# Safety and Environmental Concerns in Resin Manufacture

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# Safety and Environmental Concerns in Resin Manufacture

## I. Introduction

Significant changes have occurred in PVC manufacture in recent years because of developments in safety and environmental concerns in general and the concerns for vinyl chloride (VC) specifically. For many years the primary safety hazards of VC were thought to be its flammability and anesthetic properties, plus the need to prevent overpressuring of equipment by uncontrolled polymerization. Data became available in the 1960's which gave reason for concern at exposures below the anesthetic/explosive range. Vinyl chloride was shown to be toxic to the liver in animals, to cause acroosteolysis (AOL), a degenerative disease of the bone tufts, in humans, and by 1973 it was found to cause angiosarcoma of the liver (ASL), a rare and usually fatal liver cancer, in both animals and humans. There are lesser health concerns for the other components of the resin manufacturing process, although each has been found to have some undesirable effects. A summary of the toxicity data for VC and some of the more important constituents in PVC is presented in Part II.

These findings have resulted in regulatory action by several governmental agencies, including the Food and Drug Administration (FDA), the Consumers Product Safety Commission (CPSC), the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA), which are discussed in Part III. Extensive changes have been made in manufacturing practices and procedures in order to meet the challenge to reduce worker and environmental exposure, as well as because of technological advances. Some of these are presented in Part IV. Part V describes methods for safe disposal of the waste streams encountered in polymer manufacture, and Part VI discusses some analytical procedures specifically applicable to safety and health matters. Some problems relating to copolymer manufacture are discussed briefly in Part VII. A glossary of common acronyms can be found in Part IX.

## II. Toxicity Considerations

This section is intended to provide a general perspective on vinyl chloride and the materials most closely associated with it in PVC manufacture from which the specific safety hazards and work practices can be reviewed in the later sections.

### A. Vinyl Chloride

See Table 1 for a listing of some physical properties of VC; Table 2 contains data on selected properties of other substances often associated with VC polymerization processes.

#### 1. Acute Toxicity

The anesthetic property of VC was recognized in the early 1930's (1) and has been investigated by several workers (2-5). Death occurs rapidly in animals at concentrations much above

Table 1

Selected Physical Properties of Vinyl Chloride

| | |
|---|---|
| Formula Weight | 62.50 |
| Heat of Formation, 25°C, gas Kcal/mol | 7.5 |
| Free Energy of Formation Btu/lb | -3310 |
| Density, liquid, g/ml | |
| 32°F, 0°C | 0.9471 |
| 50°F, 10°C | 0.9293 |
| 68°F, 20°C | 0.9109 |
| 86°F, 30°C | 0.8918 |
| 104°F, 40°C | 0.8721 |
| Refractive Index, $d^{15}$ | 1.398 |
| Freezing Point, °C/°F | -153.7/-244.7 |
| Boiling Point, 760 mm °C/°F | -13.37/7.9 |
| Liquid Viscosity, absolute, CP | |
| 32°F | 0.225 |
| 50°F | 0.207 |
| 68°F | 0.193 |
| 86°F | 0.181 |
| Heat of Fusion, cal/g | 18.14 |
| Heat of Vaporization @ 57°F, Btu/lb | 158.4 |
| Specific Heat | |
| Liquid, 25°C K cal/kg | 0.38 |
| Vapor, 25°C, constant pressure, Kcal/Kg-mol | 12.83 |
| Vapor, constant volume | 10.84 |
| Heat of Polymerization, Btu/lb | 660 |
| Explosive Limits in Air | |
| Lower, wt. % | 8.3 |
| vol. % | 3.5 |
| Upper, wt. % | 37.8 |
| vol. % | 22 |
| Minimum Oxygen Content for Ignition, % | 12 |
| Flash Point, open cup | -78°C |
| Autoignition Temperature | 472°C |
| Critical Temperature, °K | 431.4 |
| Critical Pressure, atm | 52.7 |
| Critical Density, g/cc | 0.370 |
| Vapor Cloud Explosion Yield, lbs to yield the equivalent of 1 ton of TNT | 24,305 |

