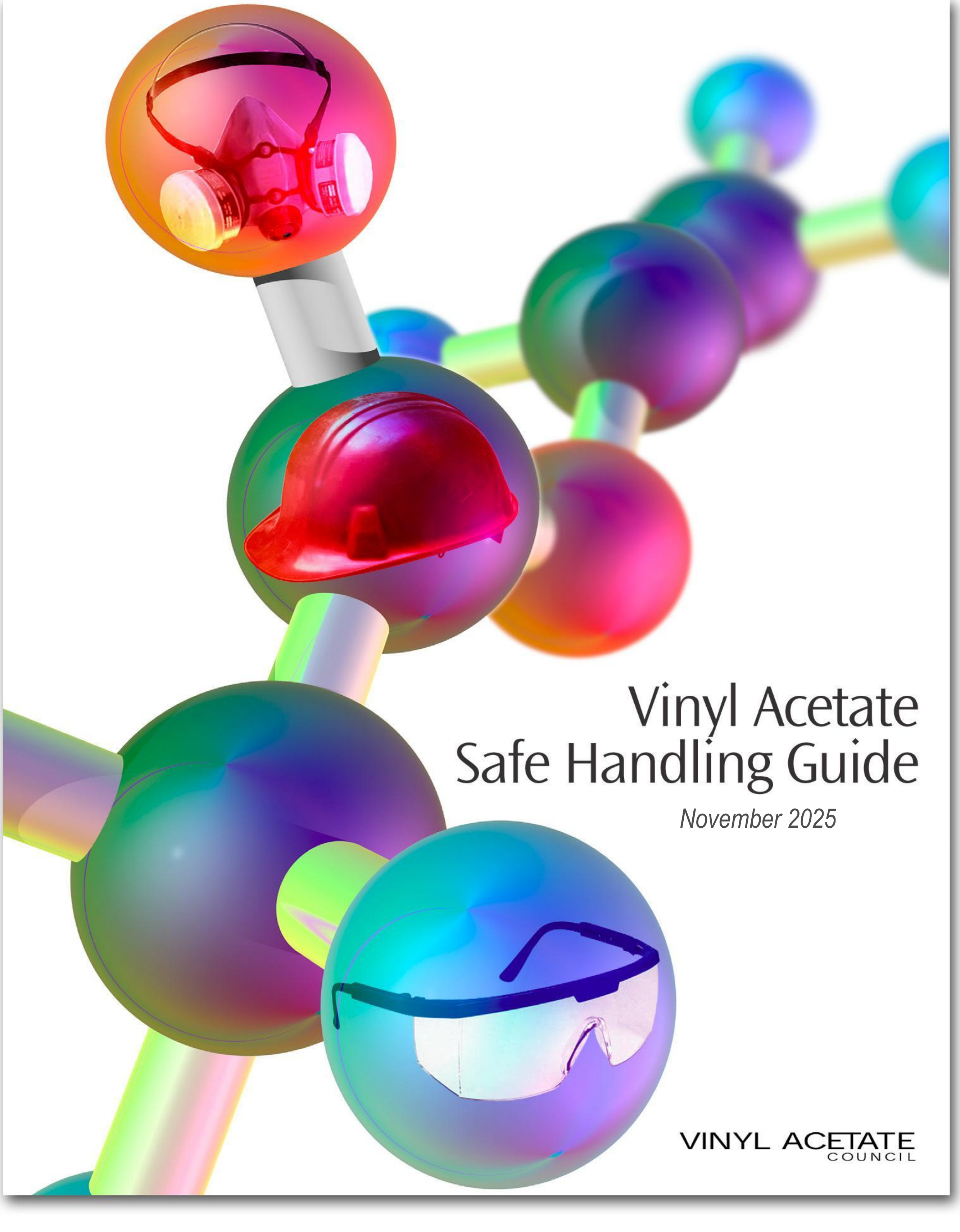

Vinyl Acetate Safe Handling Guide

November 2025

VINYL ACETATE
COUNCIL

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PREFACE

Vinyl acetate monomer (VAM) is a building block chemical used in the manufacture of polyvinyl acetate or vinyl acetate copolymers. These polymers are the base for many industrial and consumer products as well as for other polymers. When handled properly, VAM can be stored, transported and otherwise managed safely. However, if VAM is not properly managed, it can pose a serious fire, explosion, and/or health hazards.

The Vinyl Acetate Council (VAC) has developed this Safe Handling Guide to promote the safe and responsible handling and use of VAM. This document is intended primarily for North American audiences though information is included on classifications, exposure limits and transportation regulations relevant to several other jurisdictions [see Appendix II]. Information contained in this Guide was developed based on procedures currently recommended by members of the VAC and reflects best practices on the safe handling, storage and transport of VAM. This current Guide supersedes all previous editions of the "Vinyl Acetate: Safe Handling Guide."

The Guide is intended to supplement training, Safety Data Sheets (SDSs), and product labels for workers who handle, transport, process or may otherwise contact VAM, as well as for safety, engineering and health professionals responsible for implementation of safe management practices. There are also numerous national, regional and local regulations that need to be followed. All these documents should be consulted before handling VAM.

No warranty or guarantee, either expressed or implied, is made with respect to any or all of the content of this document and neither the VAC nor its members assume any legal accountability. The Guide is not intended as a statement of legal requirements or remedies. While the VAC believes that the information contained in this Guide is current and accurate as of the date published, ALWAYS CONSULT YOUR SUPPLIER'S SAFETY DATA SHEET, PRODUCT LABEL AND OTHER SAFE HANDLING INSTRUCTIONS FOR THE MOST CURRENT RECOMMENDATIONS. It is the responsibility of all persons handling VAM to respect proprietary rights and observe all existing laws. Consult with legal counsel and/or appropriate government authorities to ensure compliance with local, regional, national and international laws and regulations.

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ACKNOWLEDGEMENTS

The Vinyl Acetate Safe Handling Guide was developed by the Vinyl Acetate Council, a not-for-profit association of North American manufacturers, processors and users of vinyl acetate monomer. Current member companies of the Vinyl Acetate Council are listed below. Your manufacturing company should be contacted for any additional information or clarification of the content of this Guide. Ask your supplier for additional copies of this Guide or go to www.vinylacetate.org to request an electronic copy of this Guide.

Celanese Corporation
Transportation Emergency: 800-424-9300
Product Information: 800-835-5235
www.celanese.com

The Dow Chemical Company
North America: 800-447-4369
Europe: +800-3694-6367
Asia Pacific (except China): +800-7776-7776
China: +800-600-0015
Other Global Areas: 989-832-1560
www.dow.com

Kuraray America, Inc.
+1-800-423-9762
info@kurarayamerica.com
Emergency Numbers – CHEMTREC:
+1-800-424-9300 within the U.S.
+1-703-527-3887 outside the U.S.
http://www.kuraray.us.com/

LyondellBasell Acetyls, LLC
Contact: 713-209-7000
24-hour Emergency Number: 800-245-4532
www.lyondellbasell.com

GUIDE OVERVIEW

Using this Guide

Before using or handling vinyl acetate monomer (VAM), read the safety data sheet (SDS) and any other materials provided by your supplier. This Guide is intended to be used in conjunction with the manufacturer's information.

Section 1. Characteristics of Vinyl Acetate Monomer

Section 1 of the Guide contains an overview of the properties of VAM, including its hazards:

- Highly flammable;
- Vapor may cause flash fire;
- May polymerize spontaneously if cross contamination occurs, if the polymerization inhibitor is depleted, or if exposed to heat, radiation, oxidizing materials or strong acids or bases; may result in heat generation, rapid vaporization of VAM, and possible vessel rupture/explosion;
- May cause skin, eye and respiratory irritation;
- Harmful by inhalation; and,
- Suspect cancer hazard (GHS Category 2).

Section 2. Workplace Safety, Personal Protective Equipment and First Aid

Section 2 covers issues related to workplace training and safety, including appropriate personal protective equipment (PPE) for VAM and first aid measures.

PPE requirements for VAM will vary depending on possible exposure circumstances and activities. Proper use of PPE requires adequate training. Any garments contaminated with VAM should be removed promptly and either decontaminated by a qualified in-house or reputable external industrial cleaning service or properly disposed. Contaminated leather articles such as shoes, clothing, belts or watchbands should be properly disposed as leather cannot be thoroughly decontaminated.

First Aid

If inhaled, move to fresh air. If breathing is difficult, give oxygen. If breathing has stopped, give artificial respiration, then oxygen as needed. Contact emergency medical personnel/physician immediately. Respiratory tract irritation, bronchitis, pneumonitis or delayed pulmonary edema may develop.

In case of skin contact, immediately remove contaminated clothing and shoes. Wash affected areas with water and soap (if available) for at least 15 minutes. Call emergency medical personnel/physician if irritation and pain persist after thorough washing.

In case of eye contact, remove contact lenses if worn. Immediately flush eyes with large amounts of room temperature water for at least 15 minutes. Contact emergency medical personnel/physician immediately.

If ingested, slowly drink a glass (125-250 mL [4 to 8 oz]) of water or milk. Do not induce vomiting to prevent aspiration into lungs. Contact emergency medical personnel/physician immediately.

In case of thermal burns, immediately cool affected skin for as long as possible with cold water. Do not remove clothing if adhering to skin. Keep individual warm and quiet. Contact emergency medical personnel/physician immediately.

Section 3. Storage, Transport and Handling of Vinyl Acetate Monomer

Section 3 covers the safe storage, transport and handling of bulk quantities of VAM including storage tank conditions such as temperature and inhibitor level monitoring, and proper loading/unloading operations.

Cross contamination of VAM with other chemicals, especially oxidizing materials or strong acids or bases, may lead to spontaneous polymerization and fire. VAM should be kept away from heat, sparks and flame. Prolonged or intense exposure to heat, sunlight, ultraviolet light or x-rays may also result in spontaneous polymerization.

Section 4. Hazard Analysis and Emergency Planning for the Handling of Vinyl Acetate Monomer

Section 4 covers hazard analysis and emergency planning considerations, including Process Safety Management (PSM) and Risk Management Plans (RMPs).

Section 5. Managing Emergencies

Section 5 provides information on managing emergencies for situations including spills, fire fighting, uncontrolled polymerization responses and release reporting.

In case of spill, eliminate ignition sources. Except for properly trained and equipped emergency responders, remove non-protected personnel from area. Provide adequate ventilation until area is clean.

In case of fire, use CO_2 or dry chemical for small fires (e.g., fires that can be extinguished using a portable fire extinguisher). Use alcohol-type aqueous film-forming foam for large fires. Water spray or fog may be ineffective in fully extinguishing a VAM fire, but can be used to cool fire-exposed structures and containers. Do not use high-velocity water stream since VAM floats on water and the stream may spread the fire. If potential exists for exposure to smoke, vapors or products of combustion, wear complete personal protective equipment and SCBA with full facepiece operated in pressure-demand or other positive-pressure mode.

References

Appendices

Appendix I: Provides information for use in the design of facilities and operations handling and storing VAM.

Appendix II: Contains emergency contact information.

Appendix III: Includes a list of the acronyms and abbreviations.

Appendix IV: Includes a table of general properties of VAM.

Appendix V: The recommended guide (Guide 129) for VAM from the 20240 Emergency Response Guidebook (ERG) developed by the US DOT, Transport Canada, and the Secretariat of Transport and Communications of Mexico. Readers should check the ERG website to see if a more current version is available.

Appendix VI: Several example methods for using liquid chromatography to analyze for the level of hydroquinone in vinyl acetate monomer. Liquid chromatographic (LC) methods are recommended for the analysis of VAM that has exceeded its storage time or when the presence of soluble polymer is suspected.

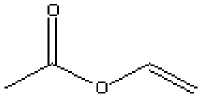
1. CHARACTERISTICS OF VINYL ACETATE MONOMER

Vinyl acetate monomer (VAM) is a flammable, reactive, colorless liquid that is partly soluble in water. It has a sweet, fruity smell in small quantities, but the odor may become sharp and irritating at higher levels. It is usually shipped and stored in clearly marked bulk containers.

VAM is a chemical building block used to manufacture a wide variety of (co)polymers that are used in a range of consumer and industrial products. There is no direct consumer use of VAM.

Chemical Name:	Vinyl Acetate
Common Name:	Vinyl Acetate
Synonyms:	Vinyl Ester Acetic Acid; Ethenyl Ester Acetic Acid; Vinyl Acetate Monomer (VAM); Ethenyl Acetate; 1-Acetoxyethylene; Acetic Acid Ethenyl Ester
CAS Name:	Ethenyl Ester Acetic Acid
CAS Registry No.:	108-05-4
Chemical Formula:	$CH_3COOCH=CH_2$

Chemical Structure:



1.1. Hazardous Properties

1.1.1. Flammability

VAM has a flash point below 37°C (100°F) and as such is considered a “flammable” liquid. When mixed with air at room temperature, VAM can form a flammable vapor. Its vapors are heavier than air and may travel a long distance to an ignition source such as a flame or electric spark and then flash back (see information on flammability classification in Section 1.2.2).

1.1.2. Reactivity

VAM is a reactive molecule. Unless inhibited, or if proper handling and storage precautions are not met, VAM can polymerize uncontrollably. VAM is typically shipped with a polymerization inhibitor, generally hydroquinone (HQ). Properly inhibited, VAM is stable under recommended storage conditions. Prolonged or intense exposure to heat, sunlight, ultraviolet light or x-rays may result in polymerization. Spontaneous polymerization may also result from exposure to amines, strong acids, alkalis, silica, alumina, oxidizing agents (e.g., peroxides, hydroperoxides, hydrogen peroxide) or polymerization initiators. Heat and pressure generated during such polymerization may rupture insufficiently vented containers, leading to liquid spill, vapor generation and possibly fire.

See Section 3 for information about storage conditions and inhibitor levels for VAM.

VAM is hydrolyzed in water. This reaction is typically not violent in nature and as such, is not considered as a hazardous reaction. While VAM has a National Fire Protection Association (NFPA) instability classification of 2 (yellow section of NFPA diamond - see Section 1.2.2) due to its ability to polymerize and to react with other chemicals, this classification and associated warnings do not apply to the mixing of VAM and water.

1.1.3. Health Effects

As with all chemical substances, the health effects associated with exposure to VAM depend largely on the exposure level and duration. VAM is irritating to the upper respiratory tract, skin and eyes so contact with vapors and liquids should be avoided. The odor detection threshold is reported to be about 0.5 ppm. If VAM gets into the eyes, it may cause irritation, redness and swelling. VAM vapors have been reported to be intolerably irritating to the eyes at 21 ppm but not at approximately 5-10 ppm. VAM is not considered to be a skin sensitizer.

Based on studies in laboratory animals, VAM is considered to have low acute toxicity potential by all routes of exposure: the oral LD50 in rats is approximately 2920 mg/kg; the inhalation 4-hour LC50 in rats is approximately 4000 ppm (14 mg/L); and the dermal LD50 in rabbits is >2000 mg/kg. High level inhalation exposure to VAM in animals results in deaths from pulmonary edema. At less than lethal exposure concentrations, single or repeated exposure to VAM may produce irritation or injury to upper respiratory tract tissues. In repeat dose studies, adverse effects were not seen below exposure concentrations of 50ppm in mice and 200ppm in rats.

