7. A drain located on the tank outlet line for removing water.

8. Ground connection.

9. A steam heating coil for keeping the benzene above the freezing point.

10. A non-freezing type of steam trap on the steam coil outlet.

11. The above steam heating coil presents a safety problem in that it might overheat the benzene to the boiling point. To reduce the hazard of boilover, the following items are suggested:

(a) A temperature indicator near the bottom of the tank to show the temperature of the benzene.

(b) A thermostatic control on the steam flowing to the coil.

(c) An orifice in the steam line which is sized to limit steam flow to coil to a rate that could not heat the benzene to the boiling point.

(d) A blank to be inserted in the steam inlet line in the summertime when no steam is required.

Pumps are usually constructed of steel. They can be a positive displacement type with sliding plastic vanes or pistons. They can also be a centrifugal type with outboard bearings preferred. Pumps are packed with asbestos (blue African preferred) impregnated with graphite.

No cast iron valves should be used in the system because of brittleness which might result in breakage. Valves should be constructed either of all-steel or as a second choice brass mounted steel.

8. TANK AND EQUIPMENT CLEANING AND REPAIRS

This work is probably the most hazardous of all operations which involve the handling of benzene in industry. All precautions pertaining to education, protective equipment and health and fire hazards should be reviewed and understood.

8.1 PREPARATION OF TANKS AND EQUIPMENT

Tank and equipment cleaning should be under the direction of thoroughly trained personnel who are fully familiar with all of the hazards and the safeguards necessary for the safe performance of the work.

Tanks and equipment, pumps, lines and valves should always be drained and thoroughly flushed with water before being repaired. Workmen should never be allowed to attempt to repair equipment while it is in operation and the lines full. If pipe sections are to be removed and flanges opened, the lower bolts should be loosened first and although the lines have been flushed, care should be taken to avoid personal contact with the liquid draining or dripping from the equipment. All spillage from the lines or equipment should be removed immediately by flushing to the drain with large quantities of water.

The tank or equipment to be repaired should first be emptied of all liquid, and all pipes leading to and from the tank (except vents) after draining should be disconnected or blanked off.

The tank should be steamed to remove residual benzene and vapors. Steam lines should be large enough to raise the tank temperature above the boiling point of benzene and the steaming should be continued until the benzene vapors have been removed.

The tank should then be cooled, preferably by filling with water and draining once or twice. The tank should then be purged with fresh air and the air should be tested for benzene vapor by an approved method before permitting personnel to enter.

NOTE: The volatilized benzene in the steam effluent should not be of sufficient concentration to contaminate the work area in excess of safe limits. The steam and water lines should be bonded to prevent the accumulation of static electricity.

8.2 ENTERING TANK

No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested and found to be safe. Furthermore, no workman should enter a tank or vessel that does not have a manhole opening large enough to admit a person wearing a safety harness, life line, and emergency respiratory equipment. It should be ascertained that the tank or vessel can be left by the original entrance.

One man on the outside of the tank should keep the men in the tank under observation and another man should be available nearby to aid in rescue if any of the men in the tank are overcome.

A supplied air respirator or self-contained breathing apparatus, together with rescue harness and life line should always be located outside the tank entrance for rescue purposes, regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank.

Special ventilation is recommended during the entire time men are cleaning, repairing, or inspecting the tank. Ventilation can be accomplished by exhausting or removing vapors from the bottom of the tank either through its bottom openings, or by exhausting the vapors from the tank bottom by means of a large flexible duct where tanks have a top opening only. The blowers or air movers used for ventilation to ensure against oxygen deficiency should be electrically grounded. They should be cleaned frequently so that moving parts will not set up friction heat which may cause ignition of the vapor. On tanks having only a top opening, care must be exercised to ensure complete removal of vapors from the entire tank. Care must also be taken to avoid having exhaust gases recycled into the tank.

During the course of the work, frequent tests should be made to determine that the atmosphere in

the tank is being maintained within the safe range. This precaution is necessary because residues not completely removed by washing may recontaminate the tank atmosphere.

In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

8.3 EMERGENCY RESCUE

Under no circumstance should a rescuer enter a tank to remove a victim of overexposure without proper respiratory protection, a safety harness and an attached life line. The free end of the life line should be manned by an attendant located outside the tank. Another attendant should be immediately available to assist in the rescue if needed. The rescuer should be in view of the outside attendant at all times or in constant communication with him.

8.4 EXTERIOR REPAIR WORK

Exterior tank repairs, including repairs to steam coils, cutting, riveting and welding, should be permitted only after thorough cleaning and testing of the tank to make sure it is free of vapors and after a work permit has been issued by an authorized person. Repeated tests with an approved combustible gas indicator should be made to fully protect the workmen.