Table 1

(continued)

| | |
|---|---|
| Vapor Pressure, psia | |
| -10°C | 18 |
| 0°C | 26 |
| 10°C | 35 |
| 30°C | 48 |
| 50°C | 115 |
| 70°C | 180 |
| Heat of Combustion, Kcal/mol | 2826 |
| Latent Heat, Btu/lb | |
| 0°C | 147 |
| 50°C | 126 |
| Solubility in Water, 30°C, % by wt. | |
| Partial Pressure, 0.5 atm | 0.5 |
| 1.0 atm | 1 |
| autogenous | 2 |
| Solubility of Water in VC, % | 0.11 |

Table 2

Selected Properties of Substances
Discussed in this Chapter

| | Vinyl Chloride | Dichloroethane | Trichloroethylene | Vinyl Acetate |
|---|---|---|---|---|
| Odor Threshold (ppm in air) | 1,000 | 50 | 20-80 | 0.4 |
| Explosive limits in Air (V%) | 3.6-33 | 6.2-15.9 | 12.5-90 | 2.6-13.4 |
| Flash Point (°F), COC | 108 | 56 | None | 18 |
| $LD_{50}$, rat (mg/kg) | 500 | 770 | 4,920 | 2,920 |
| $LC_{50}$, rat (ppm) | >50,000 | -- | 8,000 (4 hr.) | 4,000 (4 hr.) |
| Aquatic Toxicity (ppm) | >1,000 | 100-1000 | 100-1000 | 10-100 |
| Vapor Pressure, 20°C (mm Hg.) | 1,600 | 62 | 47 | 88 |
| Solubility in Water, 20°C (g/100g) | 1 (1 atm.) | 0.8 | 0.1 | 2.4 |

the anesthetic levels of 8-12% (1,6,7) but "no histological damage" was reported at 5% exposure for 100 days (8).

A review of the toxicity of VC in 1943 concluded (9) that "vinyl chloride is one of the least dangerous of the chlorinated hydrocarbons." Our present knowledge of the toxicity of this class of compounds does not let us derive as much comfort from that statement now as may have been felt then.

However, careful examination of liver effects in animals at 100-500 ppm for 4-6 months led investigators at Dow (10) to recommend a human exposure limit of 50 ppm time-weighted average (TWA). The American Conference of Governmental and Industrial Hygienists (ACGIH) accepted the 500 ppm recommendation of Harvard investigators (11) instead, and published this first as a TWA, and then as a ceiling value (12). This was the value set by OSHA in 1971 during its mass adoption of voluntary consensus standards as regulations, and remained in effect until 1974.

The Dow workers later stated (13): "Had our recommendations based upon relatively simple toxicology been followed then, the difficulties of today may never have occurred."

Human response to acute exposures is very close to that of animals. The human narcotic range is given variously as 7-10%, with 12% being dangerous (4,11). Deaths have been reported of workers exposed to high but unknown concentrations (14) and there are several anecdotal reports of workers losing consciousness temporarily (15-17, 59). The odor threshold has been reported as varying over a very wide range (17A) but the most reasonable figure seems to be either 1200-2000 ppm (18) or 500-1000 ppm (19). Some sensations from exposure are reported as confusion, intoxication, burning of the soles of the feet, and subsequent headaches (20). There are no immediate effects noticed at 50-500 ppm (21).

Vinyl chloride had been considered as a potential dental anesthetic, but the finding of serious cardiac arrhythmias in dogs and the development of sensitization (2,5,22) discouraged this application.

Vinyl chloride is autocryogenic and can cause frostbite if the liquid contacts the skin. Adequate protective clothing should be worn to avoid this contact.

2. Metabolism

Vinyl chloride is metabolized by the mixed-function oxidative action in the Cytochrome P-450 component of cells (23,23A). This pathway is saturable (24,25) and if an excess of vinyl chloride is inhaled, the liver capacity is overwhelmed and metabolism to the carcinogenic intermediate then occurs in

other organs of the body, allowing tumor formation to occur there also. This result has been seen in animals (26), and Bartsch (26A) has shown that rat and mouse lungs can metabolize VC at 10-20% of the rate of their livers. Epidemiological data (27-32) do not show it to occur in humans at either the ambient or occupational concentrations now experienced.