VAM does not cause reproductive or developmental toxicity; no observed effect levels were 1000 ppm in drinking water and 200 ppm in air, respectively.

VAM has caused tumors in laboratory animals following lifetime exposure to irritating concentrations. Tumors were localized to tissues that were directly in contact with VAM (i.e., the nose and upper respiratory tract if inhaled or in the mouth, esophagus and stomach if ingested). A threshold-based tumor mechanism is believed to exist with a key event involving the enzymatic conversion of VAM by tissue carboxylesterases to acetaldehyde and acetic acid. Acetaldehyde is ubiquitous in the environment and present in the body at low levels as a byproduct of food metabolism. If threshold exposure levels of VAM are exceeded, acetaldehyde may accumulate above background levels. Acetaldehyde is also mutagenic and thought to mediate the genotoxicity associated with VAM. However, the body of evidence indicates that carcinogenicity is not expected to occur when the levels of VAM (and acetaldehyde) are below a practical concentration threshold (EU 2008a; Canada 2009). Occupational exposure limits (see Section 2.1.1 Occupational Exposure Limits) are below the threshold level for tumors in laboratory animals (EU 2008b). Thus, tumors observed at high exposure concentrations are not considered to be relevant to humans under typical use conditions.

The International Agency for Research on Cancer (IARC) has designated VAM as a Group 2B carcinogen, meaning “possibly carcinogenic to humans” based on IARC’s classification of acetaldehyde. Classification has not been reevaluated since 1995.

1.1.4. Environmental Effects

If released into the environment, VAM will partition into the environmental compartment to which it is released.

If released to air, VAM tends to stay in the air where it is rapidly degraded by photochemical pathways. The VAM atmospheric half-life has been calculated to be 0.6 days. Some volatilization can occur following releases of VAM to soil or water.

If released to water, VAM partitions mostly to the water where it undergoes hydrolysis. The hydrolytic half-life of VAM is estimated to be approximately 7 days at pH 7 and 25°C (77°F). Acetic acid and acetaldehyde are hydrolysis products of VAM. In general, hydrolysis increases in basic conditions. VAM is not expected to adsorb to sediments or soils to a great extent.

VAM is readily biodegradable and subject to biotic and abiotic hydrolysis in soils and sediments. Anaerobic and aerobic biodegradation pathways yield acetaldehyde (transient) and acetic acid (final). An aerobic transformation half-life of 12 hours was obtained with one bacterial isolate, whereas a half-life of 60 hours was found for non-enzymatic hydrolysis of VAM in a sterile medium.

VAM acute aquatic toxicity values range from approximately 12-18 mg/L for freshwater fish, algae and invertebrates with exposure periods of 48-96 hours. Chronic toxicity has been evaluated in freshwater fish with a no-observed effect concentration of approximately 0.6 mg/L.

Given the susceptibility of VAM to be readily biodegraded and the low level of acute aquatic toxicity, VAM is not considered to represent a significant environmental or ecotoxicological risk (EU 2008a, Canada 2009).

Bioaccumulation, which is the increase in a chemical’s concentration in an organism relative to the environmental concentration under steady state conditions, of VAM is unlikely. In the European Union (EU) and Canada, VAM is not classified as an environmental hazard or persistent, bioaccumulative or toxic (PBT) in the environment (EU 2008a, Canada 2009).

1.2. Hazard Communication

1.2.1. General

So that workers, emergency responders and the public are aware of the potential hazards associated with chemicals, there are hazard communication requirements throughout the world. In the US, chemicals are subject to the labeling requirements of the Occupational Safety & Health Administration (OSHA) Hazard Communication Standard (Code of Federal Regulations (CFR) 29 CFR 1910.1200); the Department of Transportation (DOT) requires labeling and placarding during shipment (DOT, 49 CFR 172.400). Comparable requirements can be found in Canada (Workplace Hazardous Materials Information System (WHMIS)) and in the European Union (Regulation on Classification, Labeling and Packaging (CLP) of Substances and Mixtures, EC 1272/2008).

The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (currently in its 11th edition, UN 2025) was developed to provide a common basis for chemical classification and labeling throughout the world. The GHS has been implemented in the US, Canada and elsewhere in the world. In the European Union, GHS is implemented through Regulation EC 1272/2008 (see above). The US has also implemented GHS as reflected in the Hazard Communication Standard (OSHA, 2012).

Consult your supplier for appropriate labeling information.

1.2.2. Hazard Classifications

Hazard communication programs require that a substance's hazard be classified and specific precautionary symbols or safety phrases be used. Some VAM hazard classification information for various regions are provided below, though consult your SDS for complete information.

<u>US Hazard Classification</u>

VAM is addressed under several US regulations (both state and federal) and programs covering toxic, chemical and fire hazards. Below are some of the common VAM hazard classifications.

GHS , 11th edition, UN 2025

Classification	Category	Risk Phrase	Definition
Flammable Liquid	2	H225	Highly Flammable Liquid and Vapor
Acute Toxicity	4	H332	Harmful if Inhaled
STOT, Single Exposure	3	H335	May Cause Respiratory Irritation
Carcinogen	2	H351	Suspected of Causing Cancer

Sections 311, 312 of the Emergency Planning and Community Right-to-Know Act (EPCRA):

Acute: Yes
Chronic: Yes
Fire: Yes
Reactivity: Yes
Pressure: No

VAM is listed on the following:

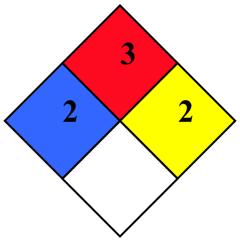
- EPCRA Section 313, the Toxics Release Inventory (TRI)
- Clean Air Act Section 112(r)
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Hazardous Substance
- EPCRA Section 302 Extremely Hazardous Substances (EHS)
- California Proposition 65: cancer

The American Conference of Governmental Industrial Hygienists (ACGIH) has classified VAM as an "A3" carcinogen - confirmed animal carcinogen with unknown relevance to humans.

US DOT regulations, require that containers of VAM bear a label in the shape of a diamond with a red background showing the flame symbol with the words "Flammable Liquid" and a number "3" signifying its designation as a flammable liquid (49 CFR 172.419(a)).

The National Fire Protection Association (NFPA) hazard, reactivity, flammability label and classification for VAM is shown below:

Flammable!



🟥 **Warning** Flammable liquid flash point below 100°F (37.78°C)
🟦 **Warning** May be harmful if inhaled or absorbed
🟨 **Warning** Violent chemical change at high temperature and pressures

Refer to Section 1.1 Hazardous Properties for information on the specific hazards of VAM.

Canada Hazard Classification

The Canadian classifications for VAM under WHMIS are presented in the table below. The disclosure level for VAM in substances is 0.1 percent.

Table 1.1: VAM Classifications in Canada (WHMIS)

Classification	Statement
B2	Flammable Liquid
D1B	Toxic Material Causing Immediate and Serious Toxic Effects
D2A	Very Toxic Material Causing other Toxic Effects
F	Dangerously Reactive Material

EU Hazard Classification

In the EU, VAM is classified under the GHS CLP classification regulation (see Section 1.2.1) as follows:

Table 1.2: GHS European CLP Classification

Classification	Category	Risk Phrase	Definition	Pictogram
Flammable Liquid	2	H225	Highly Flammable Liquid and Vapor	
Acute Toxicity	4	H332	Harmful if Inhaled	
STOT, Single Exposure	3	H335	May Cause Respiratory Irritation	
Carcinogen	2	H351	Suspected of Causing Cancer	

1.2.3. Safety Data Sheets

Safety data sheets (SDSs) provide detailed information about the hazards and precautions required for handling hazardous chemicals. SDSs are provided by suppliers; please consult your supplier for the latest SDS.

2. WORKPLACE SAFETY, PERSONAL PROTECTIVE EQUIPMENT AND FIRST AID

Everyone working with VAM, or in the vicinity of VAM, should be fully aware of its hazards and informed of appropriate safe handling and emergency response procedures.

Every workplace handling VAM is advised to have an established emergency response plan in place prior to bringing the chemical on-site. All personnel responsible for handling VAM should be thoroughly trained on the storage and handling requirements, including all applicable occupational safety, health and environmental regulations. Training should be conducted by persons with knowledge and experience in these areas and in conformance with all required local, regional and/or national regulations.

Workers engaged in the handling, storage or transport of VAM should be aware of the telephone number(s) or other emergency contacts for securing immediate assistance in response to a VAM event. Workers should also be authorized to summon emergency response personnel. Workers and supervisors should be aware of the requirements for reporting accidents and accidental releases to local, state and federal or national agencies. (An overview of these requirements is discussed in Section 4.)

2.1. Industrial Hygiene

VAM is an eye, skin and respiratory tract irritant. Workers should be warned to avoid skin and/or eye contact with VAM and to avoid breathing its vapors.

Safety showers and eyewash facilities should be provided in areas where VAM is being handled. Workers should be trained to promptly wash any area of the skin exposed to VAM with large amounts of water. All contaminated footwear and clothing should be removed immediately.

2.1.1. Occupational Exposure Limits

VAM should be handled in a well-ventilated area or in a completely closed system. Appropriate respiratory protection should be worn when exposure to vapors or mists above the established exposure limit may occur. Workers should be familiar with the location and operation of respiratory protective equipment and instructed to immediately report any incident that could result in exposure to VAM above permissible exposure limits.

The National Institute for Occupational Safety and Health (NIOSH), the American Conference of Governmental Industrial Hygienists (ACGIH), Canadian provinces, the EU SCOEL and other regulatory bodies have recommended exposure limits for VAM. Consult your supplier's SDS for any applicable occupational exposure limits on VAM for your area.

Table 2.1: VAM Occupational Exposure Limits

Organization/Agency	Limit
NIOSH	15 minute Ceiling Limit of 4 ppm (15 mg/m3)
ACGIH	8 hour Threshold Limit Value (TLV) Time-Weighted Average (TWA) of 10 ppm (35 mg/m3)
	15 minutes Short-term Exposure Limit (STEL) of 15 ppm (53 mg/m3)
Canada (Alberta, British Columbia, Ontario)	8 hour Time-Weighted Average (TWA) of 10 ppm (35 mg/m3)
	15 minutes Short-term Exposure Limit (STEL) of 15 ppm (53 mg/m3)
Mexico	8 hour Time-Weighted Average (TWA) of 10 ppm (30 mg/m3)
	15 minutes Short-term Exposure Limit (STEL) of 20 ppm (60 mg/m3)
EU SCOEL	Long-term Exposure Limit of 5 ppm (17.6 mg/m^3); Short-term Exposure Limit (STEL) of 15 minutes of 10 ppm (35.2 mg/m3)
China	8 hour Time-Weighted Average (TWA) of 10 mg/m^3
	15 minutes Short-term Exposure Limit (STEL) of 15 mg/m^3

2.2. Personal Protective Equipment

2.2.1. Availability and Use of Protective Equipment

A hazard analysis should be performed for each work activity to identify specific personal protective equipment (PPE) that should be worn by personnel working with VAM.

PPE is not an appropriate substitute for safe working conditions, such as engineering controls and compliance with safety procedures. However, in some instances PPE is the only practical means of protecting the worker, particularly in emergency situations. The proper use of PPE requires adequate training of workers. The PPE described in the following sections should be readily available for use when there is potential exposure to VAM.

For routine operations where vapor exposure is below established exposure limits, PPE typically would consist of:

- Flame retardant clothing, splash goggles, hard hat and safety shoes; and,
- Gloves are also recommended for handling hoses or drums.

For routine operations with potential for minor liquid exposure (from splashes, drips or minor spills) and where vapor exposure is below established exposure limits, PPE typically would consist of:

- As above but use impervious gloves, clothing, boots and a face shield; and,

- Wear protective clothing made of chemical- and fire-resistant materials in process areas. When both are needed, the chemical resistant clothing should be worn over flame retardant clothing.

For routine operations with potential vapor exposure up to 40 ppm, NIOSH recommends:

- use of approved full face organic vapor respirator or any supplied-air respirator with full face pieces, goggles and chemical resistant gloves.

For spills, emergencies and activities with the potential for substantial or unknown exposure use:

- supplied air respirator with full protective clothing, including a whole-body, chemical- and fire-resistant suit, impervious gloves and boots, and eye, head and respiratory protection.

For large spills where the potential exists for uncontrolled high-level exposure to VAM vapor, wear:

- complete protective suit that includes SCBA with full facepiece operated in pressure-demand or other positive-pressure mode and impervious gloves.

Permeation testing indicated that the materials in Table 2.2 may afford protection against VAM penetration. Other materials or products from other suppliers may be suitable for use with VAM if documented permeation test results are available to the user. See your supplier's SDS or contact your supplier for additional information.

2.2.2. Respiratory Protection

Respiratory protection per OSHA 29 CFR 1910.134/ANSI Z88.2-2015 should be a type approved by NIOSH. Guidelines for the use of any personal protective equipment must be followed, including medical evaluation and approval, worker fit testing, training for use and care of respiratory equipment.

Very high exposures to VAM may occur during: emergency situations; equipment cleaning and repairs; when decontaminating areas after a spill or; in case of failure of piping or equipment containing VAM. In these situations, workers need to be provided with approved full-face self-contained or supplied air respiratory protection and full protective suits.

NIOSH recommended respiratory protection levels are:

- Situations where potential exposure is unknown or could be up to 4,000 ppm: Use self-contained breathing apparatus (SCBA), which permits the wearer to carry a supply of breathing air in a cylinder or appropriate supplied air respirator. The SCBA should have a full facepiece and operate in a pressure-demand or other positive pressure mode. A supplied air respirator is also acceptable providing it has a full facepiece and is operated in a pressure demand or other positive pressure mode.

For escape: Use SCBA with full face piece or any respirator specifically approved for escape.

- <u>Situations where potential exposure could be up to 100 ppm:</u> Use full facepiece supplied air respirators, either continuous flow or positive pressure or a powered, air-purifying respirator with organic vapor cartridge. Air purifying element should have an end of service life indicator or defined replacement schedule.

- <u>Situations where potential exposure could be up to 40 ppm</u>: Use air purifying respirators (low level concentrations only) with organic vapor cartridge or air purifying respirator with full face piece and organic vapor cartridge. Note that eye irritation has been noted to occur at concentrations of 20 ppm and higher. The air purifying element should have an end of service life indicator or defined replacement schedule. A supplied air respirator is also acceptable.

SCBAs allow considerable mobility and maximal protection where exposure concentrations are unknown. The length of time this apparatus provides protection varies according to the amount of air carried and its rate of consumption. Where mobility is required, only SCBA should be used.

Supplied air respirators use breathing air from banks of compressed air cylinders or from other reliable respirable air sources. Conventional air compressors or plant air systems not specifically designed for breathing air may introduce respirable contaminants and should not be used as a source of breathing air.

Air purifying respirators are convenient and provide considerable mobility but afford limited protection. They should be used only when exposure concentrations are known to be at low levels.

