

Chemical Safety Data Sheet SD-75

PROPERTIES AND ESSENTIAL INFORMATION

FOR

SAFE HANDLING AND USE

OF

VINYL ACETATE

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.

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MCA

MANUFACTURING CHEMISTS ASSOCIATION

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Chemical Safety Data Sheet

VINYL ACETATE

PREFACE

Vinyl acetate is extremely flammable and forms explosive mixtures with air. At elevated temperatures such as in fire conditions, polymerization may take place resulting in violent rupture of a closed container. To prevent polymerization it is inhibited with diphenylamine or with hydroquinone.

Vinyl acetate is a chemical of low toxicity but it causes skin and eye irritation on contact.

The full text of this chemical safety data sheet should be consulted for details of the hazards of vinyl acetate and suggestions for their control.

FIRST AID — SEE PAGE 15

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Chemical Safety Data Sheet

VINYL ACETATE

1. NAMES

Chemical Name: Vinyl Acetate
Common Name: Vinyl Acetate
Formula: $\text{CH}_3\text{COOCH}:\text{CH}_2$

2. PROPERTIES

2.1 GRADES AND STRENGTH

Grade A—Diphenylamine inhibited
Grade H—Hydroquinone inhibited
Purity of Sample 99.8%

2.2 PROPERTIES AND CHARACTERISTICS

Physical State.....Liquid at ordinary temperature and pressure
Explosive Limits (by volume in air).....Lower 2.6% Upper 13.4%
Flash Point..... -5.5°C . (22°F .) Open Cup
Autoignition Temperature..... 427°C . (801°F .)
Boiling Point..... 72.7°C . (163°F .)
Color.....Clear and Colorless
Corrosivity.....Noncorrosive at normal atmospheric temperatures when moisture free
Critical Pressure.....22.4 Atmospheres
Critical Temperature..... 228.9°C . (444°F .)
Freezing Point (Melting Point)..... -92.8°C . (-135°F .)
Hygroscopicity.....None
Molecular Weight.....86.1
Odor.....Not unpleasant, sweetish smell in small quantities
Reactivity.....While inhibited "A" grade may be stored for an undetermined length of time, "H" grade recommended 60 days maximum storage.
Solubility at 20°C .,
weight % vinyl acetate in water.....1.98
Solubility at 20°C .,
weight % water in vinyl acetate.....0.96
Specific Gravity ($20/20^\circ\text{C}$.).....9338
Vapor Density (Air = 1.00).....2.97
Vapor Pressure (Reid).....3.7 lbs per sq. inch

3. HAZARDS

3.1 HEALTH HAZARDS

Vinyl acetate is a chemical of low toxicity. It can cause skin and eye irritation by contact. No cumulative or chronic effects in man have been noted.

3.2 FIRE AND EXPLOSION HAZARDS

Vinyl acetate forms flammable and explosive mixtures with air at temperatures of -5.5°C . and above. (See 2.2.)

3.3 REACTIVITY HAZARDS

Vinyl acetate vapor has been found to be reactive with certain desiccants such as silica gel or alumina gel.

3.4 POLYMERIZATION HAZARDS

Vinyl acetate is a monomer. When exposed to high heat such as in a fire, to peroxides, acetaldehyde or other impurities, it may polymerize violently. (See 7.4.2 (c).)

4. ENGINEERING CONTROL OF HAZARDS

4.1 BUILDING DESIGN

(a) Equipment and vessels containing vinyl acetate should preferably be isolated from other facilities by walls and floors of fire resistive construction.

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

(c) Not less than two means of exit should be provided from each separate room or building in which vinyl acetate is stored, handled, or used. No portions of such a room or building should be farther than 75 feet from the nearest exit. Additional exits should be provided depending upon the number of persons in the building. (See NFPA Standard #101 Life Safety Code)

(d) All exit doors, including fire doors, should open out in the direction of travel and should be provided with panic hardware.

(e) Operations where large quantities of vinyl acetate are used should preferably be processed in outdoor type structures or housed in one story buildings protected by automatic sprinkler systems.

(f) Explosion vents may be used to reduce destructive damage to buildings, ducts, mixers, blenders, driers, and similar equipment in which flammable vapors of vinyl acetate are liable to concentrate.

(g) Explosion venting windows, roof and wall panels, skylights, light windows, diaphragms, etc., may be used to minimize building damage due to explosion pressures.

(h) Since the required area of explosion vents depends 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. Consideration may be given to explosion suppression systems. (Reference: NFPA Fire Codes, Vol. 9—#68).