All outside welding or burning on tanks or equipment which have contained benzene should be done only after such containers have been completely purged with steam. Purging should be continued while the repair work is in progress. Filling clean, empty tanks with inert gas is another method which may be used in outside welding or burning.

In all cases, if repair work is interrupted, the tank atmosphere should be checked thoroughly and a new work permit issued before resumption of work.

9. WASTE DISPOSAL

9.1 The disposal of waste benzene and of materials contaminated with it is subject to Federal, state and local regulations regarding health and pollution.

9.2 Disposal of small quantities may be accomplished by removal of the waste to a safe location away from buildings or other combustible structures, then pouring the mixture on dry sand, or earth and then cautiously igniting it.

9.3 Waste mixtures containing benzene should not be allowed to enter drains or sewers where there might be danger of vapors becoming ignited.

10. MEDICAL MANAGEMENT

10.1 HEALTH HAZARDS

10.1.1 General

The principal hazard is from inhalation of the vapors of benzene. Acute poisoning results from inhalation of high concentrations of vapor (above 3,000 ppm. by volume in air) usually for short periods of time, often a matter of minutes. Chronic poisoning results from daily exposure to unsafe concentrations of benzene vapor over a prolonged period of time. A threshold limit value of 25 ppm. has been set by some groups for benzene. Benzene is a mild skin irritant.

10.1.2 Acute Toxicity

10.1.2.1 *Systemic Effects*

Breathing of high concentrations of benzene vapor may cause acute poisoning. A concentration of 3,000 parts per million in the air may cause no symptoms even up to an hour's exposure. The danger increases until at 20,000 parts per million death may follow after five or ten minutes' exposure. Early symptoms may include dizziness, headache, breathlessness and excitement. These may be followed by mental confusion, and hysterical symptoms, such as laughter, shouting, cursing and singing, generally with marked obstinacy. This stage is often called the "benzene jag." In extreme cases it may be followed by collapse, unconsciousness and death. The effects of acute exposure are essentially anesthetic and upon recovery from a single exposure it is most unlikely that there would follow any such changes as are noted in chronic poisoning, such as injury to the blood forming system.

Cases of injury due to swallowing benzene are rare. This is usually accidental, and may cause burning abdominal pain, vomiting, staggering gait, drowsiness and unconsciousness. It may later cause bronchitis or pneumonia probably from some benzene entering the air passages.

10.1.2.2 *Local Effects*

The liquid is a mild skin irritant.

10.1.3 **Chronic Toxicity**

10.1.3.1 *Systemic Effects*

Chronic poisoning results from repeated exposures to unsafe concentrations of benzene vapors (more than 25 ppm. by volume in air) over a prolonged period (weeks or months). This results in weakness and anemia (reduction in the number of red blood cells and other blood constituents) due to the effect on the blood-forming organs. These symptoms may occur some time after cessation of exposure.

10.1.3.2 *Local Effects*

Prolonged and repeated contact of liquid benzene with the skin can cause a defatting action with resulting drying out of the skin and dermatitis.

10.2 PREVENTIVE HEALTH MEASURES

Benzene should be handled in such a manner as to avoid excessive exposures to its vapors. These exposures may be caused by the continuous evaporation of benzene into the workroom atmosphere or its escape from partially closed apparatus without proper and adequate ventilation. Exposure to vapors should be limited to less than 25 ppm. by volume in air for continuous working exposure. Care should be exercised to prevent prolonged or repeated contact of the liquid with the skin.

10.2.1 **Personal Hygiene**

Employees should be instructed to minimize contact with benzene liquid and vapors. Where exposure to vapors is unavoidable, personal protective equipment such as that described in Section 5.2 should be used.

10.2.2 **Physical Examination**

10.2.2.1 ***Preplacement Examinations***

Most employees who can pass the usual preplacement physical examination (including a blood count) may be assigned to operations in which benzene is used. However, in order to protect the health of the individual, the examining physician may want to exclude people who present evidence or history of simple anemia or other blood cell diseases.

10.2.2.2 ***Periodic Health Examinations***

Periodic examinations should be made at least once a year on employees exposed to benzene. See Section 10.3, Suggestions to Physicians, regarding periodic blood counts and urine studies.

10.3 SUGGESTIONS TO PHYSICIANS

10.3.1 Since the most important effect of benzene is upon the bone marrow, which is the chief source of new blood cells, the first diagnostic evidence of "chronic poisoning" is obtained by a microscopic examination of the blood. If the individual has had sufficient exposure to benzene to produce a bone marrow effect, this will be indicated by a change in the number and character of white blood cells and decrease in red blood cells. Immature blood cells not usually found in the circulating blood may also be observed.