Humans and animals have similar metabolic routes (33) but that in humans is much slower. This has been used to adjust risk estimates based on animal data to give figures which are much closer to actual human experience (34-35). The rhesus monkey appears to resemble humans much better than do rodents (36-37).

An equilibrium is established quickly between the ambient and blood concentrations of vinyl chloride (3,33,36) and the blood level decreases just as rapidly upon cessation of exposure. Thus, analysis of breath samples can be used as a rough indication of recent exposure levels. It has been estimated that consumption of 20 ppm VC in all fluid intake is equivalent to 2 ppm exposure by inhalation for 24 hours (36A).

Administration of Cytochrome P-450 inhibitor blocks the respiratory uptake (38,39). Skin absorption by monkeys of the vapor is only 0.1% as rapid as absorption through the lungs (24). However, there are anecdotal reports of deep anesthesia in humans exposed to extensive skin exposure.

3. Chronic Toxicity

There are few animal studies extending past 6 months except for carcinogenic bioassays. Viola (40) attempted to reproduce AOL in rats by exposing them to 3% VC for 4 hrs/day, 5 days/week for 12 months. He reported that the animals were slightly soporific, and began to show a decrease in weight and reaction to external stimuli. Half of the animals died of cardiorespiratory complications and two of hematoperitoneum. Most showed pathological involvement of the brain, liver, kidney, and thyroid. Six showed pathological alterations of the skeleton, bone metaplasia, and changes in the cartilage. This latter effect may have been the rat equivalent of AOL. There were, in addition, tumors at various sites. Feron and Krees (41) exposed rats to 5,000 ppm, 7 hr/day, 5 days/week for up to one year and found tubular nephrosis, focal degeneration of the myocardium, and spleen damage, in addition to various primary tumors.

Several articles appeared before 1974 describing what has come to be called "VC poisoning" or "VC disease", although the latter term now has become more closely associated with AOL than gastro/neural problems. Many of these reports are not particularly useful because there are no exposure data and there often is known exposure to other recognized toxic materials. It does appear, however, in light of subsequent

information, that the exposures must have been quite high for these symptoms to have appeared so quickly. Some of these reports are listed briefly below.

One article which has been cited frequently as supplying an early warning of the toxicity of VC is that by Tribukh in 1949 which discusses health conditions in a PVC processing plant in Russia (42). The author actually does not ascribe the health problems to any specific material, but mentions diphenyl chloride, hydrogen chloride, and other toxic materials as being present. No measurements were made for VC, but it is unlikely that any signficant quantities could have been present in the workplace because of the type of PVC being used at that plant.

Other early papers reported various gastro/neural symptoms: spastic angioneurosis (43), a decrease in catalase and an increase in peroxidase activities and glutathione levels (44), a decrease in albumin and an increase in beta- and gamma-globulins (45,46), cardiac disturbances (47), and lowered thyroid activity and production of 17-ketosteroids (48,49).

Kramer and Mutchler (50) made a statistical analysis of the difference between a group who had been exposed to VC for up to 25 years' work history at up to 300 ppm versus other chemical workers, and found minor changes in certain blood chemistry and liver functions.

More recent articles have examined workers from cohorts which include AOL or ASL disease. They find portal fibrosis and portal hypertension, thrombocytopenia, espohageal varices, and abnormal sinusoidal lining cell development (49, 51-58). It has been postulated that these are early stages of ASL, but there have not been enough observations to confirm this hypothesis generally. It may well be correct for certain fibrotic conditions (58A).