(i) The question of adequate spacing of chemical storage buildings from other buildings and processing equipment should be considered.

(j) A fire resistive stairwell with self-closing fire doors should be provided where hazardous operations are carried out on upper floors.

(k) The need for segregating floor drains from sanitary or process sewer systems should be considered.

4.2 EQUIPMENT DESIGN

4.2.1 Special Equipment and Design

(a) The design of vinyl acetate piping and equipment is highly 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.

(b) Relief valves and blowdown systems should discharge to a safe location.

4.2.2 System Types

4.2.2.1 Totally Enclosed Systems

Totally enclosed systems are preferable for processes using vinyl acetate as a raw material. Opening equipment during the operation for addition or removal of materials should be avoided.

4.2.2.2 Partially Enclosed Systems

(a) Processes where solid materials are extracted or treated with vinyl acetate are usually totally enclosed, but part of the equipment is opened periodically to remove solids. A method of completely removing vinyl acetate vapors from residual materials before the equipment is opened should be provided. Heat or vacuum may be used for this purpose.

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(b) For enclosed systems that are continuously or periodically pressured with inert gas from a central supply, failsafe means of preventing backup of flammable, corrosive or toxic materials into the supply system should be furnished.

(c) Equipment that is periodically filled with vinyl acetate should be vented to the outside atmosphere and the vents should be protected with flame arresters approved for this material.

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 equipped with mechanical ventilation to prevent hazardous vapors from escaping into the working area.

4.3 VENTILATION

Good ventilation is essential in rooms or areas where vinyl acetate is handled to prevent the accumulation of explosive mixtures and/or toxic concentrations. 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.

4.4 AIR ANALYSIS

(a) Analysis of the air for vinyl acetate 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 vinyl acetate vapors from equipment and also to ascertain the order of magnitude of the health and fire hazard existing in work areas.

(b) Vinyl acetate vapor concentrations in air near or within the explosive range are most easily determined by the use of a standard combustible gas indicator. The concentration of vinyl acetate vapor may read directly on the meter which is usually graduated in percent of the lower flammable limit.

4.5 ELECTRICAL EQUIPMENT

4.5.1 To help insure safe operation, wiring should be installed in accordance with Section 500 of the National Electrical Code. (NFPA #70.) Motors, controls, switches, relays, lights, etc., should be explosion-proof or intrinsically safe or as otherwise stated in this code. No heating apparatus capable of exceeding 80% of the autoignition temperature of vinyl acetate should be used. Flashlights, if used, should be a type approved by the Bureau of Mines for use in hazardous atmospheres.

4.5.2 Overheating

Automatic temperature controls and high temperature alarms are recommended for processes where vinyl acetate 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 vinyl acetate or mixtures in which it is used.

4.5.3 Static Electricity

Sparks from static electricity can ignite some vinyl acetate vapor and air mixtures.

Before vinyl acetate is poured or discharged from one metal container to another, the two vessels should be either grounded or electrically interconnected as by bonding. All metal surfaces with which vinyl acetate comes in contact should be bonded and grounded so that the resistance to ground does not exceed one million ohms. This applies to all metal and pipelines. Glass and other non-conductive piping should also be bonded. This can be accomplished by several methods. One method commonly used is to wrap braided stainless or copper wire around the pipe in about 18 inch loops. The wire should be securely fastened at each flange and grounded. Connectors are commercially available for fastening the wire to the flange. Where drive belts are necessary, conductive "v" belts are recommended. Pulley and drive shafts should be grounded. Non-conductive drive belts are liable to accumulate a static charge and their use should be avoided.

5. EMPLOYEE SAFETY

5.1 EMPLOYEE EDUCATION AND TRAINING

5.1.1 Before undertaking any training of the employees who are engaged in handling or processing vinyl acetate, the supervisor should be thoroughly familiar with the contents of this data sheet. MCA Accident Case Histories describe accidents and in-

juries that have occurred while handling or processing vinyl acetate. Safety specialists and suppliers may also be consulted.

5.1.2 Safety Review

(See MCA publication "Guidelines for Risk Evaluation and Loss Prevention in Chemical Plants")

After becoming thoroughly familiar with the hazardous characteristics of vinyl acetate, the supervisor should review each procedure stepwise where the material is to be used and preferably do this with the assistance of the workers directly involved. During the review, all danger points should be identified and the precautionary measures determined. The review should not only be concerned with the hazards of contact or exposure to vinyl acetate, but also with those associated with any aspect of the work such as container handling and equipment operation. Procedures for all foreseeable emergencies should be established including the location and operation of safety showers, fire extinguishers, alarms, etc.

