Vinyl Acetate Monomer

Introduction

Quantum Chemical Corporation, USI Division, is one of the largest manufacturers of vinyl acetate monomer (VAM) in the United States. Our Houston, Texas, facility is the world's largest single VAM manufacturing plant.

This booklet describes applications, specifications and properties for vinyl acetate monomer. It is also a general guide to VAM's storage and handling requirements. For additional information or technical assistance of any kind, contact your nearest Quantum chemicals sales representative.

Applications

VAM is a chemical building block in the manufacture of a wide variety of industrial and consumer products, including the following:

- Polyvinyl acetate (PVA) emulsion polymers are used in paints, adhesives, textile sizings and finishes, nonwoven textile binders, paper coatings and specialty coatings for flexible substrates. Nearly half the VAM produced in the U.S. is used in PVA production.
- Polyvinyl alcohol (PVOH) is prepared by acid or base-catalyzed hydrolysis of polyvinyl acetate beads. Its applications include adhesives, paper and textile coatings and sizings, water soluble packaging films, binders for building products, photosensitive coatings, moldings, extrusions and thickening and emulsifying agents. PVOH is the second largest end use for VAM in the U.S.
- Polyvinyl acetals, the reaction products of polyvinyl alcohol and aldehydes, have significant industrial applications. Polyvinyl formal is often used as an insulating medium for magnetic wire. Polyvinyl butyral is the interlayer for auto safety glass because of its superior stability, adhesion and optical and cold break properties. Polyvinyl acetals are also used in wash primers, metal coatings, textile coatings and adhesives.
- Ethylene-vinyl acetate copolymers made by emulsion and high pressure polymerization are rapidly growing in commercial importance. Quantum Chemical Corporation's USI Division produces and markets Ultrathene® and Vynathene® copolymers containing from 2% to over 50% vinyl acetate incorporated with ethylene. Copolymers with low levels of vinyl acetate incorporated are used in flexible films and coatings. Copolymers with intermediate vinyl acetate levels incorporated are used in molding, compounding and crosslinkable wire and cable coating applications. Copolymers at the high end of the scale of vinyl acetate incorporated are used as the principal ingredient in hot melt coatings and adhesive formulations. Vynathene copolymers with more than 45% vinyl acetate incorporated are found in elastomers, specialty molded rubber applications, pour point depressants, adhesives, caulks and mastics.
- Ethylene-vinyl alcohol (EVOH) barrier resins are coextruded along with structural layers to provide a gas barrier in food, medical, pharmaceutical, cosmetic, agricultural and industrial packaging applications. Packages made from these copolymers can resist odor and flavor permeance, oil and organic solvents, static buildup and weather effects.

The production of latex paints requires polyvinyl acetate, an emulsion polymer made from VAM.

Cover: Quantum Chemical Corporation's VAM plant in Houston, TX.

The development of ethylene-vinyl alcohol barrier resins has made it possible to package in lightweight, unbreakable plastic, foods that once could be contained only in glass or metal.

EVOH resins can be coextruded as film, tube or sheet. They can be blow molded, laminated, thermoformed and vacuum and pressure molded. Scrap from multilayer structures containing EVOH can be economically recovered and reused. EVAL Company of America, a joint venture of Quantum Chemical Corporation and Kuraray Co., Ltd., of Japan, produces a line of EVOH copolymers under the trade name, EVAL® EVOH resins.

Physical Properties

The USI Division produces VAM in a process developed and patented by Quantum. Vaporized acetic acid and ethylene react with oxygen in a fixed-bed tubular reactor over a noble metal catalyst. Distillation and organic-aqueous phase separation produce a VAM-rich aqueous phase. VAM from the aqueous phase is then stripped of remaining impurities to yield a clear, colorless liquid that is 99.9% vinyl acetate by weight. Figures 1 through 3 illustrate some of the physical properties of VAM produced by Quantum.