The other major area of concern, AOL, was described earlier as a degenerative disease of the bone tufts. It usually is accompanied by Reynauds syndrome, and frequently also by scleradoma. Suciu (48) first reported this disease, then Cordier (59). These were followed by Harris and Adams (60), Wilson, et al., (61), and Basalaev (62). One industry-sponsored survey (63) identified 25 definitive cases and 16 suspect cases in the U.S. No certain etiological agent was found, but the cases were clearly associated with hand cleaning of reactors (64), where there is a combination of physical joint insult and VC exposure. The disease is most often seen in the hands and fingers, but occasionally in the feet or back (60). Dodson (65) could find no obvious medical reason for predelictiion to the disease in the four cases which he studied. It appears to be reversible after cessation of exposure (66). A total of 126 confirmed cases had been identified worldwide by 1979 (17A).

Maricq (67) found a strong association of capillary abnormalities in the hands with workers suffering from AOL. Lillis (58) reported that an abnormal Allen test for circulatory efficiency was found in many affected workers, as well as many other organic symptoms related to the liver and circulatory systems.

Bertozzi, et al., (68) studied the status as of 1975 of a group of 4,777 workers, some of whom had been employed since 1952 in VC/PVC production facilities. No control or comparison data are given, and many different laboratories performed the analyses so only relative trends within the cohort can be identified. They stated that the highest exposures were "above 800 ppm". Confirmed and suspected cases of AOL increased with the degree of exposure and the age of the worker, but not with the length of exposure. "Abnormal" liver results increased with length of exposure but not the degree. Heavy drinking appeared to act synergistically with duration of exposure in affecting hepatomegaly and elevated GGT.

Grainger, Walker, and Ward (66) reviewed the literature on symptoms associated with VC exposure, and discussed the symptoms of 88 workers from a factory, 9 of whom were stated to have definite VC disease. They report a gradiation of findings from those with the symptoms to those without, but do not make comparisons with unexposed controls. They postulate that vascular and/or immunological changes are responsible for the observed effects, and state that they expect no new cases to develop at current exposures below 5 ppm.

Knowledge of the exact exposures of these cases would be of great assistance in evaluating the concern for exposures experienced at present, but there have been no definitive estimates made. Suciu (69) reported clinical symptoms associated with exposures that appear to be far too low, in light of industry experiences since 1974. OSHA (70) estimated that reactor cleaners had been exposed to 1,600 ppm in their work. A CEFIC publication (71) has estimated the average exposure for all European PVC workers in the 1945-1960 era as "up to and beyond 1000 ppm", and there is no reason to believe that the U.S. conditions were much different, but even this is an average for all workers, and the symptoms of AOL, chronic liver damage, and ASL are more closely associated with reactor entry and cleaning than with other jobs. The National Toxicology Program (72) quotes IARC data which also cites very high potential exposures, and Fishbein (73) quotes several other sources that report high values.

The EPA requires (74) all PVC processors to displace the vapor from reactors with water before opening for entry, or to employ a procedure of equivalent efficiency. This is based on a study (75, page 4-71) which showed that this reduced the residual content of the reactor vapor to 8,000 ppm. This is a new procedure which had not been in general use before 1975. It

had been the practice of some companies to force air through an opened reactor before entry, but this was generally an unmonitored procedure. Cook, et al., (64) reported that unventilated reactors were often over 3,000 ppm, and Filatova and Gronsberg (76) stated that excursions were seen up to 34,000 ppm. These comments, coupled with the anecdotal reports of anesthesia of workers (15-17, 59), support the conclusion that reactor cleaners certainly were exposed to recurring concentrations in the several thousand ppm range. This fact must be considered in any attempt to evaluate the hazard to workers at the present time, or to the population at large.

4. Carcinogenicity

The first report of carcinogenicity in animals came as the result of the attempt by Viola to reproduce AOL-like symptoms in rats (40). This work was sponsored by a group of European VC/PVC producers, and used a 3% (30,000 ppm) concentration for 12 months. The attempt to cause AOL was not totally successful, but instead tumors developed at many sites, especially in conjunction with the Zymbal gland, and in the lungs, skin, and bones. This gland is an organ near the ear which secretes the oil used by the rat to groom itself, and is not found in humans. Most of the other tumors were thought to be metastasized from the Zymbals, and not primary tumors. Perhaps because the exposures were so high, and the tumors were not associated with human organs, this report attracted little response from regulatory agencies.