During the safety review of the operations, it will become apparent that some danger points can be eliminated. Possibly additional ventilation, machine guarding or modification of the method of handling the material or containers may avoid potential hazards. Process changes, however, should never be made without the approval of those who have developed the process. In chemical processing, even a slight deviation may have disastrous results.

All significant hazards which cannot be satisfactorily guarded by rearrangement or other modification should be explained, together with the precautions to be followed, in the standard operating procedures. Preferably these safety precautions should be an integral part of the operating instructions. For example, if eye protection is required while taking a sample, the standard operating procedure might read, "Wear goggles and take sample from Still No. 000." This type of instruction is preferable to explaining to the worker the need to take a sample and in another part of standard operating procedure having a notation to the effect that he is to wear eye protection when sampling.

If there are extremely critical steps in the process where, for example, over charge or under charge may cause uncontrollable reaction, consideration should be given to making these supervisory check points. In such instances, the standard operating procedure should specify that the employee must notify his supervisor before proceeding further or, as in this example, prior to charging the material to the reactor. It then becomes the supervisor's responsibility to verify that the employee has followed the proper procedure before undertaking the critical step.

The safety review described should be repeated periodically for all chemical processing operations and always following a change in the process.

5.2 PERSONAL PROTECTIVE EQUIPMENT

5.2.1 Availability and Use

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 vinyl acetate. It is, however, in some instances the only practical means of protecting the worker, particularly in emergency situations. One should appreciate that personal protective equipment protects only the worker wearing it, and other unprotected workers in the area may be exposed to danger.

The effectiveness of personal protective equipment requires the training of workers in proper use. The following personal protective equipment should be used when indicated:

5.2.2 Eye Protection

(a) *Chemical Safety Goggles*—Cup-type plastic or rubber-framed goggles, equipped with the approved impact-resistant glass or plastic lenses, should be worn whenever there is danger of the material coming in contact with the eyes. Goggles should be carefully fitted.

Spectacle type safety glasses without side shields offer limited protection.

(b) *Spectacle-Type Safety Goggles*—Metal or plastic-rim safety spectacles with unperforated side shields may be used where continuous eye protection is desirable, as in laboratories. Spectacles, however, should not be used where complete eye protection is needed, such as when handling bulk quantities, when there is danger of splashing, and when the material is under pressure.

(c) *Face Shields*—Plastic shields (full length, 8" 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 vinyl acetate 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 air compressed in the cylinder and the self-generating type which produces oxygen chemically, allow considerable mobility. The length of time a self-contained

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breathing apparatus provides protection varies according to the amount of air carried.

(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 alternative 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 vinyl acetate vapor, will afford protection against concentrations *not exceeding 2 percent* by volume when used in accordance with manufacturer's instructions. The oxygen content of the air must not be less than 16 percent by volume. The masks should be used for relatively short exposure periods only. They are not recommended 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. Because of the

limitations outlined, use of canister masks should be restricted.

NOTE: Where other gas having little or no odor may be encountered in addition to vinyl acetate, 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 vinyl acetate vapor. These respirators, however, are not recommended for protection where toxic concentrations may be encountered.

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.

"Bump caps" are satisfactory in areas where there is little or no hazard from falling objects. They will give protection from liquid leaks and splashes.

5.2.5 Foot Protection

Leather or rubber safety shoes with built-in steel toe caps are recommended for workers handling bulk containers of vinyl acetate. Rubbers may be worn over leather safety shoes. Rubbers and shoes should be thoroughly cleaned and ventilated after contamination.

5.2.6 Body, Skin and Hand Protection

Sustained or intermittent skin contact with liquid vinyl acetate may produce dermatitis at the site of contact. It is imperative that contaminated clothing be removed promptly and laundered or thoroughly dried before reuse. Affected areas of the body should be washed thoroughly with soap and water (except the eyes). As a general hygienic measure, facilities for personal cleanliness should be provided and washing before lunch and at the end of the day should be encouraged.

Clothing made of rubber or other impervious material may be worn to protect the body against vinyl acetate splashes. These garments must be cleaned inside and out each time they are used.

6. FIRE FIGHTING

6.1 Carbon dioxide, foam and dry chemical are recommended as extinguishing agents; water spray can also be used but water should not be used in a straight stream, except under controlled situations. Automatic sprinklers and hose lines with spray nozzles are recommended for general fire control.