For all respiratory protective equipment, follow the manufacturer's recommendations for use.

2.2.3. Hand and Skin Protection

Avoiding skin contact with VAM is very important. Using appropriate and properly fitting PPE is essential to avoid skin contact. Clothing and glove materials should be selected for suitability for the intended application prior to use and properly worn to be effective. Many common clothing and glove materials are not suitable for workplaces were VAM exposure is possible. Some potentially suitable materials are shown in the following table.

Table 2.2: VAM Permeation Test Results for Protective Clothing Materials[1]

Material	Common Uses	Results[2]
Barricade®	Suits	> 8 hours
Teflon®	Suits	> 8 hours
Responder®	Suits	> 4 hours
North Butyl B161 (16 mil) (or equivalent)	Gloves	5 hours
North Butyl B324R (32 mil) (or equivalent)	Gloves	> 8 hours
Ansell Edmont Laminate (2.5 mil) (or equivalent)	Gloves	6 hours
North Silver Shield®/4H® (2.7 mil) (or equivalent)	Gloves	> 8 hours

If other chemicals are used in conjunction with VAM, material selection should be based on protection for **all** chemicals present. These recommendations do not take into account the physical demands (e.g., puncture or heat resistance, flexibility) that may be required for the protective clothing. Alternative materials with shorter breakthrough times (e.g., Neoprene) may also provide acceptable protection as long as adequate permeation test data are available for the use scenario envisioned.

Contaminated Clothing/Apparel

Whenever garments become contaminated with VAM, they must either be cleaned by an industrial cleaning service familiar with VAM or properly disposed. Contaminated leather articles (e.g., boots, belts, gloves) must be properly discarded as contaminated leather cannot be thoroughly cleaned. Other contaminated articles (e.g., non-leather watch bands, belts) may or may not be able to be properly decontaminated; seek a reputable, professional cleaner experienced with VAM contaminated clothing.

2.2.4. Foot Protection

To prevent crushing-related injuries, safety footwear with built-in steel toe caps in accordance with (OSHA 29 CFR 1910.136/ASTM F2412-05 and ASTM F2413-05) is recommended for most industrial operations. For added protection against chemical contact, safety footwear of chemically-resistant materials should be worn over safety shoes.

All footwear contaminated with VAM, except those that are chemical-resistant to VAM, should not be reused and should be properly disposed. Chemical-resistant safety foot coverings should be thoroughly cleaned before reuse.

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[1] Testing conducted according to the American Society for Testing and Materials (ASTM), Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact. ASTM F 739-99a. Annual Book of ASTM Standards, Vol. 11.03.

[2] Results are given as resistance time to breakthrough after continuous contact.

2.2.5. Eye Protection

Safety glasses must be worn as minimum eye protection (OSHA 29 CFR 1910.133/ANSI/ASSE Z87.1-2020) but provide little protection against facial injury. Side shields and/or chemical splash goggles provide some additional protection. When handling VAM, full eye and face protection is preferred and should include face shields (full length, 20 cm [8 in.] minimum) with forehead protection in addition to chemical splash goggles. If vapor or mist exposure is likely, eye protection can be provided through the use of a full-face mask in conjunction with appropriate respiratory protection.

Each user of VAM should determine appropriate procedures for employees wearing contact lenses given the potential for VAM to irritate the eyes.

2.2.6. Head Protection

Hard hats (OSHA 29 CFR 1910.135/ANSI/ISEA Z89.1-2014) are recommended for protection from falling objects. Additional chemical resistant head covering may be required to protect against overhead liquid leaks and chemical splashes.

2.3. First Aid Treatment

The following first aid procedures should be started immediately in the event that VAM is ingested, inhaled or comes into contact with an individual's skin or eyes. Exposed individuals should be referred to emergency medical personnel, who should be provided with the details of the incident, exposure and symptoms.

<u>Inhalation (Breathing)</u>

- Remove individual from contaminated area to fresh air and monitor for sign of respiratory distress.
- Provide supplemental oxygen if breathing is difficult.
- Start artificial respiration if breathing stops, then oxygen as needed.
- If there are signs of respiratory distress or breathing difficulty, immediately contact emergency medical personnel/physician. (Respiratory tract irritation, bronchitis, pneumonitis or delayed pulmonary edema may develop.)

<u>Skin Contact</u>

- Immediately remove all contaminated clothing (e.g., garments, gloves, belts, watch bands, shoes).
- Wash exposed skin thoroughly with water and soap (if available) for at least 15 minutes or else blistering may develop 24-48 hours later.
- Contact emergency medical personnel/physician if irritation and pain persist after thorough washing.

Eye Contact

- Immediately, flush exposed eye(s) with large amounts of room temperature water for at least 15 minutes. Remove contact lenses if worn.
- Hold eyelid(s) open and away from eyeball during irrigation to ensure water contacts all tissue surfaces of eye and lid.
- Contact emergency medical personnel/physician immediately.

Ingestion (Swallowing)

- Slowly drink a glass (125-250 mL [4 to 8 oz]) of water or milk in small sips. Larger volumes of liquids may induce vomiting.
- Do not induce vomiting as VAM can be aspirated into the respiratory tract leading to severe respiratory symptoms.
- Immediately contact emergency medical personnel/physician.

Thermal Burns

- Immediately cool affected skin for as long as possible with cold water.
- Do not remove clothing if adhering to skin.
- Keep individual warm and quiet.
- Contact emergency medical personnel/physician immediately.

3. STORAGE, TRANSPORT AND HANDLING OF VINYL ACETATE MONOMER

Vinyl acetate monomer (VAM) can be stored, transported and handled safely if its hazards are understood. Two guiding principles for the proper storage, transport and handling of VAM are to avoid:

- ***Situations such as inhibitor depletion, excess heat or cross contamination that could result in spontaneous or uncontrolled polymerization.***
- ***Situations that could result in uncontrolled releases (spills, overfills, runaway polymerization) which create potential fire risks.***

VAM may be subject to rapid spontaneous polymerization if the inhibitor is not present or becomes depleted during prolonged storage. Spontaneous polymerization is especially likely if cross contamination occurs. The stability of VAM is finite and depends on the concentration of inhibitor present, the temperature of the storage vessel and other conditions. To avoid polymerization, ensure that cross contamination does not occur, that the temperature is not increasing and that the inhibitor concentration does not decrease below a minimum effective level (3 ppm).

3.1. Storage Considerations

3.1.1. Bulk/Tank Storage

Bulk storage systems for VAM should be evaluated prior to use to ensure that appropriate systems (e.g., temperature and level monitors, systems to add inhibitor and mix content of tanks) are available if necessary.

Bulk storage of VAM at ambient temperature is an acceptable practice when appropriate procedures and controls have been put in place to prevent spontaneous or uncontrolled polymerization. Most VAM shipped from the manufacturer will contain an inhibitor, typically 3-5 ppm hydroquinone[3] (HQ) for regional shipments and up to 25 ppm HQ for long-range (e.g., transoceanic) shipments. VAM storage tanks should be equipped with temperature measuring devices to monitor for unexpected VAM polymerization. The ability to sample and analyze tank contents for polymerization inhibitor concentration and add additional inhibitor may be needed. See Appendix I for more information about tank design and monitoring equipment and Figure 1 (in Appendix I) for a diagram of a typical VAM bulk unloading and storage system.

3.1.2. Maintaining and Assessing Inhibitor Levels in Bulk Storage

The rate at which the polymerization inhibitor HQ is consumed is dependent on storage conditions with temperature, oxygen concentration and presence of reactive contaminants being the key factors. Under normal storage and use conditions,

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[3] Hydroquinone is the main inhibitor used for VAM. There are other known inhibitors though these are not typically used because of their impact on the color of VAM/VA-based polymers.

routine sampling of HQ concentration should not be required providing the initial HQ inhibitor concentration is at least 3 ppm. Normal storage conditions include:

- An HQ concentration of 3 ppm or higher.
- A recommended storage temperature below 30ºC (86ºF). Temperature should not exceed 100 °F (38 °C). Tank heating is due to ambient temperature changes only. It is not recommended to heat the tank by other heating medium.
- A recommended dry blanket nitrogen in the tank headspace.
    - Dry air may be used but it results in a flammable atmosphere in the tank and promotes formation of organic peroxides, which are polymerization initiators.
- The absence of reactive contaminants.
- Turnover of the tank contents every 60 days or less for VAM at 3 ppm HQ min.; 90 days for VAM at 6 ppm min.; and 120 days for VAM at 12 ppm min.
- A rust free storage environment.

Blanketing with dry gas is important because the presence of water initiates a hydrolysis reaction of the VAM to acetic acid and acetaldehyde. Nitrogen is recommended as the blanket gas for two reasons. First, it minimizes flammability concerns. Second, the presence of oxygen promotes formation of organic peroxides, which are polymerization initiators, which leads to more rapid depletion of HQ and more rapid onset of polymerization. However, storage under dry air is acceptable with a 60-day or shorter turnover.

Turnover of the tank involves the addition of fresh, inhibited VAM with sufficient mixing in the tank to maintain a uniform HQ concentration of at least 3 ppm throughout the tank. To adjust inhibitor content, add hydroquinone (HQ) pre-dissolved in VAM. It is not recommended to dump dry inhibitor down into the tank or container vapor space. As the tank/vessel temperature increases, significant amounts of VAM vapors will be produced and there is the potential of a static charge igniting a potentially flammable vapor atmosphere. For proper uniform inhibitor mixing, tank/vessel shall be circulated long enough to provide adequate mixing and to ensure full turnover of material. Excess circulation can create heat that can cause the tank temperature to increase. A cooler may be used to remove the heat generated from the pump circulation. Contact with HQ may be harmful if personnel DO NOT wear proper PPE (consult HQ SDS for more guidance).

Under laboratory conditions, experimental data indicates that VAM stored at a temperature of 38ºC (100ºF) with a dry air blanket and containing 3-5 ppm HQ in a carbon steel container, is stable for at least 7-8 months. Stable storage times using a nitrogen blanket were even longer (Levy 1993, Levy and Hinojosa 1992). Despite evidence for stability over 6 months without polymerization, the 60 day turnover time for VAM is recommended with the minimum 3 ppm HQ inhibitor to provide conservatism when accounting for varying transit times and storage conditions.

Analysis of Inhibitor Concentrations in Bulk Storage

Under conditions that deviate from these normal storage and use conditions, periodic analysis of the HQ concentration and tank temperature monitoring may be needed to insure that polymerization is not occurring. The HQ concentration should be measured at least once every 30 days until sufficient historical data is available to define a HQ sampling schedule based on actual storage conditions.

A commonly used analytical method for HQ analysis of fresh VAM is a titration method established by the ASTM – D2193 "Standard Test Method for Hydroquinone in Vinyl Acetate" (ASTM 2012). However, for analysis of HQ in VAM when the presence of soluble polymer is suspected, a liquid chromatographic (LC) method is recommended. In these circumstances, it is possible for a solid polymer film to form during the evaporation stage included in the ASTM method, which could block the HQ and prevent its further dissolution with water during the sample preparation procedure (see Appendix VI for several sample LC HQ analytical methods). The supplier should be consulted for more information on inhibitor analysis.

Precautions Regarding Recycled/Recovered VAM

Special transfer and storage procedures must be used for recycled vinyl acetate monomer, such as unreacted VAM recovered from an incomplete polymerization process or from vent condensation. Recycled VAM will not contain sufficient levels of inhibitor to prevent polymerization and may even contain traces of polymerization initiator (Gustin 2002, 2005). Recycled or recovered VAM must not be returned to a storage tank unless special precautions are taken to ensure that adequate polymerization inhibitors have been added and that cross contamination of storage tanks does not occur.

There have been documented polymerization events that have occurred in tanks of recovered VAM. In one circumstance, VAM recovered from a polymerization operation at a polyvinyl acetate plant caused a violent, uncontrolled polymerization, resulting in catastrophic tank failure, after being stored in hot summertime conditions (Gustin 2002, 2005).

3.1.3. Containers and Drum Storage

To prevent hazardous polymerization, drums and small containers should be stored in a cool, well-ventilated area, and out of direct sunlight. Use only approved containers (per DOT, Transport Canada or other appropriate authority). Drums of VAM should be stored out of direct sunlight.

Sealed drums of VAM inhibited with 14-17 ppm hydroquinone may be stored at temperatures up to 30ºC (86ºF) for approximately one year from the date of packaging. Sealed drums of VAM inhibited with 3-5 ppm hydroquinone may be stored at temperatures up to 30ºC (86ºF) for up to six months from the date of packaging.

3.1.4. Barge, Railcar, and Truck Storage

Material stored in bulk storage containers should follow the same guidelines as bulk/tank storage in section 3.1.2. If conditions deviate from listed storage conditions, routine sampling of HQ is recommended.

3.2. Shipping Classifications and Regulations

VAM is commonly transported by highway, rail and water. In the United States, regulations for movement of VAM are established by the DOT. Based on United Nations Recommendations on the Transport of Dangerous Goods, the DOT established Hazardous Materials Regulations for hazard communication, classification and packaging requirements (http://phmsa.dot.gov/hazmat/regs). Shipping specifications for VAM were listed in the DOT Hazardous Materials Table, 49 CFR 172.101.

Table 3.1: US DOT, Canadian TDG, and EU Shipping Requirements for VAM

	US DOT	**Canadian TDG**	**EU**
Shipping Name	Vinyl Acetate, Inhibited	Vinyl Acetate, Stabilized	Vinyl Acetate, Stabilized
Hazard Class	3 (Flammable Liquid)	3	3
UN/NA ID Number	UN 1301	UN 1301	UN 1301
Packing Group	II	II	II
Reportable Quantity	5,000 lb (2270 kg)	Any quantity	
Tank Car Specification	111A100W		
Tank Truck Specification	MC 307, 312, DOT 407, 412		
Barge Specification	USCG Certified for VAM		
Placard	Flammable	Flammable Liquid	Flame
Label	Flammable Liquid	Flammable Liquid	Highly Flammable Liquid and Vapour

3.3. Loading and Unloading Bulk Shipments from Barges, Tank Rail Cars and Trucks

There are national and regional regulations regarding barges, tank cars (e.g., rail cars) and tank trucks for transporting chemicals like VAM, see Section 3.2 for more information.

The use of rail tank cars with top loading/unloading fittings is recommended to minimize the chance of leakage or spillage of the whole cars' contents. If the tank rail car does not have a suction pipe or dip tube[4] for top unloading, one can be inserted through a nozzle or

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[4] A dip tube or suction pipe is a pipe which extends from the top of the railcar at the multi-housing plate to approximately 3" from the bottom of the railcar. It allows for loading without causing splashing or turbulence that can lead to the build-up of static electricity.

opening on top of the tank car or through the manway (an opening in the tank car through which a person can enter the tank). However, appropriate fittings for the opening or manway should only be used to minimize the opening for the suction pipe or dip tube so as to minimize the opportunity for volatilization of VAM to the atmosphere.

There are two common types of tank trucks for VAM transport-center loaders/unloaders and rear loaders/unloaders; both types utilize closed system loading (open loading is inappropriate for VAM due to the potential for vapor generation). Tank trucks should be equipped with two valves and with wash out caps, one of which should be used for the vapor recovery and/or nitrogen purge.

