ASSESSMENT OF ACETONE AS A POTENTIAL AIR POLLUTION PROBLEM

VOLUME V

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U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park
North Carolina 27711

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Volume V

bу

Robert M. Patterson Mark I. Bornstein Eric Garshick

GCA CORPORATION
GCA/TECHNOLOGY DIVISION
Bedford, Massachusetts

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Contract No. 68-02-1337 Task Order No. 8

EPA Project Officer

Michael Jones

EPA Task Officer

Justice Manning

U.S. ENVIRONMENTAL PROTECTION ACENCY
Research Triangle Park
North Carolina 27711

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ABSTRACT

This report is one of a series which assesses the potential air pollution impacts of 14 industrial chemicals outside the work environment. Topics covered in each assessment include physical and chemical properties, health and welfare effects, ambient concentrations and measurement methods, emission sources, and emission controls. The chemicals investigated in this report series are:

Volume I Acetylene

Volume II Methyl Alcohol

Volume III Ethylene Dichloride

Volume IV Benzene

Volume V Acetone

Volume VI Acrylonitrile

Volume VII Cyclohexanone

Volume VIII Formaldehyde

Volume IX Methyl Methacrylate

Volume X Ortho-Xylene

Volume XI Maleic Anhydride

Volume XII Dimethyl Terephthalate

Volume XIII Adipic Acid

Volume XIV Phthalic Anhydride.

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SECTION I

SUMMARY AND CONCLUSIONS

Acetone is a colorless, highly flammable liquid with a characteristic mintlike odor and taste. It is one of the least hazardous organic solvents. Acute exposure can cause mucous membrane irritation, headache, and narcosis. No deaths due to acute exposure have been recorded. There is no systemic injury associated with chronic inhalation of low concentrations of acetone. The occupational standard for an 8-hour time weighted average exposure is 1000 ppm. Acetone has shown little reactivity in irradiation studies and is not an important component in photochemical oxidant formation.

Simple diffusion modeling estimates place the likely maximum 1-hour average ambient concentration at about 4 ppm. The maximum 24-hour average ambient concentration might be expected to be about 2 ppm.

About 2 billion pounds of acetone were produced at 12 plants in 1974, with about 30 percent being used as a solvent. Production is expected to increase by 6 percent per year through 1978. Emissions result primarily from solvent usage, production, use as an absorbent packing for acetylene, bulk storage, and end-product manufacturing. About one-third of total production is eventually lost as emissions.

Two types of emission controls are used extensively by the industry. These are vapor recovery and incineration. Control by adsorption on activated charcoal is used when recovery is economically desirable. The primary advantage of incineration is that low concentrations may be oxidized with only small supplemental fuel requirements. Fixed roof storage

tanks can be controlled by venting to an adsorber or incinerator, or they can be converted to floating roof design.

Based on the results of the health effects research presented in this report, and the ambient concentration estimates, it appears that acetone as an air pollutant does not pose a threat to the health of the general population. In addition, acetone does not appear to pose other environmental insults which would warrant further investigation or restriction of its use at the present time.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Acetone is a colorless, highly flammable liquid with a characteristic pungent, mintlike odor and taste. The main industrial methods of manufacture are the catalytic dehydrogenation of isopropanol and the oxidation of cumene. Acetone is used as an intermediate in the manufacture of methyl methacrylate and other chemicals. It is also widely used in lacquers and varnishes as a solvent, and in the rubber, dyeing, celluloid, rayon acetate and leather industries. It is a solvent for many fats and oils, a stain remover, and a common laboratory solvent. Significant properties of acetone are listed in Table 1.

