

#### 4. PRODUCTION, IMPORT, USE, AND DISPOSAL

##### 4.1 PRODUCTION

It is not known whether vinyl acetate occurs naturally (IARC 1986). Vinyl acetate is a man-made compound that was first produced in 1912 as a by product in the synthesis of ethylidene diacetate (Matthews 1974). This reaction involved bubbling acetylene through a mixture of mercurous sulfate and anhydrous acetic acid (Leonard 1970). During the 1920s, the Germans converted this liquid-phase process to a vapor phase process that allowed Germany to achieve a production volume of 12 million kg per year by the 1940s and which accounted for most of the world's production of vinyl acetate until about 1970 (Leonard 1970; Rhum 1970). The vapor phase process involved passing a 4:1 acetylene-to-acetic acid mixture over a catalyst bed made of zinc acetate-saturated activated carbon at 180°-200°C. (Daniels 1983; Llewellyn and Williams 1972). Mercury salts can also be used as a catalyst in this reaction when it is conducted at 40°-50°C (International Labour Office 1985). Originally, acetylene was generated from calcium carbide (Leonard 1970). More recently, acetylene has been produced by cracking petroleum (Llewellyn and Williams 1972).

Currently, the manufacturing process most widely used to produce vinyl acetate is the vapor phase ethylene process, an oxidative reaction in which ethylene is bubbled through acetic acid at 120°C in the presence of palladium chloride catalyst (Daniels 1983; IARC 1986). Impurities found in the reaction have been reported at less than 1% (for one manufacturer) and have included the following: acetaldehyde, ethyl acetate, and methyl acetate. The vapor phase ethylene process was developed in 1967 to take advantage of ethylene as a cheaper feedstock than acetylene, and came into widespread use in the 1970s (Daniels 1983; IARC 1986; Llewellyn and Williams 1972). By 1981, the vapor phase ethylene process accounted for 92% of U.S. production and the vapor phase acetylene process accounted for the remainder (Dylewski 1981). Various firms in the United States, Japan, West Germany, and the United Kingdom have independently and/or jointly modified the vapor phase ethylene process by using different types of catalysts in the reaction. The catalyst is usually palladium or its salt, although salts of rhodium, gold, platinum, ruthenium, vanadium, and iridium have also been used (Daniels 1983; Leonard 1970; Llewellyn and Williams 1972). The advantage of these processes is that the catalyst lasts longer and undergoes less corrosion (Mannsville 1982).

A less important commercial manufacturing process for vinyl acetate involves the reaction between acetaldehyde and acetic anhydride. The intermediate species, ethylidene diacetate, undergoes pyrolytic cleavage to vinyl acetate and acetic acid (Daniels 1983; Leonard 1970; Mannsville 1988). This process was used in the United States until the 1960s, and may still be in use at small plants in China, India, and Mexico (Daniels 1983; Mannsville 1982, 1988). Vinyl acetate can also be synthesized in high yields by reacting vinyl chloride with sodium acetate in solution at 50°-75°C, using palladium chloride as a catalyst (Daniels 1983). New methods for vinyl acetate

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manufacture were being developed in 1982 that were to utilize synthetic gas as a feedstock. The gas would undergo a series of carbonylation reactions to yield ethylidene diacetate, which can be pyrolytically converted to vinyl acetate and acetic acid (Mannsville 1982). No information has been found that would indicate whether or not such new methods have been perfected or adopted for industrial production in the United States.

Vinyl acetate is normally produced in three grades that differ only in their content of inhibitor, which is added to prevent spontaneous polymerization (Daniels 1983; Mannsville 1988). To obtain these grades, either 3-7 ppm, 12-17 ppm, or 200-300 ppm *p*-hydroquinone is added to freshly produced vinyl acetate, depending upon how long the product is to be stored prior to use. Longer storage times require higher concentrations of inhibitor (Daniels 1983). Vinyl acetate is often stored and/or shipped with a variety of other inhibitors including benzoquinones, nitrobenzenes, diphenyls, toluenes, anthracene, phenanthrene, naphthalene, and others (Operations Research Inc. 1974).