The following changes call for further study and follow-up of the case: white blood cells below 4,000, red blood cells less than 4,000,000, hemoglobin less than 12 grams per 100 cc. of blood, or 80 per cent by color test, blood platelets less than 100,000 per cmm., differential count of less than 50 per cent polymorphonuclear white cells, and the presence of more than a very few immature blood cells.

10.3.2 **Urine Sulfate Test**

In cases with unsatisfactory blood findings, the urine sulfate test may give useful information. This test is not a diagnostic test but is a measure of the degree of the current benzene exposure, as of the day of the test. The test should be taken during exposure or within two hours of exposure. It is not a measure of degree of benzene poisoning nor of blood changes present. Determinations of the ratio between inorganic and organic sulfates is obtained by dividing the amount of the former by the amount of the latter. Interpretation and significances may be given as follows:

Urine Sulfate Ratios	Benzene Exposure	Precautions Indicated
75% - 95%	None	Normal range of sulfates.
50% - 75%	Slight	Such values occasionally noted are not significant, but if repeated call for further study of exposure conditions.
25% - 50%	Unsafe	Additional control measures necessary.
0% - 25%	Dangerous	Stop exposure until control measures are improved.

10.3.3 **Oxygen Administration**

Oxygen has been found useful in the treatment of inhalation exposures of many chemicals, especially those capable of causing either immediate or delayed harmful effects in the lungs.

In most exposures, administration of 100% oxygen at atmospheric pressures has been found to be adequate. This is best accomplished by use of a face mask having a reservoir bag of the non-rebreathing type. Inhalation of 100% oxygen should not exceed one hour of continuous treatment. After each hour therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

11. FIRST AID

11.1 GENERAL PRINCIPLES

Immediate removal of the employee from further exposure is essential.

11.2 CONTACT WITH SKIN AND MUCOUS MEMBRANES

Clothing contaminated with benzene should be removed immediately.

11.3 CONTACT WITH THE EYES

If liquid benzene enters the eyes, flush thoroughly with plenty of water for at least 15 minutes. If irritation persists, secure medical attention.

11.4 TAKEN INTERNALLY

There is no specific antidote for benzene poisoning. If patient is conscious, make him vomit by giving warm salt water (2 teaspoonfuls to glass of water.) If patient does not vomit spontaneously, stimulate vomiting by sticking finger down throat. Call a physician. Keep patient warm and quiet until physician arrives. Never give anything by mouth to an unconscious person.

11.5 INHALATION

In case of unusual exposure to high concentrations of benzene vapors, call a physician immediately. Immediately remove the patient to fresh air. To prevent collapse, the patient should lie down without a pillow and be kept quiet and warm. If he is so violent that restraint is necessary, take care that in tying arms and legs, there is no interference with circulation and respiration.

If the patient is unconscious:

1. Lay the patient down, preferably on the left side with the head low. Remove any false teeth, chewing gum, tobacco, or other foreign objects which may be in the mouth.
2. If the patient is not breathing, an effective means of artificial respiration should be started at once.

If oxygen inhalation apparatus is available, oxygen should be administered but only by a person authorized for such duty by a physician.

OTHER CHEMICAL SAFETY DATA SHEETS AVAILABLE IN THIS AREA

(Date of latest available edition, as of July 1969, given in parentheses)