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - Acetone is one of the least hazardous organic solvents. At high concentrations it acts on the central nervous system, producing narcosis or stupor, ketone bodies in the blood, and inflammation of the gastrointestinal tract accompanied by vomiting. $^{\rm l}$ At lower concentrations it will produce headache and mucous membrane irritation of the eyes, nose, and throat. Some dose-reponse data are summarized in Table 2. $^{\rm l-6}$

The odor of acetone is detectable without any background interference at $100~\rm ppm$. Humans never exposed to acetone vapor complained of slight eye, nose, and throat irritation at 300 ppm and 500 ppm. After a short

Table 1. SIGNIFICANT PROPERTIES OF ACETONE

Synonyms	dimethyl ketone, 2-propanone	
	0	
Chemical formula	сн ₃ с сн ₃	
Molecular weight	58.08	
Boiling point	56.5°c	
Melting point	-95.6°c	
Specific gravity	0.792 at 20 ⁰ /4 ⁰ C	
Vapor density	2.00 (air = 1)	
Solubility	Soluble in all proportions in water, alcohol and ether	
Explosive limits	2.5 to 12.8 percent by volume	
Ignition temperature	560 ^o C	
Flash point	-17.8°C (closed cup)	
At 25°C and 760 mm Hg	1 ppm vapor = 2.372 mg/m ³ 1 mg/m ³ vapor = 0.422 ppm	

Table 2. ACUTE HUMAN RESPONSE TO ACETONE VAPOR

Dose, ppm	Exposure, hr	Response	Reference
100	2	No effect	2
100	4	lo effect	2
300	3-5 min.	Jery slight mucous membrane irritation	3
500	3-5 min.	Very slight mucous membrane irritation	3
500	2-4	No effect; awareness of the vapor	2
700		Undetectable by man after short time	1
,000-1,500	1.5-2	Transient eye, nose irritation; headache	4
2,110	8	Intoxication; begins to affect coordination	5
9,300	5 min.	Acute throat irritation	1
10,000	30-60 min.	Endurance limit with mucous membrane irritation, narcosis	6

time, workers could not detect 700 ppm. Awareness of mucous membrane irritation did not begin until 1,000 ppm to 1,500 ppm. However, many investigators have concluded that eye irritation does not become a factor until 2,500 ppm. The degree of irritation varies with individual susceptibility, with irritation disappearing after removal from the vapors. Symptoms of intoxication are similar to those seen after ethanol ingestion. Death due to acute exposure has never been recorded, but it is possible via narcosis leading to anesthesia and respiratory failure after prolonged exposure to high concentrations.

Acetone taken in doses of 15 to 20 g daily for several days produced no ill effects other than drowsiness. An occasional short exposure would not cause skin irritation. The danger of skin absorption is very slight and would not be significant in contributing to intoxication. Acetone is readily absorbed into the blood and is distributed throughout the body, with the majority exhaled unchanged by the lungs.

Chronic Poisoning There is no systemic injury associated with the chronic inhalation of low concentrations of acetone. Workers have been exposed to concentrations averaging up to 2,000 ppm for up to 15 years without any ill effects. It has been stated that the worst that can happen to men chronically exposed to such concentrations is a temporary dull headache. The United States Occupational Standard for an 8-hour time weighted average is 1,000 ppm based on studies concerning industrial exposures. However, it may not be low enough to prevent all narcotic symptoms.

Effects on Animals

Acute Poisoning - The effects of acute exposure to acetone vapor for some animals are summarized in Table 3. As in man, it acts as an irritant to the mucous membrane in addition to acting on the central nervous system. Symptoms of intoxication are salivation, lachrymation, twitchings and convulsions leading to narcosis and respiratory failure. Eye irritation is temporary and disappears upon removal from the vapor. Skin absorption of the vapor is considered slight and does not contribute to poisoning.

The only organ to be specifically injured by acetone poisoning is the kidney, with some investigators reporting lesions of the convoluted tubules, or degeneration. 8

Table 3. ACUTE ANIMAL RESPONSE TO ACETONE VAPOR

Animal	Dose, ppm	Duration, hr	Response
Guinea pig	40,000	4-8	Dangerous to life
	20,000	8-9	Loss of reflexes
Rats	126,600	1.75-2.25	Fatal
	42,200	4.5 -5.5	Fätal
•	42,200	0.25-5.0	Intoxication
Mice	46,000	1	Fatal
	20,256	1.5	Narcosis
	16,880	3.0	Narcosis

Chronic Poisoning As in man, acetone does not act as a chronic poison. Cats repeatedly exposed to 1,265 to 2,110 ppm were found to suffer no ill effects except slight irritation of the eyes and nose. Chronic exposure resulted in an increased tolerance to the vapor.