Commercial production of vinyl acetate in the United States was first reported in 1928 (U.S. Tariff Commission 1930). From 1960 to 1979, U.S. production rose from 250 million pounds to 2.0 billion pounds. Production levels were approximately 1.9 billion pounds between 1980 and 1982, and then rose from 1.96 billion pounds in 1983 to 2.1 billion pounds in 1985. Levels dropped to 1.7 billion pounds in 1986 and then climbed to 1.8 billion pounds in 1987 (Daniels 1983; USITC 1979, 1980, 1981, 1982, 1983, 1984, 1985, 1986, 1987, 1988).

In 1984, with an increasing demand for vinyl acetate derived copolymer emulsions, due primarily to strong automobile and housing industries, production (over 2 billion pounds) was rapidly approaching the "practical effective capacity" of 2.2 billion pounds and supply was limited (Greek 1984). It was forecasted in 1984 that an increased demand for vinyl acetate for making adhesives and coatings would result in a greater capacity in production (Greek 1984). By 1989, the demand for vinyl acetate reached 2.6 billion pounds and is expected to reach 2.9 billion pounds by 1993 (Van et al. 1989). In 1989, five U.S. production facilities had a combined annual production capacity of 2.8 billion pounds (Van et al. 1989).

The following chemical companies currently produce vinyl acetate in the United States: E.I. DuPont de Nemours and Company, Polymer Products Division located in La Porte, Texas; Hoechst Celanese Corporation, Commodity Chemicals located in both Bay City, Texas and Clear Lake, Texas; Quantum Chemical Corporation, U.S.I. Division located in both La Porte, Texas and Clinton, Iowa; Union Carbide Corporation, Solvents and Coatings Materials Division located in Texas City, Texas; Monsanto Company located in Trenton, Michigan (SRI 1989; TR187 1989). For further information on facilities in the United States that manufacture or process vinyl acetate, refer to Table 4-1. Vinyl acetate is also produced in Australia, Brazil, Canada, China, France, West

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TABLE 4-1. Facilities That Manufacture or Process Vinyl Acetate<sup>a</sup>

State <sup>b</sup>	No. of facilities	Range of maximum amounts on site in thousands of pounds <sup>c</sup>	Activities and uses <sup>d</sup>
AL	4	1-499,999	7, 13
CA	16	0.1-9,999	2, 7, 8, 10, 12, 13
CT	1	10-99	7
DE	2	100-999	3, 7
GA	8	10-999	2, 7, 8, 9
IA	1	100-999	1, 3, 4
IL	16 (1) <sup>e</sup>	10-9,999	7, 8, 10
IN	2	1-999	7, 8, 9
KS	2	1-999	7, 13
KY	5 (1) <sup>e</sup>	10-9,999	7, 8
LA	4	10-9,999	3, 7, 12, 13
MA	2	10-9,999	7
MD	1	1,000-9,999	7
MI	3	1-999	1, 5, 7, 13
MO	2	10-999	13
NC	5	1-999	2, 7
NH	1	10-99	7
NJ	11	10-499,999	7, 9, 10
NY	3	1-999	7, 12
OH	7	1-999	7, 8, 13
OR	2	100-999	7
PA	5	1-999	7, 12
SC	10	10-9,999	4, 7
SD	1	10-99	8, 9
TN	2	1-999	7
TX	27	0-49,999	1, 2, 3, 4, 5, 7, 8, 9, 10, 13
PR	2	100-999	7

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TABLE 4-1 (Continued)

State <sup>b</sup>	No. of facilities	Range of maximum amounts on site in thousands of pounds <sup>c</sup>	Activities and uses <sup>d</sup>
VA	2	0.1-9	7, 8
WI	1	0-0.09	8
WV	1	1,000-9,999	4, 7, 10
WY	1	1-9	7

<sup>a</sup>TRI87 1989

<sup>b</sup>Post office state abbreviations

<sup>c</sup>Data in TRI are maximum amounts on site at each facility.

<sup>d</sup>Activities/Uses:

- |                               |                                  |
|-------------------------------|----------------------------------|
| 1. produce                    | 8. as a formulation component    |
| 2. import                     | 9. as an article component       |
| 3. for on-site use/processing | 10. for repackaging only         |
| 4. for sale/distribution      | 11. as a chemical processing aid |
| 5. as a byproduct             | 12. as a manufacturing aid       |
| 6. as an impurity             | 13. ancillary or other use       |
| 7. as a reactant              |                                  |

<sup>e</sup>Number of facilities reporting "no data" regarding maximum amount of the substance on site.