Acetaldehyde (1952) SD-43
Acetic Acid (1951) SD-41
Acetic Anhydride (1962) SD-15
Acetone (1962) SD-87
Acetylene (1957) SD-7
Acrolein (1961) SD-85
Acrylonitrile (1964) SD-31
Aluminum Chloride (1956) SD-62
Ammonia Anhydrous (1960) SD-8
Ammonia Aqua (1947) SD-13
Ammonium Dichromate (1952) SD-45
Aniline (1963) SD-17
Antimony Trichloride (Anhydrous) (1957) SD-66
Arsenic Trioxide (1956) SD-60
Benzene (1960) SD-2
Benzoyl Peroxide (1960) SD-81
Benzyl Chloride (1957) SD-69
Betanaphthylamine (1949) SD-32
Boron Hydrides (1961) SD-84
Bromine (1968) SD-49
Butadiene (1954) SD-55
n-Butyllithium in Hydrocarbon Solvents (1966) SD-91
Butyraldehydes (1960) SD-78
Calcium Carbide (1967) SD-23
Carbon Disulfide (1967) SD-12
Carbon Tetrachloride (1963) SD-3
Caustic Potash (1968) SD-10
Caustic Soda (1968) SD-9
Chlorine (1960) SD-80
Chloroform (1962) SD-89
Chlorosulfonic Acid (1968) SD-33
Chromic Acid (1952) SD-44
Cresol (1952) SD-48
Cyclohexane (1957) SD-68
Diethylenetriamine (1959) SD-76
Dimethyl Sulfate (1966) SD-19
Dinitrotoluenes (1966) SD-93
Ethyl Acetate (1953) SD-51
Ethyl Chloride (1953) SD-50
Ethyl Ether (1965) SD-29
Ethylene Dichloride (1947) SD-18
Ethylene Oxide (1951) SD-38
Formaldehyde (1960) SD-1
Hydrochloric Acid (1951) SD-39
Hydrocyanic Acid (1961) SD-67
Hydrofluoric Acid (1957) SD-25
Hydrogen Peroxide (1969) SD-53
Hydrogen Sulfide (1968) SD-36
Isopropylamine (1959) SD-72
Lead Oxides (1956) SD-64
Maleic Anhydride (1962) SD-88
Methanol (1948) SD-22
Methyl Acrylate and Ethyl Acrylate (1960) SD-79
Methylamines (1955) SD-57
Methyl Bromide (1968) SD-35
Methyl Chloride (1951) SD-40
Methylene Chloride (1962) SD-86
Methyl Ethyl Ketone (1961) SD-83
Mixed Acid (1956) SD-65
Naphthalene (1956) SD-58
Nitric Acid (1961) SD-5
paraNitroaniline (1966) SD-94
Nitrobenzene (1967) SD-21
Ortho-Dichlorobenzene (1953) SD-54
Paraformaldehyde (1960) SD-6
Perchloroethylene (1948) SD-24
Perchloric Acid Solution (1965) SD-11
Phenol (1964) SD-4
Phosgene (1967) SD-95
Phosphoric Acid (1958) SD-70
Phosphoric Anhydride (1948) SD-28
Phosphorus, Elemental (1947) SD-16
Phosphorus Oxychloride (1968) SD-26
Phosphorus Pentasulfide (1958) SD-71
Phosphorus Trichloride (1948) SD-27
Phthalic Anhydride (1956) SD-61
Propylene (1956) SD-59
Sodium Chlorate (1952) SD-42
Sodium Cyanide (1967) SD-30
Sodium, Metallic (1952) SD-47
Sodium and Potassium Dichromates (1952) SD-46
Styrene Monomer (1951) SD-37
Sulfur (1959) SD-74
Sulfur Chlorides (1960) SD-77
Sulfur Dioxide (1953) SD-52
Sulfuric Acid (1963) SD-20
Tetrachloroethane (1949) SD-34
Toluene (1956) SD-63
Toluidine (1961) SD-82
Tolylene Diisocyanate (1959) SD-73
1, 1, 1-Trichloroethane (1965) SD-90
Trichloroethylene (1956) SD-14
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Reprinted 8-69

PRINTED IN U.S.A.

AUG 12 1977

INSIGHT: A Report to Managers conoco

No. 77-10, August 8, 1977

PROPOSED BENZENE EXPOSURE STANDARDS CHALLENGED BY MEDICAL WITNESSES

Expert medical witnesses testifying at a Labor Department hearing that began July 19 concur that new occupational exposure standards for benzene proposed by the Occupational Safety and Health Administration (OSHA) are unnecessary because existing safety standards are adequate.

Witnesses testified that OSHA and the petroleum industry have common interests in protecting the health of the worker. The central question in setting any OSHA health standards, they said, is to find that permissible level of exposure that adequately protects worker health, while at the same time considering the necessity for the standards and the technical feasibility of achieving them.

Present OSHA standards require that worker exposure to benzene may not be more than 10 parts of benzene per million parts of air, based on an eight-hour average. The proposed new standards would reduce this to one part per million parts of air.

OSHA issued a temporary standard containing this more stringent provision on April 29, but its implementation was stayed by the U. S. Court of Appeals for the Fifth District pending review.

Also pending is a hearing on the validity of a suit filed in the Court of Appeals for the District of Columbia by the AFL-CIO. The labor union is asking for a review of the new standard which it considers "too lenient."

Benzene is a critical hydrocarbon in the manufacture of a variety of petroleum products such as detergent intermediates, synthetic rubber, plastics, and synthetic fibers. As a result, large quantities of benzene and benzene concentrates are produced in petroleum refineries and used in the petrochemical industry. In addition, benzene can occur naturally in low concentrations in some crude oils and in some finished petroleum products, including gasoline.

Exposure to benzene has been linked with leukemia, a cancer of the blood, but the petroleum industry believes that the level at which this association may take place is much higher than the exposure standards proposed by OSHA. The new standards are not necessary to protect workers' health, say industry witnesses, and they are excessively stringent, impractical, and very costly to implement -- costs that will ultimately be borne by consumers.