Effects on Vegetation

The effects of acetone vapor on vegetation have not been well documented in the literature. Considering its properties as a solvent for oils and fats, leaf contact with acetone would probably cause a breakdown of tissue resulting in massive injury or plant death. A Russian study 10 noted the combined effect of 0.74 ppm (1.75 mg/m 3) acetone, 2.28 ppm (2.62 mg/m 3) ethylene, 0.43 ppm (1.1 mg/m 3) acetic acid, and 28 ppm (18.4 mg/m 3) methane on the growth of English oak, English hawthorne, and Tartarian dogwood near a chemical plant. The gases were seen to retard growth in the tree shoots where growth processes are usually most intense. Growth in the

crown of trees on the side near the chemical plant was retarded more than growth on the opposite side. However, growth retardation may not be due entirely to acetone, since ethylene is an extremely sensitive growth inhibitor.

Effects on Materials

There are no data in the literature documenting the effects of acetone as an air pollutant on materials. Recognizing its properties as a solvent, when present in sufficient concentration it could become active in dissolving some forms of plastic or rubber.

Other Effects

Acetone and Photochemical Smog — It is well documented that reactions involving hydrocarbons taking place in photochemical smog produce ozone and peroxyacetyl nitrate (PAN), two chemicals extremely toxic to plants and man. Acetone has shown little reactivity in irradiation studies. 11,12 Its contribution to producing significant amounts of PAN or ozone in the ambient air is negligible.

AMBIENT CONCENTRATIONS AND MEASUREMENT

Ambient Concentration Estimates

Although acetone emissions are greatest from the solvent usage source category, these sources tend to be small and geographically scattered. Production of acetone, however, occurs at a few locations for which the emissions characteristics can be fairly well defined, and which as single point or area sources have a large emission density.

The largest installation for acetone production is located in a town of about 15,000 population, and it has a capacity of about 400 million lb/yr. Assuming a 1 percent loss, this converts to an emission rate of:

(0.01 emission factor) (400 x
$$10^6$$
 lb/yr) (453.6 g/lb)
3.1536 x 10^7 sec/yr

= 57.5 g/sec of acetone.

Some assumptions must be made regarding this acetone release to the atmosphere. First of all, the emissions do not all come from one source location, but rather from a number of locations within the plant where acetone vapor leaks to the atmosphere. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Secondly, the emissions occur at different heights, and an average emission height of 10 meters is assumed.

Ground level concentrations can then be estimated at locations downwind of the facility. ¹³ To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100 \text{m}/4.3 = 23.3 \text{m}$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcast skies and light winds, the upwind distance of the virtual point source is approximately 310 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentration may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_{y}\sigma_{z}} e^{-\frac{1}{2}\left(\frac{H}{\sigma_{z}}\right)^{2}}$$

or

$$\chi = \frac{57.5}{(2)\pi(36)(18.5)} e^{-\frac{1}{2} \left(\frac{10}{18.5}\right)^2}$$
$$= 1.187 \times 10^{-2} \text{ g/m}^3$$

for a 10-minute average concentration. Over a period of an hour this becomes $(1.187 \times 10^{-2} \text{ g/m}^3)(0.72) = 0.855 \times 10^{-2} \text{ g/m}^3$ or 3.7 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to be about 2.0 ppm. '

Measurement Techniques

There are a number of techniques for determining acetone in air, including wet chemical methods, spectrographic methods, and gas chromatographic methods. All three basic analytical techniques are capable of detecting acetone in air in the parts per hundred million range.

The determination of acetone by the wet chemical methods generally involves titration of iodoform which is produced by the quantitative reaction of acetone and iodine. Acetone samples may be collected either by fritted bubblers containing water or by adsorption on silica gel. 15 Concentrations of the order of 10 ppm may be determined by this method; however, it is not specific for acetone and other methyl ketones will interfere. Collection in water using fritted bubblers is less desirable for field use due to the extra equipment requirements.