Rail tank cars and tank trucks should be equipped with pressure relief valves and vacuum breakers. For vessels/barges that have multiple compartments, there should be a sufficient number of relief devices for each compartment. These relief devices protect the integrity of the tanks/vessels/barges in an over pressure condition.

Tank trucks or rail tank cars or vessels/barges should not be loaded or unloaded during severe electrical storms.

The bulk containers (trucks, railcars, isocontainers, vessels or barges) used to load or transfer VAM into should be thoroughly cleaned and decontaminated to avoid undesirable contaminations and possible polymerization. The cleaning and decontamination procedures must be developed and critically reviewed on a case by case based on which chemical was loaded/stored previously and potential risk. Experience has shown that cross contamination can occur due to inadequate cleaning of previous chemicals in vessels. For example, high levels of benzene was detected in VAM from a vessel that previously transported benzene even though the vessel was presumably cleaned. Cleaning and decontamination may not be required if the bulk containers were loaded/stored VAM previously. Special precaution must be taken to ensure no possible polymer presence. If loading on top of VAM heels, VAM heels should be sampled to ensure adequate inhibitor is present and adjusted as needed prior to loading material on top of it.

Each loading spot should be equipped with a totalizing meter to count the desired number of gallons to be loaded. When the desired number of gallons is reached, the meter should automatically close the loading valve. Also, a back-up level probe should be provided to detect high level in the tank and to automatically close the valve in case the meter fails.

A dry nitrogen blanket for the head space should be used on all the VAM bulk containers to make the transfer or to provide suction to a pump. For VAM bulk containers (trucks, railcars, isocontainers, vessels or barges) with long transit times (more than one week), the oxygen concentration should be maintained below 8 % (including dedicated containers for VAM service when they are empty after unloading) to slow the rate of inhibitor depletion. Purging to below 8% also reduces flammability concerns.

Upon arrival at the delivery site, the tank car or tank truck should be inspected for leaks and damage. If there are any issues identified, notify the supplier, the owner of the tank car or tank truck and the trucking or railroad company, even if the tank can be unloaded safely. Always ensure that the damaged tank car or tank truck is in safe condition before it leaves the property.

When a tank car or tank truck arrives:

Complete Safety Check Preparing to Load/Unload

- Dedicated equipment is recommended, otherwise special care is required to avoid cross contamination.
- Ensure only appropriately trained and equipped personnel perform loading/ unloading operations.
- Check the shipping papers against the placards, labels and seals as appropriate to ascertain proper identification.
- Check that the car or truck is parked within the designated containment area and that the transfer hose has the correct fittings and is of appropriate length.
- Check the wheels, set the brakes and shut down the truck engine.
- Check that the tank truck driver is out of the truck during loading/unloading.
- If derails (a blocking device placed on the track to prevent unauthorized movements of the rail car) are necessary, ensure that they are in place on tank rail car tracks.
- Set up warning signs as appropriate.
- If hoses are run across vehicular byways, set up protective barricades.
- Ensure that the transfer equipment contains nothing to contaminate the VAM, especially oxidizers, acids or bases.

Check and Have Ready Necessary Safety Equipment

- Be aware of emergency procedures.
- Prior to opening any covers, check the availability and proper operating condition of the emergency water, eye wash and shower for washdown. Note pressure in the tank car and tank truck. Wear personal protective equipment appropriate for the task(s).
- Emergency equipment should be readily available and checked to confirm it is in proper working condition.
- Use electrical bonding and grounding to prevent static electricity build-up.
- Use grounded pumps or appropriately regulated, pressurized dry nitrogen (not air) for transferring VAM.
- Have vapor control systems available if regulations require.
- A flame arrester is recommended if the tank is open to the atmosphere during loading/unloading.

Preliminary Procedures

- Before opening a tank car manway cover, outlet valve cap or plug, the car should be relieved of pressure through the vent valve.
- Before removing caps on nozzles, be sure the valves are closed. In some cases a valve may have leaked, building pressure between valve and cap. Always use caution in removing caps even after having vented the tank car.
- Confirm that the tank to receive the material has sufficient room to hold the entire contents of the truck or tank.
- If sample purging is done, a metal container (not plastic or other non-conducting container) that is electrically bonded to the sample line should be used.
- Before beginning transfer, check that any necessary samples have been taken and check for proper alignment of valves in the line from the car or truck to the tank.

Making the Transfer

- VAM transfers should be continuously attended and monitored by trained personnel equipped with appropriate PPE.
- Make transfers through piping and into receiving vessels that have been properly designed to prevent the generation and accumulation of static charges. Refer to Appendix I Bulk Storage Design.
- Do not make VAM transfers during an electrical storm.

Your supplier may be consulted for advice on particular situations. Also, the Association of American Railroads provides information on methods of loading and unloading non-pressure tank cars in its Pamphlet 34 (AAR 2023).

3.4. Shipping Containers Damaged in Route

The following procedure should be followed if a bulk shipment containing or transporting VAM becomes damaged in route so that it cannot proceed safely to its destination:

- Contact local police and fire departments, the shipper, the supplier and the regional transportation emergency centers (e.g., Chemical Transportation Emergency Center (CHEMTREC) – see Appendix II for contact information).
- Remove public from the immediate area.
- Assess whether the damaged container can be moved to a safe location to transfer material to another container.
- Procedures should be in place to determine whether a reportable quantity has been released and whether the loss needs to be reported to the appropriate authorities.

3.5. Unloading into Storage Tanks

3.5.1. Storage Tank Vent Handling

When bulk shipments are loaded or unloaded, the storage tank vent gas may be returned to the shipping vessel through a dedicated vapor return line, or may be sent to the vapor collection/abatement systems such as a flare, thermal oxidizer, or incinerator. In each of these cases, the vent line should have flame and/or detonation arresters properly installed and, in some cases, may have inert gas added to render the vent gas non-flammable. See Appendix I-Figure 1 for more details.

3.5.2. Hoses

The preferred practice is to utilize dedicated equipment when unloading VAM. Prior to use, hoses should be checked for cleanliness and integrity. If hoses are used for multiple services, they should be thoroughly cleaned after each use to avoid cross-contamination.

Caution is necessary when VAM is bled from hoses to minimize employee exposure and to minimize environmental emissions of volatile organic compounds.

To help prevent static electric charge buildup, dedicated electrically continuous chemical transfer hoses should be used. Hose materials must be compatible for VAM service (see Section 1 on VAM reactivity and incompatible materials).

Caution: These hoses should not be relied on to be the primary electrical bond; separate bonding and grounding cables must be used.

Dry-disconnect hose connections are available, which have internal mechanisms that allow only a few drops of spillage when disconnected. These also prevent excessive spillage if the connection is broken during transfer.

3.5.3. Sampling

The preferred practice is the use of a 'closed loop' sampling device such as a Dopak™. If closed-loop sampling is not available and a direct collection method (e.g., via a purge line) is required, procedures should be used to insure a clean, representative sample is collected. Appropriate PPE should be utilized during the sample collection process to avoid inhalation, skin and eye contact and/or clothing contamination.

3.6. Tank and Equipment Cleaning and Repairs

The following are general guidelines and suggestions for the preparation and cleaning of VAM tanks and equipment prior to entering for inspection and repair. These guidelines are not intended to replace detailed written procedures for a specific job and situation.

3.6.1. Preparing Personnel

Tank and equipment cleaning should be performed by trained personnel who are familiar with all of the hazards and the safeguards necessary for the safe performance of the work. All precautions pertaining to education, protective equipment and health and fire hazards, as detailed elsewhere in this Guide and in company guidelines and response plans, should be reviewed and understood.

A stepwise procedure addressing all relevant tasks should be written and used to train all personnel involved with the work. The procedure should include specific instructions regarding possible hazards, and describe safe procedures and protective equipment for dealing with these hazards.

3.6.2. Preparing Tanks and Equipment

The tank, equipment and associated lines to be cleaned should first be electrically grounded and then emptied of all liquid. In the case of large tanks, it is imperative that the tank vent and make-up system be in good working condition to keep from over-pressuring or collapsing the tank.

The bulk of the liquid should be transferred to another vessel (for recovery or reprocessing, if necessary) so that any remaining liquid (i.e., heel) is minimized. The heel should then be drained into a suitable container for proper reuse or disposal. In the case of large storage tanks, it may be helpful to add about six inches of water to the tank to recover any VAM remaining in the low spots of the tank. All waste liquids should be properly disposed.

Caution: The vapor space above even dilute aqueous solutions of VAM may be flammable.

The vessel(s) and piping to be cleaned should be isolated from all other systems by closing the proper valves. Wash and flush the equipment three or four times with hot (preferably 49-66°C [120-150°F]), demineralized water. Contaminants like chlorine in raw water can deposit in corroded crevices serving as an initiator for polymerization. The dirty wash water should be collected in a sump or other suitable vessel for proper disposal, taking into consideration potential environmental effects. Steam may be used to remove final traces of VAM. Providing VAM is not present, a strong aqueous detergent or caustic solution can be used to help loosen and remove polymer residues. The tank's material of construction should be checked for compatibility with the cleaning solution to protect the mechanical integrity of the tank. All wastes should be properly disposed.

Caution: Do not use caustic or alkali detergent solutions when liquid VAM is present or with aluminum equipment.

The lines in and out of the tank or equipment should be disconnected and grounded for entry. Note: Even though the equipment has been flushed with water, proper protective equipment should be worn when opening flanges. The equipment should then be purged with fresh air and the air should be tested for VAM vapor and oxygen content by an approved method before permitting personnel to enter. Tank entry is governed by the OSHA standard for Confined Space Entry, 29 CFR 1910.146 and the Lockout/Tagout Rule for Control of Hazardous Energy, 29 CFR 1910.147.

3.7. Maintenance of Equipment*

Routine maintenance is critical to ensuring that equipment performs as designed and constructed. A maintenance schedule and program should be implemented in accordance with equipment utilized at the facility and applicable local, regional and national regulations.

In addition to regulatory inspections, a preventive maintenance schedule is advised to inspect for possible polymer formation inside storage tanks for its cleaning and removal. Frequency needs to be determined taking into consideration the results of previous inspections and the tank design. For floating roof tanks, monthly NVR testing is suggested for monitoring of possible polymer formation. For fixed roof tanks, NVR testing is suggested based on historical frequency of polymerization incidents.

For “pontoon style tanks”, annual inspections are suggested, and this frequency can be pushed out based on at least monthly non-volatile-residue (NVR) testing.

Inspection intervals for “pan” style floating roofs can reasonably set out to 5 plus years provided at least monthly NVR testing is performed.

Inspection intervals for fixed style without “cold fingers” can be reasonably set out to 5 plus years, based on history of polymer inspection. NVR testing is suggested based on historical frequency of polymerization incidents

3.8. Control of Vapors and Waste Disposal

VAM is volatile and may give rise to odorous vapors. As such, emphasis should be placed on the prevention of leaks and spills through careful design and good operating procedures. Because of the low odor threshold (about 0.5 ppm), leaks and spills may elicit complaints from workers and neighbors downwind.

If a spill occurs, only properly trained and equipped response personnel should remain in the area for cleanup. The spilled VAM should be collected and disposed of properly (see Section 5.3 for guidance on spill response).

3.8.1. Air Pollution Control

Atmospheric emissions of VAM are subject to local, regional and/or national regulations.

3.8.2. Discharge to Navigable Waters

Discharge of pollutants to any body of water is subject to local, regional and/or national regulations.

3.8.3. Disposal of Wastes

Wastes containing VAM must be treated or disposed of at an authorized facility. As a liquid, this material cannot be disposed of directly into a hazardous waste landfill. The recommended management practice for waste VAM is incineration or burning for heat recovery.

Typical plant-processed aqueous VAM waste streams can be treated in the plant-site wastewater treatment system. Plant-site wastewater treatment systems should be adequately engineered to handle the volume and concentration of VAM process waste streams.

Though adequate dilution of concentrated wastes can reduce odor problems and fire hazard, direct discharge of dilute wastes to municipal wastewater treatment systems is not appropriate. The treatment method and its impact on sewage sludge should be considered.

4. HAZARD ANALYSIS AND EMERGENCY PLANNING FOR THE HANDLING OF VINYL ACETATE MONOMER

Each step in handling and using VAM should be reviewed for possible hazards. The review should include the appropriateness of the equipment and the proper procedures for using the equipment. The review team should include personnel directly involved in all relevant activities, as well as technical and safety specialists. The safety review must meet the requirements of governmental regulations, and may include evaluations of:

- ***Process design and controls***
- ***Operational safety equipment such as ventilation, pressure relief devices, grounding devices, etc.***
- ***Prevention of cross contamination sources as this could result in spontaneous polymerization***

4.1. Emergency Planning

Facilities that handle large quantities of VAM, will likely need to develop an emergency plan in order to respond to situations such as: fires, releases to environment, off-site incidents, natural disasters, medical emergencies, loss of utilities, etc. Key elements of an emergency plan include:

- Each facility should maintain a written emergency plan outlining response procedures to incidents.
- Responsibilities for internal and external resources are defined and appropriate training provided.
- Emergency procedures are tested periodically, reviewed and revised, as necessary to maintain effective response.
- The emergency plan is periodically communicated to employees/contractors and responsible officials in the local community.
- Emergency response equipment is operated by qualified individuals and is available at the facility or locally.

4.2. Risk Management/Process Safety Regulations

Depending on where your facility is located, there may be regulations that determine what specific elements need to be in your emergency plan. Examples of possible regulations that should be considered are:

- US: EPA Clean Air Act, Section 112(r) - Risk Management Plan; 40 CFR 68.130
- US: OSHA Process Safety Management of Highly Hazardous Chemicals (HHC); 29 CFR 1910.119(n)
- US: OSHA Emergency Action Plan; 29 CFR 1910.38
- US: OSHA Hazardous Waste Operations and Emergency Response; 29 CFR 1910.120

- Europe: SEVESO II 2003/105/EC, 12/2003 & 96/82/EC, 1/1997
- Mexico: NOMO-28

Some of these regulations include specific "threshold quantities" of VAM that trigger regulatory requirements. For the US EPA CAA 112(r) RMP, the threshold quantity for VAM is 15,000 pounds. For the US OSHA Process Safety Management regulation, the threshold quantity for VAM is 10,000 pounds. Additional information about the CAA 112(r) regulations and other EPA programs designed to prevent and respond to emergencies can be found at http://www.epa.gov/emergencies/index.htm. More information on the OSHA Process Safety Management standard can be found at http://www.osha.gov/SLTC/processsafetymanagement/index.html.

4.3. Emergency Response Planning: Acute Inhalation Guidance Values

In emergency planning, acute inhalation guidance values are used to determine adverse health effect levels in populations that might be impacted by an emergency release. The American Industrial Hygiene Association's Emergency Response Planning Guidelines[5] (ERPG) and the US EPA Acute Exposure Guideline Levels (AEGLs), are listed in Table 4.1. In the event that an accidental or unscheduled release results in community exposures at these levels, sheltering, evacuation or other actions may be required.