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

7. SHIPPING, LABELING, HANDLING AND STORAGE

7.1 SHIPPING

7.1.1 DOT Classification and Regulations

Vinyl acetate inhibited, is classified by the Department of Transportation as a "Flammable Liquid." When shipped by rail, water, or highway, it must be packaged in authorized containers and shippers must comply with all DOT Regulations regarding loading, handling, and labeling.

7.1.2 Type and Size of Shipping Containers

Authorized containers for vinyl acetate are indicated in DOT Regulations, paragraph 173.119. Containers usually used for this commodity are as follows:

7.1.2.1 DOT Spec 12B fiberboard boxes with inside containers of metal cans not over one gallon each.

7.1.2.2 DOT Spec 15A, 15B, 15C, 16A, 19A, or 19B wooden boxes with inside containers of metal cans not over ten gallons each.

7.1.2.3 DOT Spec 17E metal drums.

7.1.2.4 DOT Spec 103, 103W tank cars.

7.1.2.5 DOT Spec MC-300, MC-301, MC-302, MC-303, or MC-304 tank motor vehicles.

7.2 LABELING AND IDENTIFICATION

7.2.1 DOT Requirements

7.2.1.1 Each container must carry an identifying label or stencil (DOT Regulations paragraph 173.401(a)).

7.2.1.2 Tank cars and box cars must bear the DOT "Dangerous" placard as specified in DOT paragraph 174.541.

7.2.1.3 Each drum or box containing inside containers must bear the DOT Red Label for flammable liquids as indicated in DOT paragraph 173.405.

7.2.1.4 Packages containing inside containers of one-quart capacity or larger must be packed with filling holes up and the outside container must be plainly marked "THIS SIDE UP" as per DOT paragraph 173.401(c).

7.2.1.5 Motor vehicles and trailers other than tank trucks transporting 1,000 pounds or more gross weight of vinyl acetate must be placarded or marked at the front, rear and each side with the word "FLAMMABLE" per DOT paragraph 177.823(a)(1). If the vehicle is carrying more than one kind of dangerous article (1,000 pounds or more gross weight), it must be marked or placarded at the front, rear and each side with the word "DANGEROUS" per DOT paragraph 177.823(a)(4).

7.2.1.6 Tank trucks of vinyl acetate must be marked or placarded as specified in DOT paragraph 177.823(b) with the word "FLAMMABLE."

7.2.2 Precautionary Labeling

The Manufacturing Chemists Association recommends that all containers of vinyl acetate should bear a label as shown. The text is designed for the

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VINYL ACETATE

**DANGER! EXTREMELY FLAMMABLE
MAY POLYMERIZE VIOLENTLY UNDER FIRE
CONDITIONS OR LOSS OR REMOVAL OF
INHIBITOR
CAUSES SKIN IRRITATION**

Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.
Avoid prolonged or repeated contact with skin.
Drum should be grounded when being emptied.

FIRST AID: In case of contact, flush skin with water. Wash clothing before reuse.

FIREFIGHTING: In case of fire, use water spray, foam, dry chemical, or carbon dioxide.

SPILL OR LEAK: Flush spill area with water spray.

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product as shipped for industrial use. It should be used in addition to or in combination with any specific wording required by law. Since individual statutes, regulations, or ordinances may require that particular information be included in a label, that certain information be displayed in a particular manner, or that a specific label be affixed to a container, the use of this label will not necessarily insure compliance with such laws. Such laws include the Federal Hazardous Substances Labeling Act; Federal Insecticide, Fungicide and Rodenticide Act; and similar state and municipal legislation.

7.3 HANDLING

7.3.1 Handling—General

7.3.1.1 All precautions must be taken to guard against explosion and fire hazards wherever vinyl acetate is handled. The area should be posted with "No Smoking" signs as required by the operation. Leaking containers should be removed to the outside or to an isolated, well ventilated area, and the contents transferred to other suitable containers. All spills should be flushed away with water. Excessive quantities of vinyl acetate should not be permitted to enter drains or sewers where there is danger of the vapors becoming ignited.

7.3.1.2 The unloading dock and the surrounding area should be considered as a Class 1 hazardous location as defined by the National Electrical Code. Conformance of electrical installations in the area to Division 1 and 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 should be consulted.

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

7.3.2 Drums

7.3.2.1 Handling

When a carload or truckload of drums containing vinyl acetate 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.

7.3.2.2 Emptying

(a) 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.

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

(c) To remove the body plug from a drum of vinyl acetate, 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.