The sponsors then undertook a much larger study at lower concentrations under the direction of Maltoni. Partial reports from this study began appearing by 1973 (76A), but final results were not available until 1979 (26).

In summary, it was found that tumors appeared in rats at several sites depending on the concentration used. The lowest doses at which statistically significant elevations of various tumors were seen were reported as:

| | |
|---|---|
| Forestomach Papillomas | 30,000 ppm |
| Neuroblastomas | 10,000 ppm |
| Zymbal Gland Carcinomas | 10,000 ppm |
| Nephrolastomas | 250 ppm |
| ASL, Male | 250 ppm, 50 mg/kg |
| Female | 50 ppm, 16.7 mg/kg |
| Mammary Adenocarcinoma | 5 ppm |

The reported finding of an increase in mammary adenoma at very low exposures led to concern for female workers, particularly when a study of fabricator employees found an excess of breast cancer among females (30). However, a case-control follow-up (31) found no relationship to VC exposure in the cases seen in those workers. In any event, the very high and variable incidence of such tumors in the controls, about which Maltoni has often commented in his oral presentations, makes it very difficult to support a conclusion that the test animals actually did respond at such doses.

Schaeffer and coworkers (76A) found that the Maltoni data fit an exponential expression which predicts a no-effect level for liver cancer in rats at about 3 ppm, and predicted an average latency period greater than normal lifetime at about 29 ppm. Many attempts have been made to estimate human risk from the animal data, but none of these have been successful unless proper biotransformation factors were applied (265).

A number of other bioassays were conducted by various industrial and governmental groups (41,77-83). In general, these confirmed the findings by Maltoni. It was determined that mice are the most sensitive species, followed by rats. Wistar rats appear more resistant than the Sprague-Dawley strain. Rabbits and hamsters are much more resistant. Either ingestion or inhalation produces tumors, with the latter route tending to give tumors at more diverse sites. This result is consistent with the saturable metabolic process discussed earlier. Both very young and older rats appear more sensitive than juveniles. This may be explainable by the differing repair and detoxification capacities at various ages. There is a regular decrease in the latency period as the dose increases, with liver tumors appearing only at the end of the lifetime at 50 ppm or less (26) in rats. Mice show a dose response to below 10 ppm for pulmonary tumors after exposure for 4 weeks (83A).

Drew and coworkers published data (88A) which they believe contradict the statements by Maltoni (26) and Groth (88B) that older animals appear more susceptible. They found that withholding exposures until later in life produced fewer tumors in the animals. They did not take into consideration that the low doses used (50 ppm for mice, 100 ppm for rats) yield long latency times, and thus the animals died of other causes before the VC-induced tumors could kill them. It is true that fewer deaths occur if exposure is delayed, but that is not necessarily because of increased resistance. In fact, the time-to-tumor increased in Drew's experiments, as the age at exposure decreased. Thus, any rigorous examination of such data must include a proper consideration of the time factor.

The first connection between VC and cancer in humans was made in 1973 when physicians at the Louisville, Kentucky plant of B. F. Goodrich, Inc. recognized the association between three

deaths of workers from ASL (84). A review of company records (85) revealed several other cases at that plant.

This tumor is rare. A review (86) of all cases reported in the United States for the period from 1964 to 1974 revealed 167 cases, of which 19 were ascribed at that time to occupational VC exposure, 26 to Thorotrast given medically, and 9 to arsenic in Fowler's solution, also used medically. The remainder were of unknown etiology, with no connection to VC. There are references in the literature to one case (87) thought to be associated with hair spray use. The high level of interest in this specific tumor is such that any subsequent cases associated with environmental exposure to VC would most certainly have been reported, and none have. For a time, NIOSH published a summary of VC-related cases, but this task was taken over by Dr. John Stafford of ICI, England (88). His most recent compilation shows a total of 32 cases in the U.S., and 107 worldwide. A summary of the number of cases by countries and of the U.S. cases by company and by date of death as given in Stafford's reports are shown in Tables 3-5, respectively.