Figure 1. Vapor Pressure of Vinyl Acetate.[1]

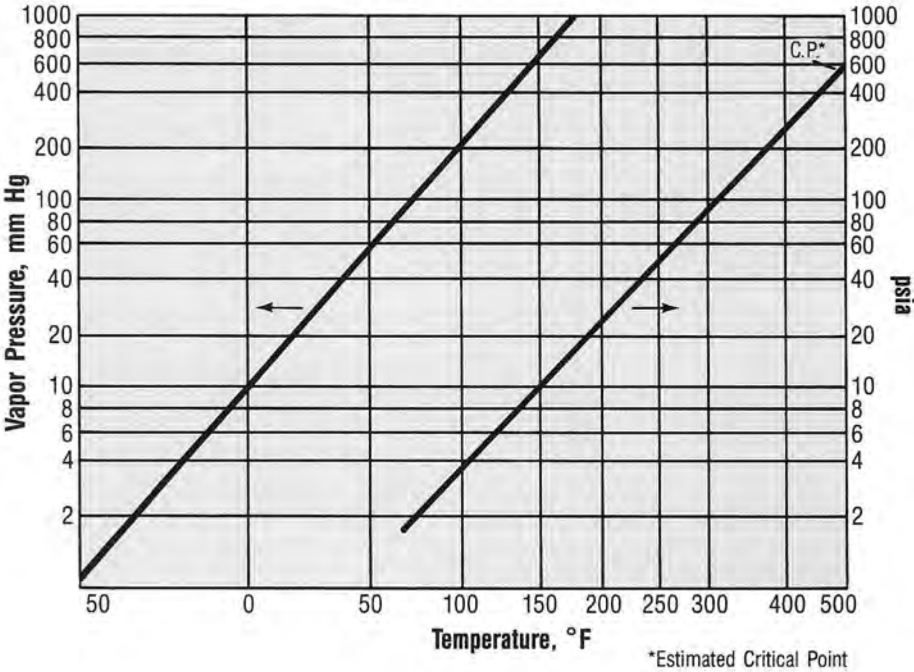
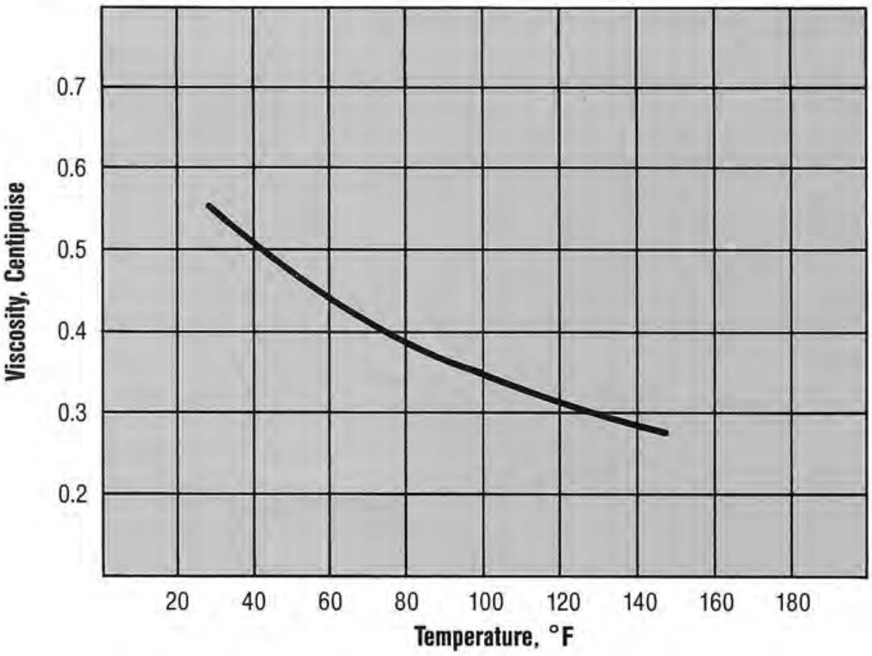


Figure 2. Viscosity of Liquid Vinyl Acetate, Ibid.



[1] Gallant, R.W., Physical Properties of Hydrocarbons, vol. 2, Houston: Gulf Publishing, 1970, pp. 51-55.