Table 4.1: ERPG and AEGL Values for VAM

AEGL/ ERPG	Value
ERPG-1	5 ppm (1-hour) Threshold for Mild, Transient Adverse Health Effects
AEGL-1	6.7 ppm (up to 8-hours) Threshold for Irritation
ERPG-2	75 ppm (1-hour) Threshold for Irreversible Health Effects and Escape Impairment
AEGL-2	36 ppm (1-hour)
ERPG-3	500 ppm (1-hour) Threshold for Lethality
AEGL-3	180 ppm (1-hour)

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[5] Emergency Response Planning Guidelines are health-based threshold values used to assist health and safety professionals in the development of emergency response strategies for protecting workers and the general public against the harmful effects of specific chemical substances. They represent the concentration that nearly all individuals could be exposed to for up to one hour without experiencing or developing the indicated effect.

5. MANAGING EMERGENCIES

An essential component of Emergency Management is incident prevention. Through adequate facility design, safe storage and handling practices, personnel training and disaster preplanning, many of the consequences of an emergency can be minimized or avoided altogether.

In the event of a major release of VAM, the area should be evacuated immediately based on the facility risk management plan (RMP) or other emergency response plan. Only trained personnel equipped with appropriate safety equipment should enter the area. Full personal protective equipment (Section 2.2) should be worn when it is necessary to work in an environment containing VAM where exposure may occur at levels in excess of permissible limits.

As part of the emergency response plan, regular communications and/or disaster training sessions with the local/municipal fire departments are encouraged in anticipation of fires, spills or emergencies.

The following sections describe the materials and procedures to be used in the event of emergency situations involving VAM, including fires, spills or first aid requirements. Much of this information comes from the 2024 Emergency Response Guidebook (ERG 20240), which may be obtained from the US DOT at https://www.phmsa.dot.gov/training/hazmat/erg/emergency-response-guidebook-erg or from Transport Canada at http://www.tc.gc.ca/eng/canutec/guide-menu-227.htm. Guide 129 is specific to VAM (see Appendix V).

5.1. Fire and Explosion

5.1.1. Preventing Fires

Since VAM vapors are heavier than air, they may concentrate and travel along the ground some distance to an ignition source and flash back. Therefore, every precaution should be taken to prevent exposure to flames, sparks or other ignition sources. The following are general guidelines for preventing VAM fires (see Section 3 for more detailed handling information):

- Locate VAM storage, handling and processing equipment outside or in a non-combustible or fire-resistant building.
- Do not allow combustible material such as brush or weeds to accumulate around storage tanks or drums.
- Provide adequate venting for emergency conditions in vessels used for storage, handling and processing. (As described elsewhere, relief devices must be sized according to engineering calculations.)
- Provide proper electrical equipment and adequate grounding for static electrical discharge.

- When filling, circulating or agitating VAM in a storage tank, care should be taken not to vigorously disrupt the liquid surface (causing a static charge).
- Regularly inspect equipment and storage facilities for corrosion and leaks, especially vents and flame arresters.
- Immediately fix any leaks in equipment.
- Provide adequate local exhaust and general ventilation in the working area and carry out regular tests with a combustible gas indicator in any area where vapors might accumulate.
- Provide proper facilities to handle any accidental spillage.
- Provide adequate fire extinguishing equipment including automatic sprinklers in storage and work areas.

5.1.2. Fighting Fires

In the event of a fire involving VAM, the following extinguishing materials should be used and procedures followed:

Extinguishing Materials

- Use carbon dioxide or dry chemical extinguishers for small[6] fires.
- Use dry-chemical or alcohol type foam for large fires. When these extinguishing materials are not immediately present, the fire can be fought with water spray, especially to keep fire-exposed containers and structures cool and to reduce vaporization. However, water spray may not be completely effective in fully extinguishing the fire because VAM floats on water.
- Use of high-velocity water stream should be avoided in order to prevent the spread of burning monomer or the accumulation of fire-fighting water. Since VAM is lighter than water and does not appreciably mix with water, it will float on water, thereby spreading the fire.

Procedures

- Firefighting individuals should wear SCBA and complete personal protective equipment (PPE) for protection from smoke, fumes or hazardous decomposition products (see Section 2 for more information on PPE).
- Use water spray to cool fire-exposed structures and containers.
- Use water spray to disperse vapor cloud if fire is not present and to flush spills.
- Firefighters must stay well away from involved vessels since explosion may be possible.
- Any drums or containers of VAM exposed to fire should be kept cool by water spray to prevent uncontrolled polymerization, which in turn can cause auto-ignition and explosion.
- If the involved VAM storage vessel is no longer venting, it could still be dangerous. Unless the vent is obviously unobstructed, other indications

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[6] A "small fire" is a fire that can be extinguished using a portable fire extinguisher.

such as pressure, temperatures and no longer making normal venting sounds must be considered to avoid undetected pressure buildup and possible container rupture.

- Have the proper SDS ready for arriving municipal emergency responders along with directions from the Incident Commander (IC) on-scene.
- In the event of a massive fire, use unmanned hose holder or monitor nozzles; if this is impossible, withdraw from area and let fire burn (ERG 2016).

Evacuation

- If tank, rail car or tank truck is involved in a fire, US DOT (ERG 2016) recommends that the area be isolated for 800 meters (1/2 mile) in all directions.

5.2. Uncontrolled Polymerization

As discussed in Section 3, VAM is typically inhibited with hydroquinone and is stable under recommended storage conditions (see Section 1.1.2 on polymerization hazards).

Polymerization of VAM is highly exothermic and a rapid release of heat may cause a rapid increase in pressure resulting in an uncontrolled release and/or vessel rupture. The only reliable method to stop an uncontrolled polymerization is the addition and proper mixing of an inhibitor. Cooling water sprayed on the exterior of a storage tank to remove heat will retard, but not stop, an uncontrolled polymerization. As conversion increases, increased viscosity of tank contents may prevent effective addition and distribution of inhibitor and may limit heat transfer. In addition, the hazards of approaching a container or vessel of VAM that is undergoing an uncontrolled polymerization must be considered in the response plan.

An abnormally high and increasing storage tank temperature trend (ex. 2.5 deg C in 30 min or 9 deg C above ambient temperature), indicates that VAM polymerization may be occurring. In this situation, additional polymerization inhibitor should be promptly added to the tank. The specific inhibitor quantity to be added will depend upon your specific situation. Where the polymerization rate is low and the temperature is gradually increasing, enough HQ should be added to raise the concentration in the tank by 5 ppm to replace HQ that has been consumed. A chiller or fire monitor could be used to quickly cool the tank contents and slow down the reaction. For more rapid or continuing polymerization and increasing temperature, it may be necessary to add more inhibitor initially until polymerization is stopped as indicated by temperature stabilization in the tank. When rapid polymerization has already started occurring, a carbon radical scavenging inhibitor like PBQ, PTZ, 4-hydroxy-Tempo or Tempo is acceptable. Until the storage tank temperature can be brought back to normal conditions, more frequent monitoring of tank temperature and inhibitor concentration is recommended due to the increased potential for recurring polymerization due to inhibitor depletion at higher temperatures. The ability to mix the inhibitor with the **entire contents** of the tank is critical and must be considered during the design of storage tanks and supporting equipment. The system for adding the inhibitor should be designed to prevent personnel exposure to the inhibitor and VAM vapors. Addition of inhibitor through a closed loop system such as a dip tube or bottoms valve is recommended to prevent flammability risks.

5.3. Managing Spills

Only professionally trained personnel provided with full personal protective gear should be involved in a VAM spill response and cleanup. The following procedures should be followed for cleaning VAM spills:

Initial Response

- Call emergency response telephone number provided from facility, supplier, SDS, shipping paper or other source.
- As an immediate precautionary measure, isolate the spill or leak area for at least 50 meters (150 feet) in all directions (ERG 2016). Larger spills will likely involve the need to isolate larger areas and/or the potential for downwind evacuation.
- Evacuate non-protected and non-professional personnel from the affected area.
- Keep non-emergency response personnel away.
- Stay upwind.
- Keep personnel out of low areas, where VAM may collect.
- Immediately turn off or remove all possible sources of ignition.
- Ensure containers and transfer lines are grounded during loading/offloading.
- Implement initial downwind evacuation based on consequence analysis of accidental catastrophic releases from the risk management plan. The 2016 Emergency Response Guidebook recommends an evacuating area of at least 300 meters (1,000 feet) downwind, though this recommendation expands to 800 meters (2,600 feet; ½ mile) in all directions if fire is involved (see Section 5.1.2 on Fire Fighting/ Evacuation).
- Provide adequate ventilation until area is clean.
- Prevent VAM from contacting peroxides, hydroperoxides, hydrogen peroxide, azo compounds and other polymerization initiators, as well as strong acids, alkalis or oxidizing agents.

Containing and Managing Small Spills

- Place leaking containers in well ventilated areas with spill containment.
- Cover liquid VAM with nonflammable absorbent material (e.g., diatomaceous earth, absorbing pads) and allow it to soak up the spilled material.
- Commercially available spill cleanup kits are suggested for small spills. Choice of spill kit should be appropriate for amount of VAM handled, size of containers and site conditions.
- If odor problems persist after a small spill has been thoroughly cleaned, lime or other alkaline material may be used to deodorize the area.

Containing and Managing Large Spills

- Locate and correct source of spill or leak, if possible to do so safely.
- Contain the spill in a diked area if possible.

- Cover the liquid with alcohol type foam to decrease vaporization and/or chance of ignition. Water spray may be used to reduce vapors.
- Keep the material out of sewers (explosion danger) and surface waters. Should accidental spillage reach surface waters or the municipal sewer system, notify appropriate pollution control and water supply agencies.
- Floating booms should be kept on hand where the possibility of spillage to water exists for use in pulling the floating monomer into a smaller area where it can be skimmed off.
- Determine if release is reportable under applicable laws and regulations and notify appropriate authorities.

<u>Disposal</u>

- Dispose of spilled material by biological oxidation if initial VAM concentration is below toxic levels for microorganisms, otherwise dispose of by controlled incineration.
- Properly dispose of contaminated dirt or absorbent material in compliance with applicable local, regional, and/or national waste regulations.
- Do not wash spillage or leakage into sewer system. Prevent runoff into storm sewers and ditching leading to natural waterways.

5.4. Reporting Releases to the Environment

Under the US Federal Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 and EPCRA, unauthorized releases of listed substances to the environment above their “Reportable Quantity” (RQ) must be reported. Transportation spills greater than the reportable quantity are also reportable. In the US, the RQ for VAM is set at 5,000 pounds. As such, any single unauthorized release above 5,000 pounds must immediately be reported to the appropriate authorities. Facilities that have on-site more than 1,000 pounds of VAM are subject to this reporting requirement. Reports are to be filed with the National Response Center (see Appendix II for contact information), the appropriate State Emergency Response Commission (SERC) and the Local Emergency Planning Committee (LEPC). (Appendix II identifies sources of additional information on these reporting requirements.)

Some states or regional authorities have established their own environmental reporting programs that can be more stringent than the national requirements. As such, facilities handling VAM should be familiar with all regulatory requirements.

In Canada, under the Canadian Transportation of Dangerous Goods (TDG) regulations, the RQ for Class 3, Category II, substances like VAM is any quantity. In the event of an accidental release of that quantity or more, an “immediate report” is required to be made with the following:

- Appropriate provincial authority
- Employer of the person who has possession of the dangerous goods
- Consignor of the dangerous goods
- For a road vehicle, the owner, lessee or charterer of the road vehicle

- For a railway vehicle, Canadian Transport Emergency Centre of the Department of Transport (CANUTEC); see Appendix II for contact information
- For a ship, CANUTEC, a Vessel Traffic Services Centre or a Canadian Coast Guard radio station
- For an aircraft, an aerodrome or an air cargo facility, CANUTEC and the nearest Regional Civil Aviation Office of the Department of Transport and, if the aerodrome is an airport, the operator of the airport
- For an accidental release from a cylinder that has suffered a catastrophic failure, CANUTEC

Follow-up reports may be required in both the US and Canada after initial notification of a release. Some state and local governments in the US have additional requirements.

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AIChE Center for Chemical Process Safety http://www.aiche.org/ccps/
AIChE Design Institute for Emergency Relief Systems
http://www.aiche.org/TechnicalSocieties/DIERS/index.aspx
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APPENDIX I: BULK STORAGE DESIGN

1. Building Design

Equipment and vessels containing vinyl acetate monomer (VAM) should be isolated from other facilities by good design practices and the use of fire resistant materials. Standard firewalls are recommended for the isolation of larger equipment and storage tanks, while partitions of plaster on metal framing may be used to isolate smaller equipment from other combustible materials.

At least two means of exit should be provided from each room or building in which VAM is stored or used. No area of such a room or building should be further than 75 feet from the nearest exit. Additional exits should be provided depending on the number of persons in the building (see NFPA 101). All exit doors should open out in the direction of travel and should be provided with panic hardware (e.g., emergency exit bar door). Fire doors should be of an approved type. A fire resistant stairwell with self-closing fire doors should be provided where hazardous operations are carried out on upper floors.

Operations where large quantities of VAM are used should preferably be processed in outdoor type structures or housed in one-story buildings protected by automatic sprinkler systems. Explosion vents may be used to reduce destructive damage to buildings, ducts, mixers, blenders, dryers and similar equipment in places where flammable vapors of VAM are liable to concentrate. Explosion venting windows, roof and wall panels, skylights, light windows, diaphragms, etc., may be used to minimize building damage due to explosion.

Since the required surface area of explosion vents depends upon such factors as the intensity of an explosion, vapor temperature, type of structure, type of vent closure, etc., the determination of required vent capacity should be made by experienced engineers. Consideration may be given to explosion suppression systems (see NFPA 68).

Static electricity is a particular problem when handling flammable materials. Consequently, shipping and storage containers, reaction vessels and transfer lines should be electrically grounded and bonded. NFPA 77: Recommended Practice on Static Electricity provides instructions for proper grounding procedures. Electrical devices and installations in areas where VAM is handled should be suitable for Class I, Group D hazardous locations (as defined by Articles 500 and 501 of the National Electrical Code). In setting up storage and handling facilities and procedures, care should be taken to conform with local ordinances and any regulations of underwriters and insurance companies. The need to segregate floor drains from sanitary or process sewer systems should be considered as well as the question of adequate distances between chemical storage buildings and other buildings and processing equipment.

Buildings used for processing or storing VAM should be well ventilated to prevent accumulation of vapors and exposure to personnel. Ventilation methods include local exhaust and general dilution procedures. Regional standards and regulations governing air exchange rates in buildings that handle toxic and/or flammable gases should be consulted. Local exhaust is most effective where vapors are emitted from point sources, such as liquid transfer points, pump houses and the reactor area. General dilution ventilation may be used when vapors are emitted from scattered points throughout an area. Because of VAM’s low odor threshold, the ventilated air may require odor abatement.