(d) The preferred method for emptying drums is by hand pump, or electrical pump with explosion-proof motor. If drums are emptied by gravity, the faucets should be self-closing. The use of pressure for emptying drums is dangerous and should be strictly prohibited.

7.3.2.3 Disposal

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

7.3.3 Tank Trucks

7.3.3.1 Unloading

(a) The use of tank trucks is authorized by DOT 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 also be observed.

(b) The operating mechanism for unloading valves or faucets should have a secondary control, remote from the fill openings and discharge faucets, for use in the event of accidents or fire during delivery operations.

(c) The control mechanism should have a fusible section which will permit valves to close automatically in case of fire.

(d) 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.

(e) The shipper should be consulted for details of proper unloading procedures.

(f) *Damage Enroute.* In case a tank truck becomes damaged enroute so that it cannot proceed safely to destination, every effort should be made to park it where it will not endanger traffic or property. The police and fire department should be notified and public warned to stay away. The truck should be parked, if possible, in a vacant lot and away from an area in which there are concentrations of people. Follow MCA Chem Card precautions as available or *contact producer* for safe disposal instructions.

(g) 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.

(h) Truck brakes should be set, the wheels blocked, and the driver out of cab.

(i) 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.

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

(k) *Air pressure should never be used for unloading tank trucks of vinyl acetate.* It is preferable to unload from the top through a dome fitting which will prevent escape of flammable vapors to the atmosphere.

7.3.3.2 Fittings

(a) The packing and lubricant for pumps, glands, etc., must be of a material recommended for vinyl acetate handling.

(b) The pump glands, flanged fittings, and valve stems may be provided with splash collars in cases where personnel would be exposed to major vinyl acetate leaks or sprays if the material should escape.

(c) Where access to the top of the tank truck is needed, the spot should be provided with stairs and platform. Non-combustible construction is preferred. Overhead loading equipment should be counter balanced.

7.3.4 Tank Cars

7.3.4.1 Unloading

(a) Because of the flammable properties of vinyl acetate, 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 recommended guide to assist unloaders in performing this operation safely.

(b) Shipper's instructions should always be followed and all caution markings on both sides of tank and dome should be read and observed.

(c) See that train or engine crew accurately spots the car at the unloading line. The unloading track should be level.

(d) Brakes must be set and wheels blocked on all cars being unloaded.

(e) It is considered good practice to place derails at open ends of the unloading track approximately one car-length from the car being unloaded, unless the car is protected by a closed and locked switch or gate.

(f) Caution signs, described in DOT Regulations, Section 174.561(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.

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

(h) All tools and implements used in unloading tank cars should be spark resistant and should be kept free from oil, dirt, and grit.

(i) Before manhole cover or outlet valve cap is removed, tank car must be relieved of all internal pressure by cooling with water or venting 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.

(j) 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.

(k) Tank cars of vinyl acetate may be unloaded through either the top or bottom outlet unless restricted by state or municipal regulations. When unloading through the bottom outlet, special precautions should be taken. Tank cars approved for bottom unloading must be equipped with valving approved by the Association of American Railroads' Committee on Tank Cars and consistent with DOT Regulations. The purpose of such valving is to contain the product and to control safely the flow during unloading. As an added precaution it is desirable, where practical

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and where conditions warrant, to apply a supplementary control in the unloading system to provide a secondary and remotely actuated closure in the event of accidents involving fire or car movement. (See NOTE.) For tank cars which are equipped only for bottom unloading but which have a suitable manway, consignees who prefer or are restricted to top unloading can use a special device which consists of a cover equipped with a flame arrester and breather vent, a vapor return connection, or a vacuum relief valve. This assembly is placed over the open manway and a pipe installed so that top unloading may be accomplished.

NOTE: Devices for shutting off liquid flow are usually incorporated in the unloading line and may include fusible links and shear sections in conjunction with mechanically, pneumatically or hydraulically actuated valves of a fail-safe type.

(l) Air pressure must never be used for unloading flammable liquids. Use of a pump is the recommended method. Consignees desiring to unload cars from the top by water displacement method or with the aid of a standard system employing an inert gas such as carbon dioxide or nitrogen as a pressure generating medium, should contact the shipper for details on unloading procedure.

(m) If necessary to discontinue unloading a tank car for any reason, all unloading connections must be disconnected. All valves must first be tightly closed, and all other closures securely applied.

7.3.4.2 Return Precautions

(a) 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. DOT Regulations Section 74.562(b) concerning return placarding must be observed.

(b) 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.