Concentrations as low as 0.04 ppm may be determined by spectrophotometry. 16 The sample is collected in 2,4-dinitrophenylhydrazine, treated with carbon tetrachloride and sodium hydroxide, and read in a spectrophotometer at 420 nanometers.

In the gas chromatographic method the sample is collected on charcoal and subsequently desorbed with carbon disulfide. The presence and concentration of acetone are determined by the characteristic retention time and the area of the breakthrough curve. 17

SOURCES OF ACETONE EMISSIONS

Acetone Production and Consumption

The production of acetone in 1974 was 2,073 million pounds, ¹⁸ and it is expected to increase at 6 percent ¹⁹ per year through 1978. Approximately 30 percent of all acetone produced is used as 'a solvent for protective coatings and chemical processing. Presently 12 companies using the cumene or isopropyl alcohol process are manufacturing acetone (see Appendix A). The consumption of acetone for final products is shown in Table 4. This table also presents the expected growth rates for each sector of the market.

Acetone Sources and Emission Estimates

Primary sources of emissions of acetone result from solvent usage, acetone manufacturing, absorbent packing for acetylene, bulk storage, and end product manufacturing. Total emissions from all categories are estimated to be 698 million pounds, representing 34 percent of total production. See Table 5.

The major source of acetone emissions results from its use as a solvent, mainly for protective coatings. It is assumed that all acetone used as a solvent will evaporate to the atmosphere. In 1974, an estimated 85 million pounds were used in paints, varnishes and lacquers, and 125 million pounds were used in thinners and wash solvents. Consumption of acetone for pharmaceuticals (toiletries and cosmetics) accounted for 123 million pounds. Its use as a chemical processing solvent amounted to approximately 107 million pounds. The production of cellulose acetate consumed 80

Table 4. ACETONE CONSUMPTION - 1974 19

	Million	Percent
	pounds	annual growth
Methyl Methacrylate	524	10
Methyl Isobutyl Ketone	259	-1.5
Solvent for Protective Coatings	210	5
Pharmaceuticals (toiletries, cosmetics)	123	7
Chemical Processing Solvent	107	7
Methacrylic Acid and Higher Methacrylates	107	7
Bisphenol A	101	12
Cellulose Acetate Spinning Solvent	80	0
Hexylene Glycol	52	3
Diacetone Alcohol	50	4
Methyl Isobutyl Carbinol	45	3
Isophorone	36	2
Mesityl Oxide	28	3
Absorbent Packing for Acetylene	15	0
Exports	131	6
Miscellaneous Chemical Production	88	5
Other Solvent Usage (painting, inks,	117	6
adhesives, clean printed circuits)		
		_
Total	2,073	6

Table 5. SOURCES AND EMISSION ESTIMATES OF ACETONE

	Million pounds/year
Solvent for Protective Coatings	210
Pharmaceuticals	123
Chemical Processing Solvent	107
Cellulose Acetate Spinning Solvent	80
Acetone Manufacturing (1% loss)	21
Absorbent Packing for Acetylene	15
Bulk Storage	13
End Product Manufacturing (1% loss)	12
Other Solvent Usage	117
Total	698

million pounds, and an additional 117 million pounds were used for printing inks, adhesives and as a degreaser for printed circuit boards.

The second major source of emissions, other than from solvent usage, is the manufacture of acetone. In 1974, 58 percent of total acetone capacity in the United States and Puerto Rico was based on cumene oxidation, the remaining 42 percent was based on isopropyl alcohol.