Figure 3. Physical Properties Data

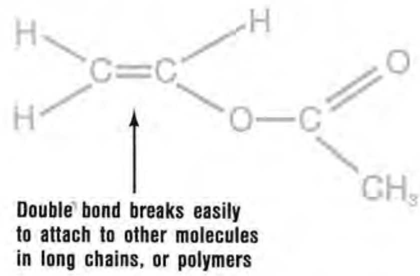
Property	Value	Units	Test Method
Molecular weight	86.088		
Boiling point at 760 mm. Hg	72.5 (162.5)	°C (°F)	
Freezing point	-93.2 (-134.8)	°C (°F)	
Specific gravity at 20/20°C	0.9338		
Weight per gallon at 20°C	7.77	lbs	
Specific heat of liquid at 20°C	0.46	BTU/lb	
Viscosity at 20°C	0.432	centipoises	
Solubility in water at 20°C	2.3	wt %	
Solubility of water in vinyl acetate at 20°C	0.96	wt %	
Flash point, Tag open cup	30	°F	ASTM D 1310
Flash point, Tag closed cup	15	°F	ASTM D 56
Auto ignition temperature	427 (801)	°C (°F)	
Flammable limits in air	2.6 - 13.4	Parts by volume	
Critical temperature	259.4 (498.9)	°C (°F)	
Critical pressure	44.6	atmospheres	
Heat of combustion, at 25°C	489.0	Kcal/mole	
Heat of formation	-92.34	Kcal/mole	
Heat of vaporization, at 72.7°C	90.6	calories/g	
Heat of polymerization	21.3	Kcal/mole	
Reid vapor pressure	3.7	lbs	
Refractive index, n_D^{20}	1.3956		
Surface tension, at 20°C	23.95	dynes/cm	
Vapor density	2.97	air = 1.0	
Coefficient of cubical expansion, 20-40°C	0.00152	per °C	
Solubility in organic solvents at 25°C (acetone, benzene, ethyl ether, heptane, methanol, carbon tetrachloride)	complete		
Color	colorless liquid		

From Kirk, Othmer, eds., Encyclopedia of Chemical Technology, 3rd. ed., vol. 23, New York: John Wiley & Sons, 1983, pp. 817-847.

Polymerization

VAM is an unsaturated compound containing an ethylenic grouping in its molecule. The ethylenic group is extremely active, making VAM a "hot" monomer that polymerizes easily.

Figure 4. The Vinyl Acetate Molecule



Hydroquinone is added to VAM at 3-5 ppm by weight as an inhibitor to prevent premature polymerization. This level maintains stability under normal storage conditions, but does not interfere with polymerization under manufacturing conditions.

When storing VAM, check the inhibitor content every month. You may have to add additional hydroquinone to maintain the concentration at 3-5 ppm. Storing VAM for longer than two months is not recommended. Quantum can supply VAM with higher levels of hydroquinone to meet customers' requirements.

VAM's importance as a chemical building block stems from its readiness to polymerize with other vinyl monomers, with acrylate comonomers, even with itself. In the presence of initiators (or catalysts), VAM adds other molecules across the double bond of its ethylenic group to produce large polymers.

Polymerization Methods

VAM polymerization reactions are fast and highly exothermic. The reaction vessel must be cooled (usually with a refrigerated jacket), the polymerization catalyst thoughtfully chosen and the amount of VAM in the reactor carefully adjusted to control reaction rate and direction.

Carton-sealing adhesives, shown here as solid chips and blocks, are compounded from ethylene-vinyl acetate copolymers and other materials.

VAM can be polymerized by using any of the major polymerization techniques discussed below:

- In **bulk polymerization**, heat is applied to small amounts of catalyst dissolved in the monomer. As the polymerization proceeds, the heat of polymerization and the resulting increase in viscosity may cause difficult problems of heat-removal and reaction control. Regular additions of monomer at the reflux temperature can help control the process.
- In **suspension or bead polymerization**, small droplets of the monomer are suspended in a medium which will not dissolve it. To maximize the monomer's insolubility, the droplets are coated with a protective colloid. Catalyst addition and elevated temperatures initiate the polymerization of the suspended droplets. Agitation and dispersing agents keep the insoluble beads from clumping together. Bead polymerization produces small solid beads.
- In **solution polymerization**, the monomer is dissolved in a pure organic solvent like acetone, methyl ethyl ketone, ethyl acetate or butanol. Catalyst addition and elevated temperatures initiate the polymerization, which usually produces low molecular weight polymers. Solution polymerization is not used as widely as bulk, bead or emulsion polymerization.
- In **emulsion polymerization**, the monomer is agitated with a surfactant in water to disperse it. Adding catalyst and applying heat initiates the polymerization reaction. Emulsion polymerization typically produces very fine polymer particles (1.0 micron to 10 microns in size) dispersed through a milky white medium. The product is used as is or is compounded with a number of other ingredients in latex paints, adhesives, paper coatings, textile coatings and other applications.

Three emulsion polymerization processes are commonly used commercially: batch, semi-continuous and delayed addition. For the batch process, all the ingredients -- solvent (water), comonomers, surfactants, colloids, initiators (catalysts) and buffers -- are added to the reactor and heated to initiate the catalyst. Polymerization occurs at 66°C, completion at 90°C. The resulting product is a high molecular weight, large particle size polymer.

For the semi-continuous process, ingredients are continuously fed to the first reactor. Partially polymerized polymer is continuously moved to one or two additional reactors for completion of the polymerization. The product is a polymer with broad particle size and molecular weight distribution.