7.4 STORAGE

7.4.1 Indoor Storage

(a) When filled drums or other containers are stored indoors, they should be stored in non-combustible well-ventilated structures. When stored in separate storage rooms, trapped floor drains should be provided. The floors should be pitched to the drains and the drains should lead to safe location through proper trapping. In case no drains are provided, 4" curbs or a drained gutter, covered with appropriate grill, should be constructed at door openings. In either case, only those properly pro-

tected should clean up areas in which vinyl acetate has been spilled. All storage areas should be provided with automatic sprinklers or other extinguishing system suitable for interior storage.

(b) Oxidizing materials or other incompatible chemicals should not be stored in the same area.

(c) The storage of vinyl acetate in glass containers is to be avoided.

7.4.2 Bulk Storage

(a) The storage of vinyl acetate in above and below ground tanks poses certain problems relating to such factors as size of vents, diking, and separation distances, which depend upon other variables such as tank sizes, tank design, and tank protection. It is recommended that tank storage requirements be determined through consultation with qualified fire protection engineers.

(b) The use of an inert gas venting system may be indicated where drying devices (desiccants) are required because of possible reactivity between the vinyl acetate and the desiccant. The desiccant to be used should be checked for reactivity with vinyl acetate.

(c) Spontaneous Polymerization

Where storage of low hydroquinone stabilized monomer is under hot, moist conditions, there is a potential hazard of "spontaneous polymerization" unless further stabilization is done. A low inhibitor level could reduce the storage period of 60 days which is the maximum recommended period of storage to avoid possible polymerization.

The steps involved in "spontaneous polymerization" of vinyl acetate are as follows:

1. Auto-oxidation of the acetaldehyde impurity by the oxygen dissolved in the vinyl acetate, or at the liquid-air interface.

2. Slow decomposition of the resultant peroxide to initiate polymerization.

3. Early termination of the free radical chain by the inhibitor or by the oxygen dissolved in the monomer. NOTE: The oxygen plays a dual role. It forms the peroxide, but it also acts as a chain terminator.

4. Additional formation of acetaldehyde by hydrolysis of the vinyl acetate. Hydrolysis is promoted by normal tank breathing of moist air, and so back to steps 1-3 until neither oxygen nor inhibitor are sufficient to terminate the growing chain.

5. Heat evolution then occurs, the peroxide decomposes more rapidly, etc.

8. TANK AND EQUIPMENT CLEANING AND REPAIRS

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

8.1 PREPARATION OF TANKS AND EQUIPMENT

(a) 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.

(b) 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, all necessary personal protective equipment must be worn. The lower bolts should be loosened first and although the lines have been flushed, care should be taken to avoid personal contact with any 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.

(c) 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.

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

(e) The tank should then be cooled, preferably by filling with water and draining once or twice.

NOTE: The volatilized vinyl acetate in the steam effluent must 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.

(f) The tank should then be purged with fresh air and the air should be tested for vinyl acetate vapor by an approved method before permitting personnel to enter.

8.2 ENTERING TANK

(a) 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.

(b) 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 sparkproof and they should be cleaned frequently so that moving parts will not set up friction heat which may cause ignition of vapors. 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.

(c) 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.

(d) 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

(a) A supplied-air respirator (hose mask) 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. The air intake of the hose mask must be located in an uncontaminated area.

(b) One man stationed on the outside of the tank should keep the workmen in the tank under observation and another man should be nearby and instantly available with self-contained breathing apparatus and necessary equipment to aid in the rescue if a man in the tank is overcome. Protective clothing should be worn, if required.

(c) Under no circumstances 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

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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.

(d) If a tank cleaner or repairman is overcome by fumes, he should be removed to fresh air immediately. Artificial respiration should be applied if breathing has stopped, and a physician summoned at once.

8.4 EXTERIOR REPAIR WORK

(a) Repairs to interiors or exteriors of tanks or equipment, 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.

(b) All outside welding or burning on tanks or equipment which have contained vinyl acetate 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 empty tanks with inert gas is another method which may be used in outside welding or burning.

(c) 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 vinyl acetate by burning or discharge by drainage to natural waterways should be conducted in accordance with Federal, state and/or local regulations regarding pollution.

9.2 Provisions must be made to prevent vinyl acetate spills from entering public sewers or drains in sufficient amounts to cause explosion hazards. Connections to such sewers or drains should be provided

with separator boxes or other approved means whereby the entry of vinyl acetate is precluded.