2. Storage Tank Construction and Location

Type:	Suitable for flammable liquids
Material:	Rust free steel, cured phenolic-lined steel, stainless steel or aluminum
Design:	American Petroleum Institute (API 620 and 650)
Fittings:	Nozzles for temperature, pressure, and level sensors, manhole cover, dip pipe, vent line, pressure and vacuum relief devices, emergency relief devices, manometer level gauge, high level alarm and/or interlock, overflow, fill and discharge

Other common lining materials such as copper, copper alloys (e.g., brass and admiralty metal), zinc and galvanized steel should **not** come into contact with VAM because these can have adverse effects on end uses.

A newly constructed carbon steel tank should be prepared for service by sandblasting and vacuum cleaning. If the cleaned tank is not to be immediately filled with monomer, it should be closed and blanketed with dry air or inert gas to retard rusting.

VAM is typically stored in a vertical (API 620 or 650 design) above ground tank. There may be local regulations that require additional design aspects (e.g., internal floating roofs). The design selected should allow for mixing of the contents with new deliveries or when additional inhibitor is added in order to achieve uniform distribution of the inhibitor. The tank should be set on a concrete pad within a concrete dike of sufficient capacity capable of holding a minimum of the entire tank’s contents. Storage tanks containing materials that are incompatible with VAM must not be placed in the same dike. A tank well with a bottom drain line through the tank pad will provide complete tank drainage.

For VAM floating roof tank designs, a “pan” style design is suggested over “pontoon” for floating roof tanks, as the “pan” style has greater resistance to polymer buildup than the “pontoon” style.

Tanks normally used for VAM storage may be coated with a heat or light reflective coating (e.g., white or reflective paint) in order to minimize heat absorption and to reduce possible air emissions.

Tanks must be electrically grounded to prevent accumulation of static electricity, which could discharge and ignite flammable VAM vapors. The design, testing and maintenance of grounding systems are beyond the scope of this document. Refer to applicable regulations and design standards (e.g., NFPA 70, 70B and 77, IEEE Standards 81 and 142).

When filling, circulating or agitating VAM in a storage tank, care should be taken to not vigorously disrupt the liquid surface, which will cause generation and accumulation of a static charge within the liquid. This applies even if the tank vapor space is made inert with nitrogen. If VAM is fed into a storage tank through a dip pipe, the dip pipe must be electrically grounded to prevent the buildup of a static electrical charge.

Equipment such as emergency vents and instrumentation that are attached to a VAM storage tank should be designed to prevent accumulation and polymerization of VAM. Vapors of VAM can condense in equipment such as emergency vents, vacuum breakers, instrumentation tubing, nozzles and piping.

Caution: It is critical to note that the condensate will not contain any polymerization inhibitor and may begin to polymerize.

Polymerization will occur and could affect performance of critical safety and operational devices. Therefore, equipment attached to a tank should be designed such than all condensate drains into the tank. In the case of instrumentation tubing, VAM vapors can be kept out of the tubing with a small nitrogen purge. VAM storage tanks and supporting equipment (e.g., pipes, pumps, and valves) should be designed and operated to prevent stagnant areas where liquid VAM could remain for long periods of time and lead to polymerization.

3. Storage Tank Equipment

3.1. Temperature Measuring Device

An unusual increase in temperature may be an indication of VAM polymerization. Therefore, continuous temperature monitoring with the ability to observe trends in tank temperature is a valuable tool for early detection of polymerization. One temperature sensing element should be placed near the tank bottom to ensure that it is always in liquid. In large bulk storage tanks, additional sensing elements should be installed at different elevations in the tank as localized polymerization can occur in tanks that are poorly mixed. Additionally, a high temperature alarm should also be installed to warn of polymerization. It should activate at a temperature of about 5°C above the normal maximum temperature of the stored liquid, however this value may be revised based on historical experience and as needed to account for ambient and process conditions. Refer to Section 5.2 on addition of inhibitor if tank temperature exceeds alarm level.

3.2. Emergency Vent-Pressure Relief Devices

Storage tanks containing VAM should be equipped with one or more emergency vents sized according to local, regional and/or national regulations (e.g., NFPA 30 or ATEX 95). It should be noted that despite conformance with engineering standards, such devices may not provide sufficient pressure relief in the event of an uncontrolled or runaway polymerization. Runaway polymerization can be prevented by maintaining an adequate concentration of polymerization inhibitor and preventing exposure to high temperature and reactive contaminants. Vacuum relief is also required to prevent collapse or rupture of the tank should the tank pressure control system fail during withdrawal of liquid from the tank. It is recommended to design the tank at full vacuum. As ambient air is drawn into the tank via the vacuum breaker, moisture and other contaminants may enter the tank and lead to undesirable consequence.

For further guidance on emergency pressure relief device designs, contact organizations such as the AIChE Design Institute for Emergency Relief Systems (DIERS) or the AIChE Center for Chemical Process Safety (CCPS).

3.3. Reducing Air Emissions

VAM emissions from point sources can be reduced by vapor recovery systems that recapture the monomer or emission control devises such as flares or incinerators. These (or other) emission reduction systems should only be installed after consulting with appropriate technical and regulatory experts.

3.4. Tank Head Space Considerations

It is recommended to have a dry blanket nitrogen in the tank headspace.

Dry air may be used but it results in a flammable atmosphere in the tank and oxygen promotes formation of organic peroxides which are polymerization initiators.

In cases where air is used instead of nitrogen in the tank headspace, the air should be dry. Drying agents (typically, molecular sieves or calcium chloride) can be used. The drying agent should be renewed as needed to maintain a dry headspace. Silica and alumina are not recommended due to incompatibility with VAM.

3.5. Flame Arrester

Flame arresters should be used on vent lines for tanks holding flammable liquids and are frequently required by regulation. They are not used on emergency vents that vent directly to the atmosphere. Flame arresters should be regularly inspected for blockage by vinyl acetate polymer deposits. Initial inspection frequency should be at least once every 6-12 months and then can be modified based on experience and performance history. When using closed circuit unloading, an additional flame arrester should be installed in the vapor return line.

3.6. Overflow Protection

Safe guards such as high-level interlocks or other systems should be used to prevent overfilling the tank. If the capacity of the tank is exceeded during transfer of monomer from a delivery vehicle, the excess monomer should flow through a properly designed overflow protection system such as an overflow vent, seal pot/loop (collection devices connected to the tank) into a suitable receiver.

3.7. Liquid Level Measurement and Control

A differential pressure transmitter is the preferred method for measuring liquid level. The transmitter tap to the tank vapor space should be purged using dry nitrogen to prevent condensation of VAM vapor in the tap, which would cause an erroneous level measurement. Use of a differential pressure transmitter also allows continuous readout of the liquid level at remote locations (e.g., control room).

A separate high level switch or differential pressure transmitter should be used to trigger liquid flow shut off into the tank in cases where overfilling the tank would create unsafe (e.g., spill) or undesirable (e.g., tank damage) consequences. The measurement device used for the high level shutoff should not be the same device used to control the tank level so that both control and shut off functions are not disabled by a single instrument failure. The high level sensor should be set based on tank capacity, fill rate and time required for manual intervention should the automated shut off fail to work (e.g., shut off at 90 percent of tank maximum liquid level). A high level alarm (e.g., 85 percent level) can provide a warning that the shutoff level is being approached. While alarm levels can vary from these values, users are responsible for determining the maximal safe tank levels and alarm settings consistent with safe operating conditions.

3.8. Pumps

Double mechanical seals are typically used as the sealing mechanism for VAM process pumps. Double mechanical seals, specifically the barrier fluid seal pot, provide containment of the VAM in the event of a seal failure. Seal-less (e.g., mag-drive) or canned pumps are also acceptable. If tank cars or tank trucks are to be unloaded from the top, a self-priming centrifugal pump is recommended. Consult your pump supplier to match material compatibility with VAM.

Caution: If seal-less or canned pumps are used, heat generation can cause polymerization in the pump if flow is stopped.

Care should be taken to prevent dead-heading (i.e., running pump with a blocked discharge line) of any pump used with VAM. Pump discharge piping and any related components must be capable of handling the maximum pump dead-head pressure, or suitable over pressure protection (e.g., a relief valve discharging to a safe location) can be provided. To prevent heat buildup, a pump should not be allowed to circulate through a relief valve or other recirculation line for extended periods of time. Dead-heading of the pump or continued circulation without adequate cooling will lead to polymerization of VAM over time. Dead-heading a pump may result in a seal leak, pump failure, loss of containment and possibly a fire. An automated pump shut-off system should be considered where pump dead-heading could create safety and material quality issues.

3.9. Pipe

Steel piping should be cleaned of all grease and scale adhering to the inner walls. All pipes should be painted white or otherwise protected from the heat of direct sunlight. All pipes should be pitched to drain and not retain VAM that could subsequently polymerize. Pipelines and associated systems that will be dormant should be drained and cleared as any VAM remaining in the lines may polymerize.

Nitrogen should be used to blow pipelines clean, due to the potential for generating flammable vapors and static charges.

3.10. Valves

Type:	Polytetrafluoroethylene (PTFE)-sleeved plug valves, globe valves, gate valves, ball valves
Material:	Carbon steel, ductile iron or stainless steel

Ball valves with PTFE seals are suggested for on-off service.

3.11. Gaskets

Consult your gasket supplier to ascertain material and design compatibility.

Note: The impact of heat from external fires may compromise gasket integrity and should be considered in gasket selection given VAM’s flammability.

3.12. Filter

Rust particles or other particulate matter can be satisfactorily removed from VAM by means of a cartridge filter.

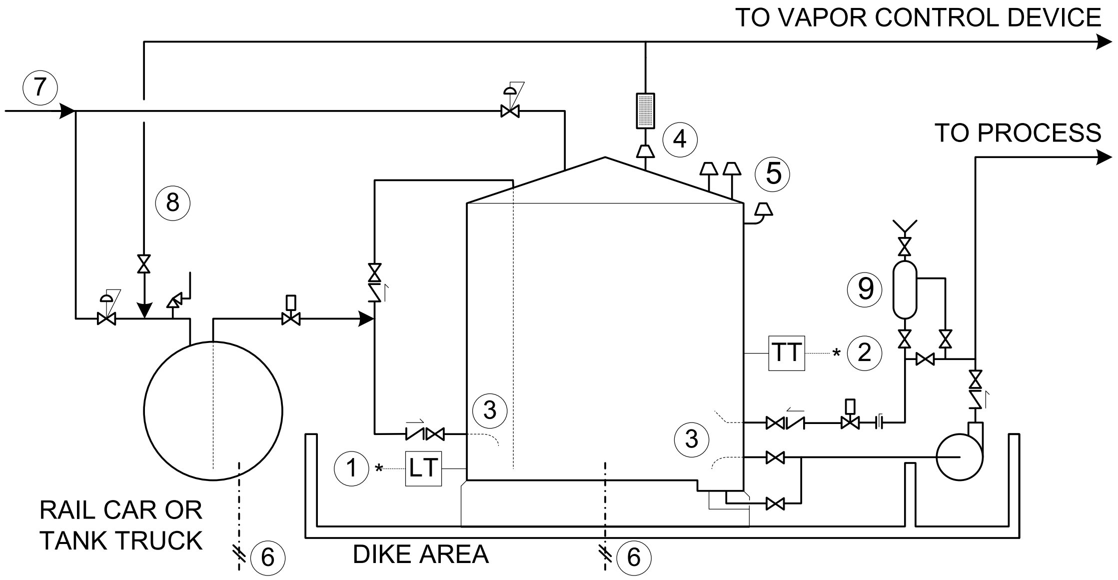
Type:	In-line cartridge filter
Material:	White cotton fiber or polypropylene wound on a stainless core or stainless steel mesh

3.13. Prevention of Spills from Storage Tank Piping

Designers and operators of VAM storage tanks should consider the potential for large releases of liquid due to failure of piping connected to the tanks. Check valves on inlet lines and remote shutoff valves on outlet lines may be used to minimize the risk of emptying tanks through failed piping. Some localities may require the installation of fusible link valves to stop the flow of monomer from storage tanks in case of a fire in the vicinity of the tank. Valves used to prevent releases from VAM storage tanks should be located close to the tanks to minimize the amount of unprotected piping between the valves and tanks. Other considerations include the proper design, installation and inspection of piping and adoption of safe work practices to prevent damage to piping.

3.14. Diagram of Storage Tank

Figure 1 – Typical VAM Unloading and Storage Facility



① Level transmitter(s) providing level indication in control room. High level alarm(s) and automated shutoff(s) of liquid feeds to prevent overfilling tank. Low level alarm(s) and automated shutoff(s) of liquid flow to internal mixing nozzle to prevent generation of static electricity due to spray above liquid surface. Separate transmitters may be required for level control and safety shutoff(s).

② Temperature transmitter at bottom of tank providing temperature indication and high temperature alarm(s) in control room. Multiple measurements at different tank elevations may be needed for large tanks.

③ Typical options for liquid feeds with internal dip tubes and mixing nozzles.

④ Pressure control device and detonation arrestor in vent to control device.

⑤ Emergency vent(s), vacuum vent with flame arrestor, and overflow vent.

⑥ Grounding systems.

⑦ Dry nitrogen (preferred) or dry air supply for maintaining positive pressure in head space of tank.

⑧ Vapor return line from tank to shipping container.

⑨ Inhibitor addition tank.