The average latency period in the U.S. has been 25 years, but with a mode of about 22 years. The latency period in Europe, and particularly Germany, has been somewhat shorter. There is an unusual clustering of cases in relatively few plants (Table 4). All of the U.S. occupational cases, and almost all of the cases in the rest of the world, are closely associated with the job of reactor cleaning, which was once done manually at the end of the polymerization cycle. It may be speculated that differing work programs and job progressions have had some effect on the rates at various plants.

Ten cases of ASL have been reported in one plant in Canada, the last in 1976, with no new cases since that time (89,90). These cases are completely typical, both as to the clustering and the medical symptoms.

It also is worthy of note that there is, at most, one case of both AOL and ASL in the same person (88), although both of these diseases are associated with VC exposure as a reactor cleaner.

An industry-sponsored epidemiological survey of workers in the VC/PVC industry covered 8,384 men with at least one year of exposure before 1973. The expected excess of ASL was found. There were also suggestions of an excess of cancers in the brain, respiratory, and at unknown sites, and of lymphoma. This study was expanded to 10,173 workers (27,92), where the excess of brain and respiratory cancers continued to be seen without, however, an association between the brain cancer and exposure. In addition, most of the lung cancer cases come from the same facility, with many plants having no cases. A follow-up study of this cohort to determine the status of the workers as of the end of 1980 is underway.

Table 3

Angiosarcoma Cases in the VC/PVC Industry by Country

| | |
|---|---|
| United States | 32 |
| West Germany | 21 |
| France | 17 |
| Canada | 10 |
| United Kingdom | 8 |
| Sweden | 5 |
| Yugoslavia | 4 |
| Italy | 4 |
| Czechoslovakia | 2 |
| Japan | 2 |
| Norway | 1 |
| Belgium | 1 |
| Total | 107 |

Includes 3 U.S.A. cases still alive.
Adapted from Stafford (88).

Table 4

Angiosarcoma Cases in the U.S.
by Company

| | |
|---|---|
| Goodrich, Louisville | 14 |
| Union Carbide, S. Charleston | 9 |
| Goodyear, Niagara | 4 |
| 5 Others | 5 |
| Total | 32 |

Table 5

Chronology of U.S. Deaths From Angiosarcoma

| | Deaths | Year of First Exposure |
|---|---|---|
| 1961 | 1 | 1946 |
| 1962 | 0 | |
| 1963 | 0 | |
| 1964 | 1 | 1944 |
| 1965 | 0 | |
| 1966 | 0 | |
| 1967 | 0 | |
| 1968 | 3 | 1944, 1951, 1952 |
| 1969 | 2 | 1949, 1950 |
| 1970 | 1 | 1946 |
| 1971 | 1 | 1955 |
| 1972 | 0 | |
| 1973 | 3 | 1945, 1948, 1958 |
| 1974 | 1 | 1942 |
| 1975 | 4 | 1945, 1947, 1954, 1962 |
| 1976 | 3 | 1943, 1947, 1955 |
| 1977 | 1 | 1946 |
| 1978 | 2 | 1941, 1944 |
| 1979 | 0 | |
| 1980 | 4 | 1942, 1951, 1955, 1964 |
| 1981 | 0 | |
| 1982 | 1 | 1946 |
| 1983 | 1 | 1944 |
| Total | 29 | |

Three cases living (first exposures 1954, 1955, and 1956).
Data from Stafford (88).

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Marsh (92A) followed 2,490 workers who had been exposed for at least one year between 1949 and 1966 in a plastics-producing plant which included PVC production. Vital status was determined for 99.7% of these as of the end of 1976. Death records for 98% of the 603 deceased workers showed a slight, but not statistically significant, excess of genitourinary system cancer (SMR=154). A follow-up case-control study did not relate these findings to either type or length of occupational exposure. One case of ASL occurred in this cohort in 1979 (88).