9.3 The MCA Laboratory Waste Disposal Manual recommends the following for handling of small spills.

Eliminate all sources of ignition and flammables. Absorb the liquid on paper. Evaporate on an iron pan in a hood. Burn the paper.

10. MEDICAL MANAGEMENT

10.1 HEALTH HAZARDS

10.1.1 General

Vinyl acetate is a chemical of low toxicity. This is substantiated by animal experimentation and by many years of large volume production and use experience.

10.1.2 Acute Toxicity

There are no reported instances of organic injury from industrial exposure.

As tested in animals, vinyl acetate is approximately twice as toxic as isopropyl alcohol when given orally. Inhalation by animals gives an LC_{50} in the range 4500 ppm.

10.1.3 Chronic Toxicity

Cumulative and chronic effects and sensitization are not known to occur.

10.1.4 Toxic Effects and External Contact

10.1.4.1 Skin

Contact with the uncovered skin may cause

formation of blisters, particularly on the finger webs and on the thin skin of the under side of the wrists. If contact is covered and continuous, as from clothing wet with the chemical, severe irritation and blistering may result.

10.1.4.2 Eyes

Vinyl acetate produces significant irritation of the eyes upon contact.

10.1.5 Toxic Effects By Inhalation

High concentrations may produce anesthetic effects. This is characterized by incoordination, drowsiness and confusion. Central nervous system depression and respiratory depression may occur if exposure is extreme.

10.1.6 Toxic Effects After Oral Intake

Swallowing amounts that might be splashed in ordinary industrial handling should present no problem. The swallowing of substantial amounts may cause illness.

10.2 PREVENTIVE HEALTH MEASURES

Provision of adequate ventilation and prevention of contact with skin and eyes will prevent injury by vinyl acetate. The threshold limit value is set at 10 ppm (ACGIH-1969—tentative).

10.2.1 Personal Hygiene

Employees should be instructed to report any signs or symptoms of a substandard physical condition and receive medical attention.

Facilities for personal cleanliness should be provided.

10.2.2 Physical Examination

A standard pre-employment and periodic physical examination will be adequate for the protection

of the health of employees working with vinyl acetate. There are no known physical abnormalities or diseases that make exposure to vinyl acetate unusually hazardous.

10.3 SUGGESTIONS TO PHYSICIANS

There are no specific antidotes for vinyl acetate. If swallowed, evacuate the stomach. For contact with skin or eyes wash thoroughly with plenty of water. Treatment is symptomatic and supportive.

10.3.1 Oxygen Administration

If a person is overcome by vinyl acetate but is still breathing, oxygen should be administered by qualified personnel.

11. FIRST AID

11.1 GENERAL PRINCIPLES

Most important in the case of any exposure is quick removal. In the case of vinyl acetate exposure, this means first removing the subject from the contaminated atmosphere and insofar as possible removing the vinyl acetate from the respiratory tract, skin, eyes, or gastrointestinal tract. Give the subject fresh air by moving him to a well ventilated room and dispersing any crowd. If breathing has stopped, start artificial respiration at once. Keep the subject quiet and comfortably warm, but not hot.

Call a physician immediately, explaining briefly and clearly what has happened and the exact location of the patient. Do not give anything by mouth to an unconscious person.

11.2 SPECIFIC ACTIONS

11.2.1 Inhalation

A person showing symptoms of overexposure to vinyl acetate should be removed promptly from the contaminated area into fresh air. In case breathing has stopped, give mouth to mouth resuscitation until spontaneous respiration resumes or until mechanical oxygenated ventilation is available. Oxygen

should be given when breathing resumes as well as in cases in which there has been no interruption of respiration.

11.2.2 Skin Contact

Immediately flush with plenty of water for at least 15 minutes. All contaminated clothing and shoes should be removed at once and washed thoroughly before reusing.

11.2.3 Contact With Eyes

Immediately flush thoroughly with plenty of water for at least 15 minutes. If pain and irritation persist after this initial irrigation refer to a physician.

11.2.4 Taken Internally

If a person has swallowed more than an incidental amount of vinyl acetate, he should be made to vomit immediately. Have him drink at least a pint of warm salt water (2 tablespoons of salt per pint of water), or of warm soapy water. If necessary, the patient should be encouraged to stick his finger down his throat to induce vomiting. This procedure should be repeated at least three times and then followed by the administration of a tablespoon full of Epsom salts. A physician should be called at once.