APPENDIX II: CONTACTS: EMERGENCY RESPONSE, TRANSPORTATION AND OTHER REGULATORY AUTHORITIES

North America

- CHEMTREC: 800-424-9300 or http://www.chemtrec.com/Chemtrec/

Canada

- CANUTEC: 613-996-6666

United States

- National Response Center: 800-424-8802 or http://www.nrc.uscg.mil/nrchp.html
- State Emergency Response Commission (SERC): obtain individual state contacts at: http://www.epa.gov/emergencies/content/epcra/serc_contacts.htm
- Local Emergency Planning Committee (LEPC): obtain contacts at: http://yosemite.epa.gov/oswer/LEPCDb.nsf/HomePage?Openform
- Federal Emergency Management Act (FEMA) State Offices and Agencies of Emergency Management: obtain contact information at: http://home.fema.gov/about/contact/index.shtm
- National Emergency Management Association (NEMA): http://www.nemaweb.org/home.aspx

European Union

- ICE – European Emergency Response Network http://www.cefic.org/Templates/shwStory.asp?NID=492&HID=379

APPENDIX III: ACRONYMS AND ABBREVIATIONS USED THROUGHOUT GUIDE

AAR	Association of American Railroads
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guideline Level
AIChE	American Institute of Chemical Engineers
AIHA	American Industrial Hygiene Association
ANSI	American National Standards Institute
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATEX	ATmosphere EXplosive; ATEX 95 is an EU Directive on Equipment and Protective Systems Intended for Use in Potentially Explosive Atmospheres; ATEX 137 is an EU Directive on Minimum Requirements for Improving the Safety and Health Protection of Workers Potentially at Risk from Explosive Atmospheres
CAA	Clean Air Act
CANUTEC	Canadian Transport Emergency Centre of the Department of Transport
CCPS	Center for Chemical Process Safety
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act (also commonly known as “Superfund”)
CFR	Code of Federal Regulations
CHEMTREC	Chemical Transportation Emergency Center
DIERS	Design Institute for Emergency Relief Systems
DIPPR	Design Institute for Physical Properties®
DOT	Department of Transportation
EHS	Extremely Hazardous Substances
EPA	Environmental Protection Agency

EPCRA	Emergency Planning and Community Right-to-Know Act (also commonly known as “Superfund Amendments and Reauthorization Act (SARA) Title III”)
ERG	Emergency Response Guidebook
ERPG	Emergency Response Planning Guidelines
EU	European Union
FEMA	Federal Emergency Management Act
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
HHC	Highly Hazardous Chemicals
HQ	Hydroquinone
IARC	International Agency for Research on Cancer
IC	Incident Commander
IEEE	Institute of Electrical and Electronics Engineers, Inc.
LC50	Median Lethal Concentration
LD50	Median Lethal Dose
LEPC	Local Emergency Planning Committee
SDS	Safety Data Sheet
NA	North America
NEMA	National Emergency Management Association
NFPA	National Fire Protection Association
NIOSH	The National Institute for Occupational Safety and Health
OECD	Organisation for Economic Co-Operation and Development
OEL	Occupational Exposure Limit
OSHA	Occupational Safety & Health Administration
PPE	Personal Protective Equipment

PPM	Parts Per Million
PSM	Process Safety Management
PTFE	Polytetrafluoroethylene
RCRA	Resource Conservation and Recovery Act
RMP	Risk Management Plan
RQ	Reportable Quantity
SCBA	Self-Contained Breathing Apparatus
SCOEL	Scientific Committee on Occupational Exposure Limits
SERC	State Emergency Response Commission
STEL	Short Term Exposure Limit
STOT	Specific Target Organ Toxicity
TDG	Transportation of Dangerous Goods
TLV	Threshold Limit Value
TRI	Toxics Release Inventory
TWA	Time-Weighted Average
UN	United Nations
VAC	Vinyl Acetate Council
VAM	Vinyl Acetate Monomer
WHMIS	Workplace Hazardous Material Information System (Canada)

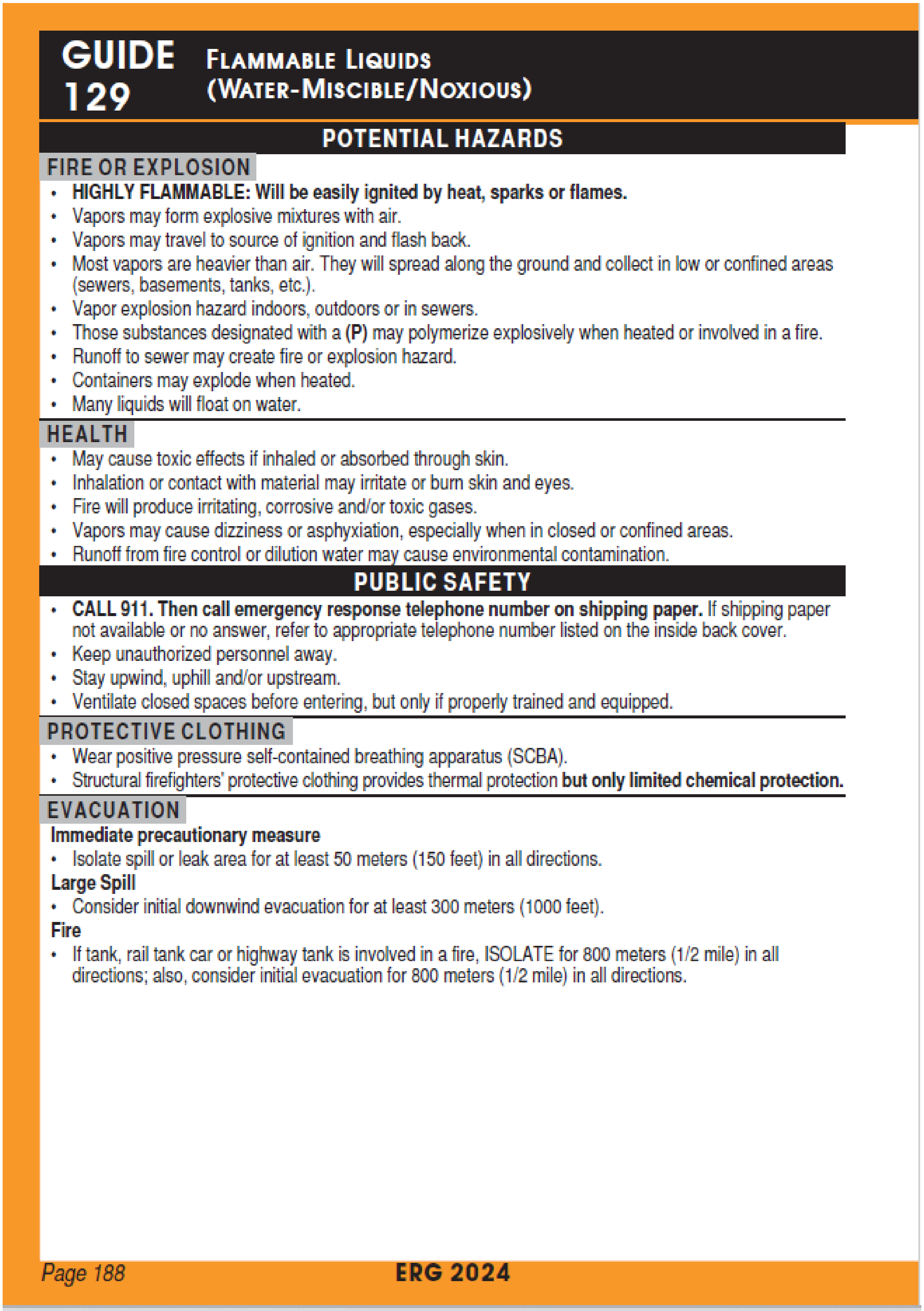
APPENDIX IV: GENERAL PROPERTIES OF VINYL ACETATE MONOMER

PROPERTY	VALUE
Formula Weight	86.09
Critical Temperature	246°C (474.8°F)
Critical Pressure	574.0 psia (39.0 atm)
Normal Boiling Point	@ 760 mm Hg = 72.7°C (162.9°F)
Standard Heat of Formation	Liquid @ 25°C = -83.5 Kcal/mole
Heat of Combustion	@ 25°C = -495 Kcal/mole
Refractive Index	(n_D^{20}) 1.3953
Flash Point	Tag Closed Cup = -8°C (18°F); Tag Open Cup = -4°C (25°F)
Autoignition Temperature	385-426.9°C (725-800°F)
Physical State	Liquid
Relative Evaporation Rate (n-butyl acetate = 1)	8.9
Vapor Pressure @ 60°C	487.4 mm Hg
Vapor Pressure @ 40°C	222.1 mm Hg
Vapor Pressure @ 20°C	89.1 mm Hg
Antoine Equation	Log P = A - [B/(T+C)] - Log = Base 10 - T = °C - P = mm Hg - Range = 10 to 83°C
Equation Coefficients	- A = 7.51868 - B = 1452.058 - C = 240.588

PROPERTY	VALUE
Color	Clear and colorless
Specific Gravity (20/20°C)	0.934
Vapor Density (Air = 1.00)	2.97
Viscosity @ 20°C	0.43 cps
Melting Point	-92.8°C (-135°F)
Heat of Vaporization (1 atm)	87.6 cal/g
Heat of Polymerization	21.3 Kcal/mole
Specific Heat @ 20°C (liq.)	0.46 cal/g °C
Odor	Not unpleasant, sweetish smell in small quantities
Odor Threshold	Approx. 0.25-0.5 ppm
Reactivity	Reactive with self and variety of other chemicals. Stable when properly stored and inhibited.
Water Solubility: - VA in Water @ 20°C	2.3% by weight
- Water in VA @ 20°C	1% by weight
Light Sensitivity	Light promotes polymerization
Electrical Conductivity @ 23°C	2.6 x 10^4 pS/m (1 S = 1 mho)
Surface Tension (20°C)	23.6 dynes/cm
Coefficient of Cubical Expansion	0.00137 per °C at 20°C
Upper Flammability Limit	13.4 vol% in air
Lower Flammability Limit	2.6 vol% in air

Data presented in Appendix IV are largely extracted from the AIChE Design Institute for Physical Properties (DIPPR®) (www.aiche.org/DIPPR/) and also from the EU Risk Assessment Report on VAM (EU 2008a) and the EU Substance Evaluation report (ECHA 2020).

APPENDIX V: GUIDES 129 FROM 2024 EMERGENCY RESPONSE GUIDEBOOK



GUIDE 129 FLAMMABLE LIQUIDS (WATER-MISCIBLE/NOXIOUS)

POTENTIAL HAZARDS

FIRE OR EXPLOSION

- **HIGHLY FLAMMABLE: Will be easily ignited by heat, sparks or flames.**
- Vapors may form explosive mixtures with air.
- Vapors may travel to source of ignition and flash back.
- Most vapors are heavier than air. They will spread along the ground and collect in low or confined areas (sewers, basements, tanks, etc.).
- Vapor explosion hazard indoors, outdoors or in sewers.
- Those substances designated with a **(P)** may polymerize explosively when heated or involved in a fire.
- Runoff to sewer may create fire or explosion hazard.
- Containers may explode when heated.
- Many liquids will float on water.

HEALTH

- May cause toxic effects if inhaled or absorbed through skin.
- Inhalation or contact with material may irritate or burn skin and eyes.
- Fire will produce irritating, corrosive and/or toxic gases.
- Vapors may cause dizziness or asphyxiation, especially when in closed or confined areas.
- Runoff from fire control or dilution water may cause environmental contamination.

PUBLIC SAFETY

- **CALL 911. Then call emergency response telephone number on shipping paper.** If shipping paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.
- Keep unauthorized personnel away.
- Stay upwind, uphill and/or upstream.
- Ventilate closed spaces before entering, but only if properly trained and equipped.

PROTECTIVE CLOTHING

- Wear positive pressure self-contained breathing apparatus (SCBA).
- Structural firefighters' protective clothing provides thermal protection **but only limited chemical protection.**

EVACUATION

Immediate precautionary measure

- Isolate spill or leak area for at least 50 meters (150 feet) in all directions.

Large Spill

- Consider initial downwind evacuation for at least 300 meters (1000 feet).

Fire

- If tank, rail tank car or highway tank is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

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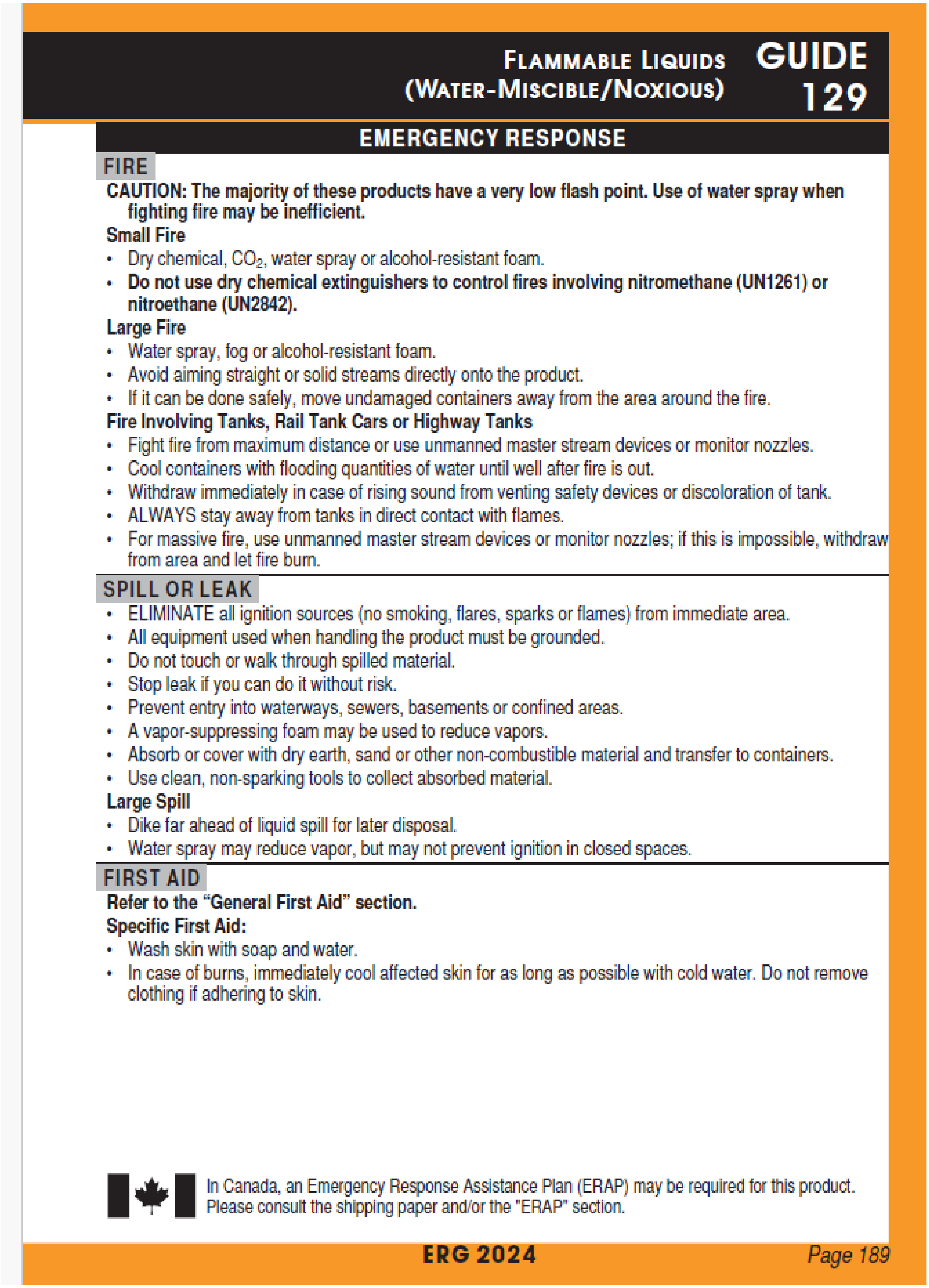

FLAMMABLE LIQUIDS (WATER-MISCIBLE/NOXIOUS)

GUIDE 129

EMERGENCY RESPONSE

FIRE

CAUTION: The majority of these products have a very low flash point. Use of water spray when fighting fire may be inefficient.

Small Fire

- Dry chemical, CO_2, water spray or alcohol-resistant foam.
- **Do not use dry chemical extinguishers to control fires involving nitromethane (UN1261) or nitroethane (UN2842).**

Large Fire

- Water spray, fog or alcohol-resistant foam.
- Avoid aiming straight or solid streams directly onto the product.
- If it can be done safely, move undamaged containers away from the area around the fire.

Fire Involving Tanks, Rail Tank Cars or Highway Tanks

- Fight fire from maximum distance or use unmanned master stream devices or monitor nozzles.
- Cool containers with flooding quantities of water until well after fire is out.
- Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
- ALWAYS stay away from tanks in direct contact with flames.
- For massive fire, use unmanned master stream devices or monitor nozzles; if this is impossible, withdraw from area and let fire burn.