Ethylene-vinyl acetate, such as Quantum's Ultrathene copolymers, can be foamed to provide cushioning in the soles and heels of athletic shoes.

For the delayed addition process, the monomer (or comonomers) are added incrementally during the process. Polymerization occurs at a temperature higher than 75°C. The other ingredients (catalyst, surfactant, protective colloids) may also be added gradually. The product is an extremely stable polymer with small particle size.

Physical Forms and Uses of Polymers

Commercial polymer products come in three common forms: solid, liquid and emulsion, with the emulsion products by far the most commonly used.

- Solid polymers -- mainly polyvinyl acetate (PVA) homopolymers produced from solution polymerization -- are processed into large pellets or chunks. They are low molecular weight products that tend to cold-flow together at moderate temperatures and become brittle at 10-15°C. Solid PVA is used in adhesives and specialty coating applications.

  Solid polymers produced from suspension polymerization function as intermediates in the production of polyvinyl alcohol, polyvinyl butyral and polyvinyl formal. The beads are high molecular weight polymers, also used in adhesives and reprographic resins. Suspension polymerization can also produce a powdered homopolymer or copolymer that is typically used in adhesive applications.
- Liquid solutions of homopolymerized vinyl acetate from solution polymerization are often directly used in adhesive applications.
- Emulsion VAM products are the dominant commercial form. Their molecular weight is usually high, but it often varies over a broad range. The colloidal properties of the emulsion and the properties of the dispersed polymer particles can be adjusted somewhat independently, so it is possible to customize products for specific applications.

Quantum's production facility in Houston is the world's largest single VAM plant. Statistical Process Control has been installed at all of Quantum' s plant laboratories to assure that products meet customer requirements.

Storage and Handling

VAM's physical and chemical properties require that you handle it carefully.

- VAM is flammable. The U.S. Department of Transportation (DOT) classifies it as a "flammable liquid." It forms flammable mixtures with air. Always keep it away from heat, sparks, flame or other sources of ignition. Use electrical grounding and bonding when transferring between containers. You must comply with all DOT and other regulations for labeling, loading, transporting, handling and storing flammable liquids.
- VAM is highly reactive. Do not ship or store it without an inhibitor. Keep it away from oxidizing agents and strong acids and bases. Typical materials to avoid include peroxides, ethylenediamine, 2-aminoethanol, ethyleneimine, chlorosulfonic acid, hydrochloric acid, phosphoric acid, sulfuric acid, nitric acid, hydrofluoric acid, sodium hydroxide and potassium hydroxide.
- VAM irritates the eyes, skin and mucous membranes. Do not breathe VAM vapors; work only in areas with adequate ventilation. Do not get the liquid on your skin or in your eyes. Wash thoroughly after working with it. Repeated, prolonged exposures to high airborne concentrations of VAM have resulted in respiratory tract tumors in some laboratory animals.

Material Safety Data Sheets available from your Quantum chemical sales representative provide more detailed information about working safely with VAM.

Labeling Requirements

All Quantum VAM containers are labeled in accordance with applicable Occupational Safety and Health Administration (OSHA) and DOT regulations and good hazard communications practices.

Loading/Unloading Requirements

When loading or unloading a tank truck:

1. Always load with a submerged pipe. Free-falling VAM may produce static electricity which could be a source of ignition.
2. Ground the truck before you connect any part of it to the unloading line or equipment.
3. Electrically bond all containers to the grounded truck before you start filling them.
4. Use a level, paved and accessible station for all unloading activities.
5. If pneumatic pressure is used to aid unloading, an inert gas, such as nitrogen, should be used.

DOT regulations authorize tank truck usage. Where applicable, follow Section 173.115 to 173.119 inclusive and Part 177 of those regulations. Observe all local rules, regulations and ordinances.

When loading or unloading tank cars:

1. Use only clean, oil- and dirt-free, spark-resistant tools and implements.
2. Make sure the tank car's internal pressure has been relieved before you remove the manhole or outlet valve cap. Cool the cap with water, vent it, raise the safety valve or open the vent on the dome at short intervals.
3. Do not vent the car if venting will cause a dangerous amount of vapor to collect outside the car. Wait until pressure is reduced. Let the car stand overnight; or cool the car with water.
4. Ground the tank car before you connect any part of it to the unloading lines or equipment.
5. Unload the car through the dome connection or through the bottom outlet.
6. Never use air pressure for unloading tank cars.
7. Use an approved pump to unload the tank car. If the car does not have an eductor pipe, insert a pipe through the open dome and pump its contents out that way.
8. Vent the car through a flame arrester during unloading.
9. If unloading is interrupted, disconnect all unloading connections, close all valves tightly and securely apply all other closures.