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OTHER CHEMICAL SAFETY DATA SHEETS AVAILABLE

(Date of latest available edition, as of Nov. 1970, given in parentheses)

Acetaldehyde	(1952) SD-43	Cresol	(1952) SD-48	Ortho-Dichlorobenzene	(1953) SD-54
Acetic Acid	(1951) SD-41	Cyclohexane	(1957) SD-68	Paraformaldehyde	(1960) SD-6
Acetic Anhydride	(1962) SD-15	Diethylenetriamine	(1959) SD-76	Perchloroethylene	(1948) SD-24
Acetone	(1962) SD-87	Dimethyl Sulfate	(1966) SD-19	Perchloric Acid Solution	(1965) SD-11
Acetylene	(1957) SD-7	Dinitrotoluenes	(1966) SD-93	Phenol	(1964) SD-4
Acrolein	(1961) SD-85	Ethyl Acetate	(1953) SD-51	Phosgene	(1967) SD-95
Acrylonitrile	(1964) SD-31	Ethyl Chloride	(1953) SD-50	Phosphoric Acid	(1958) SD-70
Aluminum Chloride	(1956) SD-62	Ethyl Ether	(1965) SD-29	Phosphoric Anhydride	(1948) SD-28
Ammonia Anhydrous	(1960) SD-8	Ethylene Dichloride	(1947) SD-18	Phosphorus, Elemental	(1947) SD-16
Ammonia Aqua	(1947) SD-13	Ethylene Oxide	(1951) SD-38	Phosphorus Oxychloride	(1968) SD-26
Ammonium Dichromate	(1952) SD-45	Formaldehyde	(1960) SD-1	Phosphorus Pentasulfide	(1958) SD-71
Aniline	(1963) SD-17	Hydrochloric Acid	(1970) SD-39	Phosphorus Trichloride	(1948) SD-27
Antimony Trichloride (Anhydrous)	(1957) SD-66	Hydrocyanic Acid	(1961) SD-67	Phthalic Anhydride	(1956) SD-61
Arsenic Trioxide	(1956) SD-60	Hydrofluoric Acid	(1970) SD-25	Propylene	(1956) SD-59
Benzene	(1960) SD-2	Hydrogen Peroxide	(1969) SD-53	Sodium Chlorate	(1952) SD-42
Benzoyl Peroxide	(1960) SD-81	Hydrogen Sulfide	(1968) SD-36	Sodium Cyanide	(1967) SD-30
Benzyl Chloride	(1957) SD-69	Isopropylamine	(1959) SD-72	Sodium, Metallic	(1952) SD-47
Betanaphthylamine	(1949) SD-32	Lead Oxides	(1956) SD-64	Sodium and Potassium Dichromates	(1952) SD-46
Boron Hydrides	(1961) SD-84	Maleic Anhydride	(1962) SD-88	Styrene Monomer	(1951) SD-37
Bromine	(1968) SD-49	Methanol	(1970) SD-22	Sulfur	(1959) SD-74
Butadiene	(1954) SD-55	Methyl Acrylate and Ethyl Acrylate	(1960) SD-79	Sulfur Chlorides	(1960) SD-77
n-Butyllithium in Hydrocarbon Solvents	(1966) SD-91	Methylamines	(1955) SD-57	Sulfur Dioxide	(1953) SD-52
Butyraldehydes	(1960) SD-78	Methyl Bromide	(1968) SD-35	Sulfuric Acid	(1963) SD-20
Calcium Carbide	(1967) SD-23	Methyl Chloride	(1970) SD-40	Tetrachloroethane	(1949) SD-34
Carbon Disulfide	(1967) SD-12	Methylene Chloride	(1962) SD-86	Toluene	(1956) SD-63
Carbon Tetrachloride	(1963) SD-3	Methyl Ethyl Ketone	(1961) SD-83	Toluidine	(1961) SD-82
Caustic Potash	(1968) SD-10	Mixed Acid	(1956) SD-65	Tolylene Diisocyanate	(1959) SD-73
Caustic Soda	(1968) SD-9	Naphthalene	(1956) SD-58	1, 1, 1-Trichloroethane	(1965) SD-90
Chlorine	(1970) SD-80	Nitric Acid	(1961) SD-5	Trichloroethylene	(1956) SD-14
Chloroform	(1962) SD-89	paraNitroaniline	(1966) SD-94	Vinyl Acetate	(1970) SD-75
Chlorosulfonic Acid	(1968) SD-33	Nitrobenzene	(1967) SD-21	Vinyl Chloride	(1954) SD-56
Chromic Acid	(1952) SD-44	Nitrocellulose (Wet Types)	(1970) SD-96	Zirconium and Hafnium Powder	(1966) SD-92

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