Several studies have been conducted on smaller groups of workers which are also subsets of the larger study discussed above. Monson, Peters, and Johnson (93) found an excess of brain and lung cancers in the plant which developed the most ASL cases in the United States. Waxweiler, et al., (94) studied 1,151 workers who had at least five years' exposure in four older PVC plants, and reported an excess of brain, respiratory, and lymphatic cancer, as well as the known cases of ASL. A later study (95,96) expressed the opinion that it was not VC exposure that was responsible for the excess of respiratory cancer, and speculated that it may be due to PVC dust. However, preliminary results on a study of subsequent lung cancer cases in that same plant (97) do not show an association with PVC dust. Theriault and Allard (90) and Falk and Waxweiler (98) also state that it is unlikely that PVC exposure is responsible. The method used in the follow-up study was an elaborate method for determination of exposure indices for workers potentially exposed to several chemicals (99) which is useful in identifying which exposure may be most closely associated with the cases.

Beaumont and Breslow (100) evaluated the statistical power of nine epidemiological studies dealing with possible lung cancer from VC exposure and concluded that the lack of a general trend in these results indicated that VC is not a human lung carcinogen. This was supported by the negative results in the two studies with the highest statistical power (27, 29). They concluded that the reported studies were compatible with a relationship between VC and brain cancer. This was based, however, on the assumption that the result of the EEH study (27) was positive, a conclusion that is not altogether clear.

Tamburro and his associates at the University of Louisville have followed closely the histories of the ASL cases at the Goodrich plant. This work has been summarized by Dannaher, et al., (101). Diagnostic methods, treatment, and survival are described. The progression of the disease from the initial focal nodular hyperplasia through fibrosis to necrosis is described in more detail by Tamburro (102). An extensive medical regimen for VC-exposed workers was proposed by Tamburro, et al., (103). A liver scan appears to be the most effective diagnostic tool (103,103A). Of the various tests required by the OSHA medical program, the GGTP test provided

the highest positive predictive value, but the least specificity, and the ICG clearance test was recommended as the preferred screen (104), although none is very effective.

It has been suggested that human data shows the transport of some metabolic intermediate from the hepatocyte to the adjacent sinusoidal lining to initiate the first stage of tumor development (87,105-6). Ottenwalder and Bolt (107) came to the same conclusion from animal studies, and this mechanism is supported by other work at Louisville (108).

An extensive multiyear research program at the University of Louisville was sponsored by the Chemical Manufacturing Association. Much unpublished material on the subjects of metabolism, immune response, and ASL detection and surveillance methods is contained in the final report on this project (108A). In addition, more than 40 papers and talks have resulted from this effort. Many of these articles have been cited in the preceding paragraphs.

Duck, Carter, and Coombes (109) found no excess of mortality, including cancer, in British workers for 1948-1973, while following 2,120 workers. Wagoner, Infante, and Saracci (110) criticized the mathematical treatment of the data and stated that there was an excess mortality in the longer-exposed group. Duck and Carter (111) then made corrections to the numerical results, but did not change the conclusion. Berry and Rossiter (112) criticized both the original calculations and the changes proposed by Wagoner and Infante, as did Fox (113) but neither found any evidence of excess mortality in the group. Fox and Collier (29) studied 7,000 men who had worked with VC in Great Britain between 1940 and 1974 and found no evidence that cancers other than that of the liver are associated with VC exposure.

Frentzel-Beyme, Schmitz, and Thiess (32) reported on 1,618 VC-PVC workers in Germany, and could not confirm the U.S. reports that tumors at other sites than the liver were in excess, and suggested that this may be because of the consistently low exposures at the plant which they studied. A paper by Reinl, et al., (114) reported excess deaths in German workers, but the authors have since found calculation errors in the processing of the data. A later summary of this study (115) found an elevation of lymphatic tumors in addition to the expected ASL cases, but no elevation of lung or brain tumors in PVC production workers. PVC processing employees did have a small elevation of brain tumors. Molina, et al., (116) found that the Swedish work group had an elevated heart disease rate, but no tumors other than ASL. A follow-up study of Texas chemical workers found no relationship between vinyl chloride exposure and brain tumors (116A). A case-control study of 7,736 Japanese beauticians who may have used hair spray containing a VC propellant showed a slight elevation for stomach cancer, but not for liver, lung, or brain (116B).