Production process improvments are constantly under study through Quantum's Research and Development Department.

Storage Requirements

When storing VAM in tanks:

1. Carbon steel and mild steel are the recommended construction materials for storage tanks. Aluminum or stainless steel may also be used.

2. Do not use bronze or brass valves, fittings, etc. for VAM storage. Their copper content tends to inhibit polymerization.

3. If tanks are to be painted, paint them white to reduce heat absorption.

4. Pad storage tanks with nitrogen.

5. Inspect all tank flame arresters for presence of polymer and/or dirt regularly.

6. Make sure all tanks are adequately vented.

7. Never use air to pad a VAM storage tank. Air is seldom dry and the moisture, oxygen, carbon dioxide or sulfur dioxide in the air may promote polymerization.

8. Keep VAM away from oxidizing agents like HTH or chlorine bleach.

9. Keep storage temperatures below 100°F.

10. Do not place tanks close to a heat-generating source.

Check National Fire Protection Agency (NFPA) 30 "Flammable and Combustible Liquids Code" and consult with qualified fire protection specialists to determine specific tank storage requirements, such as size of vents, diking and separation distances.

When storing VAM indoors in drums or other containers:

1. Store all VAM containers in noncombustible, well-ventilated structures.

2. Provide trapped floor drains for VAM storage rooms. Pitch the floor to the drains. Make sure the drains lead to a safe location through proper trapping.

3. If no drains are provided, build curbs or a drained gutter covered with an appropriate grill at the door openings.

4. Provide proper protective clothing and equipment for personnel who clean up VAM spills.

5. Provide automatic sprinklers or some other adequate extinguishing system for the VAM storage areas.

6. Do not store oxidizing materials or other incompatible chemicals in the same area.

7. Do not store vinyl acetate in glass containers. Use safety cans with pouring outlets equipped with flame arresters and tight-fitting caps.

8. To store small analytical samples for a short time, use sealed, amber glass bottles with an aluminum-lined closure.

Suggestions for Transfer Equipment

When transferring VAM, follow these equipment specification guidelines:

- Pumps should be centrifugal-type, made of ductile iron, cast iron or carbon steel with no copper-bearing alloys in the construction material. Typical VAM transfer pumps are Ingersoll-Rand Inline Centrifugal pumps, Peerless Horizontal Centrifugal pumps or Gould AVS Centrifugal pumps.
- Gaskets should be Teflon* envelope-type, such as Garlock #900 or Johns Manville 61.
- Hoses and couplings should be made of materials that contain no brass. Carbon steel or stainless should be used whenever possible. Use only butyl and ethylene propylene (EPR) rubber. Recommended hoses and couplings are:

  1. Raybestos Manhattan RB 150, S & D Type R/M Chem Tube-butyl (special formulation) fitted with an 8-inch, 150-pound brass-Vanstone flange on one end and a 6-inch raised face carbon steel flange on the other side (the brass-Vanstone flange does not come in contact with the product).

  2. Raybestos R/M Chem Solve 44 or 45 with a 2-inch female Boss type connector on the other side.
- Rupture discs should be used underneath relief valves when storing VAM under pressure. A means of detecting rupture disc failure should be placed between the disc and the relief valve. Recommended are a BS & B bolted safety head assembly drilled for ASA 150-pound flange bolting and a BS & B rupture disc, Type PLDV, Teflon*-coated on both sides.

*Teflon is a registered trademark of E.I. duPont de Nemours & Co., Inc.

Sampling Procedures

To sample VAM for analysis:

1. Follow standard safety practices for electrical grounding. Use personal protective equipment and obey all regulations.

2. Purge all sample points before you take a sample.

3. Double-flush a small amber glass container with an aluminum-lined closure by shaking it with the closure on.

4. Fill the container to a level which allows enough vapor space for expansion.

5. Retighten the closure a few minutes after closing to create a tighter seal and prevent air diffusion. Moisture seeps in with air to produce invalid high values for acid and aldehyde coming from hydrolysis.

6. If you need to keep a sample, store it at temperatures no higher than 75°F. For long-term storage, check the inhibitor content periodically to prevent polymerization. Add hydroquinone if its level falls below 3 ppm by weight.

Follow the procedures outlined when taking a VAM sample for testing and analysis.