The oxidation of cumene is used by 9 of the 12 acetone producers. In this process acetone is produced as a coproduct with phenol by cleaving the cumene hydroperoxide obtained from the air oxidation of cumene. The reactions are presented below:

Two processes for the production of acetone from isopropyl alcohol are currently used: catalytic dehydrogenation and oxidation. The dehydrogenation process converts isopropyl alcohol to acetone by heating it to 400°C in the presence of a brass or copper catalyst. The reaction is as follows:

The oxidation process converts isopropyl alcohol to hydroperoxide with oxygen, which on hydrolysis produces hydrogen peroxide and acetone. The reaction is presented below:

$$^{\text{CH}}_3$$
 $^{\text{CH}}_1$ $^{\text{CH}}_3$ $^{\text{CH}}_2$ $^{\text{H}}_2$ $^{\text{O}}_2$ $^{\text{H}}_2$ $^{\text{CH}}_3$ $^{\text{CO}}_3$ $^{\text{CH}}_3$ $^{\text{ONS}}_3$ $^{\text{ONS}_3$ $^{\text{ONS}}_3$

Since there are no data available concerning emissions from these processes, based on other similar chemical processes ²⁰ it is estimated that 1 percent of production is emitted as acetone. On this basis 21 million pounds of acetone are lost during the production cycle. Using the same emission factor, losses from end product manufacturing are 12 million pounds.

The next major source of acetone emission results when it is used to saturate absorbent packing in acetylene cylinders. This mitigates excessive pressure so that the cylinders can be shipped safely. Emissions from this source are estimated to have been 15 million pounds in 1974.

The last major source of emissions results from bulk storage of acetone. Using the emission factors in $AP-42^{20}$ and assuming all storage tanks are fixed roof, emissions are 13 million pounds.

ACETONE EMISSION CONTROL METHODS

The literature does not report specific control equipment for acetone emissions, but it does report on control devices for other similar hydrocarbons. Two types of control devices are presently used by the industry to control hydrocarbon emissions: vapor recovery and incineration. Both systems have reported efficiencies of at least 95 percent.

Control of hydrocarbon emissions by adsorption on activated charcoal is generally applied when recovery of adsorbed material is economically desirable. Adsorption is generally used when concentrations of hydrocarbons are greater than 2500 ppm. ²¹ Other applications are for the control of very low concentration hydrocarbons that are poisonous to catalytic incinerators, and for collection and concentration of low concentration emissions for subsequent disposal by incineration. Cost data for the cases utilizing adsorption are presented in Tables 6 and 7. The three cases presented are adsorption with solvent recovery, adsorption with incineration, and adsorption with incineration plus heat recovery.

Table 6. ESTIMATED INSTALLED COSTS^a OF ADSORPTION SYSTEMS²²

Adsorber capacity, SCFM - Based on 25% lower explosive limit	1,000	10,000	20,000
With solvent recovery, \$	74,000	162,300	280,000
With thermal incineration/ no heat recovery, \$	89,500	202,000	344,000
With thermal incineration/ primary heat recovery, \$	101,500	255,000	431,000

^aCost data updated to first quarter of 1975.

Table 7. ESTIMATED ANNUAL OPERATING COSTS OF ADSORPTION SYSTEMS 22

Adsorber capacity, SCFM - Based on 25% lower explosive limit	1,000	10,000	20,000
With solvent recovery, \$/yr	13,200	10,479 ^b	37,200 ^b
With thermal incineration/ no heat recovery, \$/yr	23,400	64,300	123,200
With thermal incineration/ primary heat recovery, \$/yr	25,600	82,000	141,600

aCost data updated to first quarter of 1975.

b Indicates a savings.

Control of acetone emissions by incineration or catalytic oxidation involves direct oxidation of the combustible portion of the effluent, the desired ultimate products being water and carbon dioxide.

The primary advantage of catalytic incineration is that extremely small concentrations of organics can be oxidized with only small amounts of supplemental fuel required. The main disadvantages are the higher capital cost and the fact that certain hydrocarbons may poison the catalyst. Cost data for thermal and catalytic incinerators with and without heat recovery are presented in Tables 8 and 9.²²

Control of emissions from storage tanks will require the use of floating roof tanks or venting the emissions to the previously mentioned adsorber or incinerator. Emissions from fixed roof tanks can be vented to either system without any major increase in cost. If these systems are not available, the fixed roof tanks should be switched to floating roof tanks resulting in a 90 percent reduction of emissions. Figure 1 provides estimated costs of various gasoline storage tanks. These equipment cost estimates can also be applied to acetone. As can be seen, conversion of fixed roof to floating roof tanks by installation of internal floating covers is more economical than the installation of new pontoon floating tanks.