SPILL OR LEAK

- ELIMINATE all ignition sources (no smoking, flares, sparks or flames) from immediate area.
- All equipment used when handling the product must be grounded.
- Do not touch or walk through spilled material.
- Stop leak if you can do it without risk.
- Prevent entry into waterways, sewers, basements or confined areas.
- A vapor-suppressing foam may be used to reduce vapors.
- Absorb or cover with dry earth, sand or other non-combustible material and transfer to containers.
- Use clean, non-sparking tools to collect absorbed material.

Large Spill

- Dike far ahead of liquid spill for later disposal.
- Water spray may reduce vapor, but may not prevent ignition in closed spaces.

FIRST AID

Refer to the "General First Aid" section.

Specific First Aid:

- Wash skin with soap and water.
- In case of burns, immediately cool affected skin for as long as possible with cold water. Do not remove clothing if adhering to skin.

In Canada, an Emergency Response Assistance Plan (ERAP) may be required for this product. Please consult the shipping paper and/or the "ERAP" section.

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APPENDIX VI: EXAMPLE LIQUID CHROMATOGRAPHIC METHODS FOR HYDROQUINONE IN VINYL ACETATE MONOMER

Liquid Chromatic Method for HQ in VAM: Example 1

SCOPE:

This method describes procedure for determining the concentration of Hydroquinone (HQ) in vinyl acetate monomer (VAM) by liquid chromatography.

SAFETY

All of the reagents used in this method are hazardous. Consult the Safety Data Sheet for the reagents listed for hazard information.

APPARATUS

1. v
2. HPLC column: Phenomenex Synergi Polar-RP, 250 mm x 4.6 mm, catalog # 00G-4336-E0

REAGENTS

1. Mobile Phase A: 0.1 % v/v Phosphoric acid in nanopure water (1 ml H3PO4 in 1L nanopure water).
2. Mobile Phase B: HPLC grade Acetonitrile.
3. Hydroquinone (HQ)
4. Vinyl Acetate Monomer, purity 99%+
5. Ortho-phosphoric acid, purity 85%
6. Acetonitrile, HPLC grade
7. Water, purified by Barnstead Nanopure water purification system or equivalent.

INSTRUMENT CONDITIONS

HP 1100 Quaternary Pump

Control

Flow:	1.000 ml/min
Stoptime:	20.00 min
Posttime:	3.00 min

Solvents

Solvent A :	80.0 % (H20, 0.1% H3PO4)
Solvent B:	20.0 % (Acetonitrile)

PressureLimits

Minimum Pressure :	20 bar
Maximum Pressure:	400 bar

Timetable

Time	Solv.B (%)	Flow
0.00	20.0	1.000
3.00	20.0	1.000
15.00	95.0	1.000
20.00	20.0	1.000

HP 1100 Variable Wavelength Detector
Signal
Wavelength: 294 nm
Peakwidth: > 0.1 min
Time
Stoptime: As pump
Posttime: Off
Autobalance
Prerun balancing: Yes
Postrun balancing: No

HP 1100 Autosampler
Injection Mode : Standard
Injector volume: 7.0 µl

RetTime (min)	Name
4.932	HQ

CALIBRATION AND STANDARDIZATION

As the HQ component in the standard is not very stable, the calibration must be carried out immediately after the standard is made from a freshly prepared stock standard.

Prepare 100 ppm of HQ in Vinyl Acetate Monomer.

1. Accurately weigh 0.05g of HQ into a 1000 ml standard flask.
2. Add accurately Vinyl Acetate Monomer to have the final weight at 500 g.
3. Cap and shake the content of the standard flask to ensure proper mixing of HQ.

Prepare 3 ppm of HQ in Vinyl Acetate Monomer.

1. Weigh 3 g of 100 ppm standard into a glass bottle. (Record the weight)
2. Add 97 g of vinyl acetate monomer. (record the total weight).

Prepare 8 ppm of HQ in Vinyl Acetate Monomer.

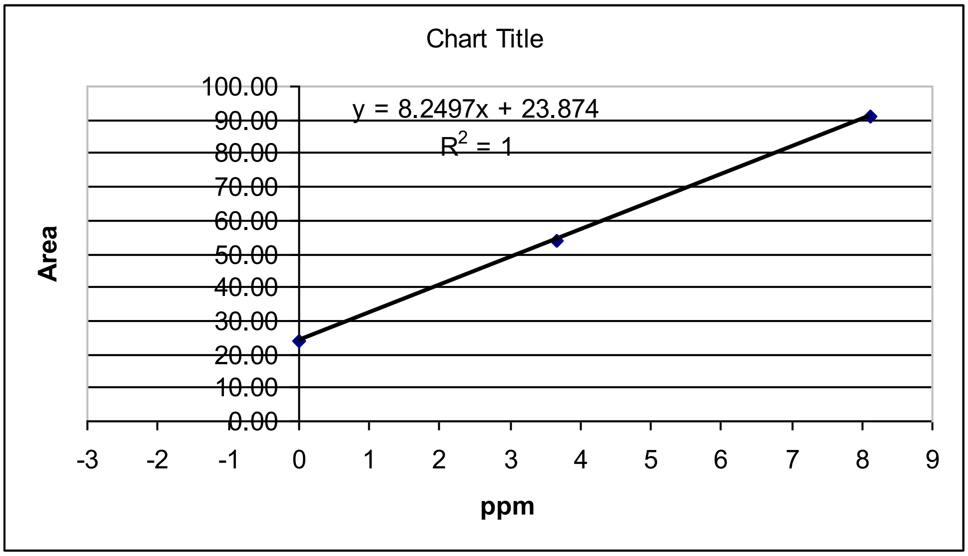
1. Weigh 8 g of 100 ppm standard into a glass bottle. (Record the weight)
2. Add 92 g of vinyl acetate monomer. (record the total weight).

Determine HQ concentrations in the vinyl acetate monomer blank by Standard Addition.

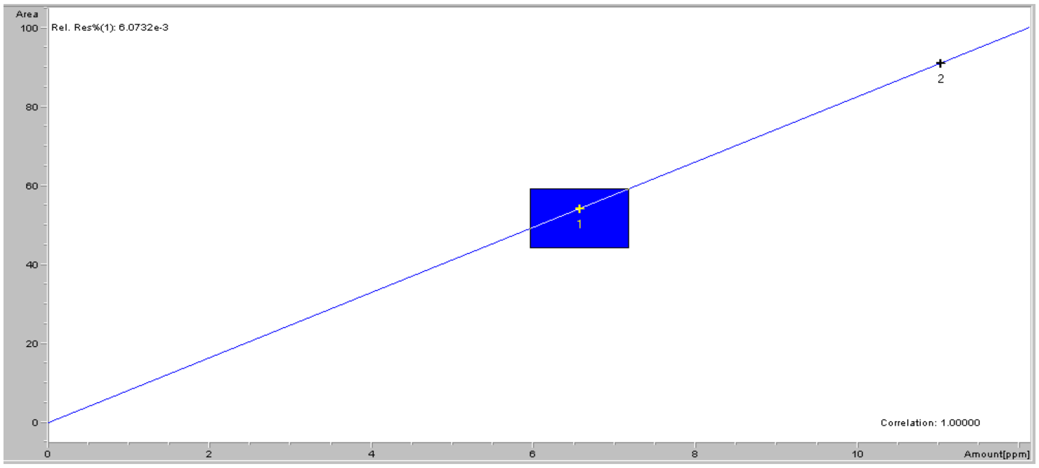
1. Analyze vinyl acetate monomer blank, 3 ppm standard, and 8 ppm standard.
2. Plot peak area vs. 0, 3, 8 ppm.
3. Use the equation obtained from the plot to calculate the HQ concentration in the vinyl acetate monomer blank.
4. Calculate the final concentration of HQ in the standards by adding the concentration in the blank to the spiked HQ concentration.

	Blank	**Standard 1**	**Standard 2**
	HQ	HQ	HQ
Spiked Conc.	0	3.670	8.132
Peak Area	23.87	54.15	90.96
Final Conc.	2.894	6.564	11.026

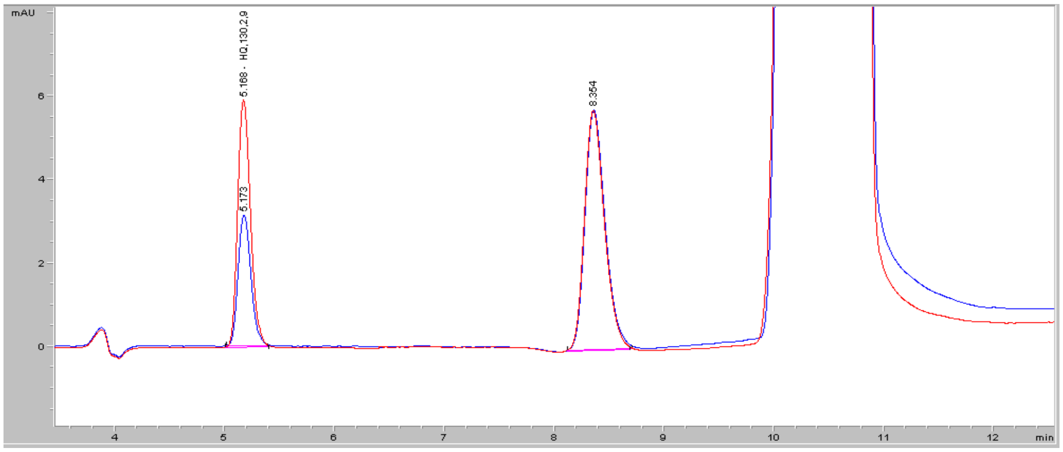
HQ (x) concentration in the vinyl acetate monomer blank is calculated from the equation:
$y = 8.2497x + 23.874$
$x = - 23.874/8.2497 = - 2.894$ ppm



Establish Calibration Curve.
Plot the peak area against the final concentration in above standards to obtain the external calibration curve.



TYPICAL CHROMATOGRAMS OF HQ. Red trace is HQ spiked.



SAMPLE ANALYSIS

1. Place the sample on the respective autosampler tray position.
2. When the sample run is over, the computer prints out the data sheet with result.

REPORTING

Report the HQ in part per million, ppm.

Liquid ChromatographicMethod for HQ in VAM: Example 2

HYDROQUINONE (HQ)

a) Analyze a portion of the sample using the following reverse phase high pressure liquid chromatographic procedure.

b) Instrument parameters

Instrument	Hewlett Packard Model 1090 High Pressure Liquid Chromatograph, or equivalent.
Column	Merck LiChrospher Reverse Phase High Pressure Liquid Chromatographic Column, LiChrospher 100 RP 18. 12.5cm x 4.0 mm with 5 µm spherical particles. Available from VWR Scientific.
Eluent (A)	Phosphoric acid (0.01%) in water.
Eluent (B)	Acetonitrile.
Gradient Program	90% A:10% B for 4 minutes; programmed to 50% A:50% B at 12 minutes; programmed to 100% B at 19 minutes. Hold at 100% B for 6 minutes.
Total Run Time	25 minutes.
Instrument Equilibration Time (between analyses)	5 minutes.
Column Temperature	40°C.
Detectors	Ultraviolet/Visible detector operated at 285 nm.
Sample size	20 µL.
Sparge gas	Helium.

NOTE: The refined vinyl acetate monomer should not be filtered due to the possibility of contamination from the filter.

c) Procedure: Analyze a portion of the sample according to the parameters described in paragraph 6b.

d) Prior to running a sequence of VAM samples, or if the instrument has not been used for greater than 2 hours, perform an injector wash sequence.

e) If the UV lamp has been turned off for any length of time, turn on and allow about 15 minutes for warm-up and equilibrium.

f) Calibration: Hydroquinone standards are prepared by weighing about 0.2500 g of HQ into approximately 26 g of refined vinyl acetate. This gives a solution containing about 0.9 weight percent inhibitor. Sequential dilution of this material with ethyl acetate are made to obtain a series of standards containing about 0.45, 0.10, 0.015, 0.01, 0.001 and 0.0005 weight percent of inhibitor.

g) Analyze the standards according to the parameters shown in paragraph 6b.

h) On graph paper plot the known weight percent inhibitor (y-axis) versus peak area count. The calibration factor for HQ is the slope of its given calibration curve (y/x or weight percent/peak area count).

i) Calculation: Calculate the concentration of inhibitor in the sample using the equation below:

Weight percent inhibitor, i = Slope i x peak area count i x 100

Where

Slope *i* = slope of the calibration curve for HQ, generated in paragraph 6h.
peak area count *i* = Peak area of HQ taken from chromatogram of the sample.

Alternate Method

j) Ceric sulfate, standard 0.002 N solution, Reagent number 29M12.2: Dissolve 1.096 g of ceric ammonium nitrate $(NH_4)_2Ce_3(NO_3)_6$, in 28.0 mL of concentrated sulfuric acid. With stirring, slowly pour the ceric solution into 200 mL of distilled water contained in a 600-mL beaker. When the solution is complete, transfer to a 1-liter flask and dilute to the mark with distilled water.
k) Diphenylamine indicator, Reagent number B7C3.2: Dissolve 0.1 g of diphenylamine in 100 mL of concentrated sulfuric acid. Store in a brown bottle.
l) Hydroquinone standard: Weigh 0.2000 g of hydroquinone to the nearest 0.1 mg. Dissolve and dilute with distilled water to exactly 1000 mL in a volumetric flask. This is an unstable solution. The HQ slowly oxidizes to benzoquinone which is inert to the reagent, hence the solution must be discarded after one week of normal use.
m) Reagent standardization: Pipet 10-mL portions of the hydroquinone solution into each of two 100-mL flasks. Add 3 drops of the diphenylamine indicator and titrate with the ceric sulfate reagent to a light-blue end point, using a 25-mL buret. The titrations should be approximately 20 mL and should agree within 0.5 mL. Average the two values and use in the calculations.
n) Procedure: Pipet 50 mL of the sample into a 250-mL flask.
o) Evaporate the sample at room temperature by passing a stream of nitrogen gas or clean air into the flask. Bench-line air should pass through a fiberglass filter before entering the sample flask. Maintain the flow of air just short of a level causing splattering of the sample. That part of the delivery tube in the flask must be metal, glass, or an inert plastic such as polyethylene or Teflon.
p) After complete evaporation, which requires 45 to 60 minutes, remove the gas stream and dissolve the hydroquinone in 25 mL of distilled water.
q) Add 3 drops of diphenylamine indicator, using the same dropper as in the reagent standardization, and titrate with the ceric sulfate solution to a light-blue end point, permanent for 15 seconds. At the 4-ppm level, this requires approximately 2 mL titration.
r) Calculation:

$$[(V \times F)/(S)] \times 1000 = \text{ppm HQ in sample}$$

V = mL $Ce(HSO_4)_4$ reagent required for the sample titration, from paragraph 6r.
F = factor = (mg HQ in 10-mL aliquot, paragraph 6m) ÷ (average mL $Ce(HSO_4)_4$ reagent, paragraph 6n).
S = grams of sample used = 50 x specific gravity

s) Reference: ASTM Method D 2193.

VINYL ACETATE COUNCIL

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