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Germany, Great Britain, India, Italy, Japan, Mexico, South Africa, and Spain (CIS 1988; IARC 1986; Mannsville 1988). In Japan alone there are eight manufacturers of vinyl acetate (CIS 1988). Five Japanese companies reported a combined production capacity of 1.3 billion pounds in 1981 (IARC 1986).

##### 4.2 IMPORT / EXPORT

U.S. imports of vinyl acetate declined, with large fluctuations from 31 million pounds in 1970 to 1 million pounds in 1984 (Mannsville 1988). Imports remained at 1 million pounds until 1986, when a sharp rise to 12 million pounds was observed. Imports then decreased to 1 million pounds in 1987 (Mannsville 1988). Only a small fraction of the vinyl acetate consumed in the U.S. is imported.

Exports of vinyl acetate increased rapidly from 15 million pounds in 1965 to 645 million pounds in 1980 (Mannsville 1988). In 1984, as the demand for vinyl acetate increased and supply was limited, it was predicted that any surplus demand that existed after anticipated increases in production capacity would be satisfied by diversion of the chemical from exports (Greek 1984). Exports were down in 1984 at 515 million pounds, compared with 589.9 million pounds in 1983 (Anonymous 1984; Mannsville 1988). Exports increased steadily after 1984 to a level of 736 million pounds in 1987 (Mannsville 1988). In 1987, U.S. exports of vinyl acetate accounted for approximately 40% of the total production volume (1.8 billion pounds in 1987).

##### 4.3 USE

The primary use for vinyl acetate is as a monomer in the production of polyvinyl acetate and polyvinyl alcohol (IARC 1986). These products, synthesized via polymerization of vinyl acetate, accounted for 75%-80% of total U.S. consumption in 1982 (Mannsville 1982, 1988). Vinyl acetate is also polymerized with vinyl chloride to produce copolymers. Polyvinyl butyral, polyvinyl acetals, ethylene-vinyl acetate copolymers, and acrylonitrile copolymers (for acrylic fibers) are also produced. It is also used in polymeric lubrication oil additives (Daniels 1983; IARC 1986).

Polyvinyl acetate emulsions (homopolymer and copolymer), the major derivatives of vinyl acetate, are widely used in adhesives for packaging and construction (wood gluing) and in water-based paints (IARC 1986; Mannsville 1988). Other important uses include nonwoven textile fibers, textile sizings and finishes, paper coatings, and inks. Polyvinyl alcohol is widely used in textile finishing, adhesives, and as a raw material for polyvinyl butyral, which is used as the adhesive interlayer in architectural and automobile laminated safety glass (Cincera 1983; Mannsville 1988). Uses of other polymers made from vinyl acetate include barriers in packaging, paint and coatings applications, plastic floor coverings, phonograph records, flexible film and sheeting (including plastic films used for wrapping food), food starch modifier, and moulding and extrusion compounds.

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In 1987, the estimated end-use distribution pattern for vinyl acetate was as follows: 55% was used to produce polyvinyl acetate emulsions (homopolymer and copolymer), for use in adhesives (23%), paint emulsions (20%) and textile and paper emulsions (12%); 20% was used to produce polyvinyl alcohol; 10% to produce ethylene/vinyl acetate; 5% to produce polyvinyl butyral; 5% to produce polyvinyl chloride copolymers; and 5% to produce miscellaneous products (Mannsville 1988).

##### 4.4 DISPOSAL

The disposal method for vinyl acetate recommended in Japan, as reported in 1982 by its International Technical Information Institute, was to incinerate the compound by mixing it with a more flammable solvent and spraying it into a furnace (ITII 1982). Information on disposal methods for vinyl acetate that have been accepted or commonly used in the United States is limited. Since underground injection accounts for 2.1 million pounds of vinyl acetate releases, it is a probable method of disposal (TRI87 1989); however, additional information on this method of disposal for vinyl acetate is not available.