Table 8. ESTIMATED INSTALLED COSTS a OF THERMAL AND CATALYTIC INCINERATORS 22

	,		
Incinerator capacity, SCFM - Based on 25% lower explosive limit	1,000	10,000	20,000
Installed costs, \$			
Catalytic without heat recovery	43,500	272,000	504,600
Catalytic with primary heat recovery	54,100	306,000	573,900
Catalytic with primary and secondary heat recovery	68,300	361,800	666,400
Thermal without heat recovery	27,200	92,500	137,400
Thermal with primary heat recovery	40,300	144,000	232,600
Thermal with primary and secondary heat recovery	54,400	200,000	322,300

^aCost data updated to first quarter of 1975.

Table 9. ESTIMATED ANNUAL OPERATING COSTS^a OF THERMAL AND CATALYTIC INCINERATORS²²

Incinerator capacity, SCFM - Based on 25% lower explosive limit	1,000	10,000	20,000
Operating costs, \$/yr Catalytic without heat recovery	16,200	102,800	195,000
Catalytic with primary heat recovery	16,400	78,500	177,900
Catalytic with primary and secondary heat recovery	19,300	108,700	203,700
Thermal without heat recovery	12,000	54,300	96,700
Thermal with primary heat recovery	11,500	36,300	59,200
Thermal with primary and secondary heat recovery	14,400	50,800	84,500

^aCost data updated to first quarter of 1975.

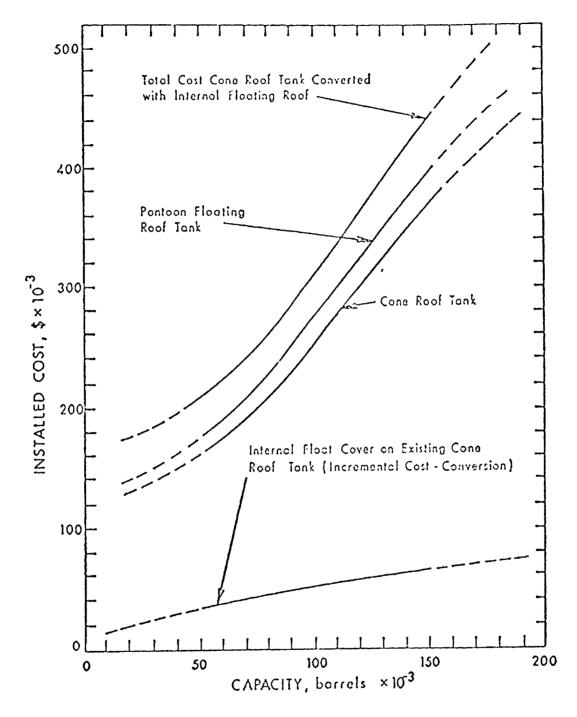


Figure 1. Estimated installed cost of acetone storage tanks (equipment costs assumed to be the same as gasoline storage tanks)²²

SECTION III

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APPENDIX A

ACETONE MANUFACTURERS

		Capacity,* million lb/yr;
Allied Chemical	Frankford, Penn.	315
Clark Oil and Refinery	Blue Island, Illinois	5 3
Dow Chemical	Oyster Creek, Texas	240
Eastman Kodak	Kingsport, Tenn.	80
Exxon	Bayway, N.J.	140
Georgia-Pacific	Plaquemine, Louisiana	172
Monsanto	Chocolate Bayou, Texas	270
Shell Chemical	Deer Park, Texas	400
Shell Chemical	Domiquez, California	100
Shell Chemical	Norco, Louisiana	100
Skelly Oil	El Dorado, Kansas	57
Standard Oil of California	Richmond, California	33
Union Carbide	Bound Brook, N.J.	90
Union Carbide	Institute, W.V.	150
Union Carbide	Texas City, Texas	110
Union Carbide Caribe	Ponce, Puerto Rico	120
U.S. Steel	Haverhill, Ohio	168
Total Capacity		2,598

^{*}As of 1974.