Workers who fabricated PVC were of interest as a group whose exposure to VC was significantly less than the workers in the VC/PVC industry (117), but much higher than any expected exposure to the general population. Chiazze, Nichols, and Wong (30) studied 4,341 deaths of employees of 17 PVC fabricators, and found no ASL. There was an excess of deaths from intestinal cancer in both sexes, and breast and urinary cancer in females, using proportionate mortality ratios based on an external standard. A case-study follow-up on the breast cancer deaths showed (31) no relationship to VC exposure. Baxter and Fox (118) found very similar results in a study of 707 deaths of male fabrication workers in Great Britain. There was no excess of lung or brain cancer in either cohort.

There is no consistent trend in these occupational studies for an excess of tumors other than ASL, and it appears that the occasional report of elevated incidence at some other site is only a quirk of statistics because of the many site/incidence ratios being evaluated.

On an overall basis, about 0.1% of the estimated working population in VC-PVC plants has been affected by ASL. All of these have been in the most exposed group of reactor cleaners or associated duties, and in this group the incidence is about 1%. It has been suggested that some genetic difference, such as metabolic or repair rates, distinguish this susceptible fraction from the 99% who have not developed the disease from similar exposures. However, it is difficult to see how that explanation is compatible with the geographic clustering which is observed. Those who did develop ASL probably inhaled more than 25 Kg of VC during their work exposure (17A).

Several studies have been made of the general population using ASL as the marker disease in an effort to detect an association with possible environmental exposure to VC. There was no association with living near a VC handling plant in the general U.S. survey conducted by the Center for Disease Control (86). Brady, et al., (119) surveyed 26 ASL deaths in New York State between 1970 and 1975, and found five who lived nearer VC handling plants than did their matched controls, but could not establish a direct connection with the disease to exposure. Ten cases of ASL in Wisconsin were examined for possible connection with VC exposure, and none was found (120). Baxter, et al., (121) found no relationship between distance of residence from VC emitters and the 47 cases of ASL in the general population of Great Britain reported in 1963-1973. A later update (122) found one case which had lived the last six years of his life near a PVC plant and three cases where the man had worked in the plastics fabricating industry, but for whom there were no records to indicate exposure to VC. The lack of relationship between residence near vinyl chloride operations and cases of unknown etiology was confirmed. Saric, et al., (123) studied the deaths during the years 1968-1971 in an area surrounding a PVC plant that had been in operation

since 1949 and in which three workers had died of ASL. No relationship was found for liver or lung/bronchial cancer and place of residence for the general population. A similar study for communities near a Swedish plant which had operated since 1945 and had found four ASL cases showed (124) no unexpected elevation of fetal mortality, deaths from all cancers, or cancer of the liver or lungs during the years 1961-1974. Pancreatic cancer in males was elevated in the age group over 60. All ASL cases in Holland since 1950 (27 cases) were studied, and none had any traceable contact with VC (125). Iturra (126) observed an excess of cancer deaths in a city in Canada with a PVC plant as compared to a similar nearby city. This difference was principally found in males aged 20-64, which is not indicative of a general pollution effect. The author drew no conclusion as to why the condition existed.

Representatives of the Environmental Protection Agency have stated (127-8) that it has been unable to establish a link between living near VC handling plants and ASL. It awarded a contract in 1978 (Contract 68-02-2986 to Science Application Incorporated) to examine the present health of a cohort which was presumed to have been exposed to VC as children, but this project was not completed.

The disease ASL is difficult to diagnose (129-30), is almost invariably fatal within a short time, and presents a variety of symptoms including portal fibrosis and hypertension with splenomegaly and varices, proliferation of the sinusoidal lining, megalocytosia, and thrombocytopenia (54,131). Metastasis is frequently involved. These symptoms are very similar to those seen in the mouse (132) and rat (41) and the pathology also is similar (133). No really adequate early warning tests have been devised (103-4), although the gammaglutamyl transpepsidase test is promising, along with ICG clearance and SGOT. Radiographic liver scans and tomography and sonography (134) are said to be useful confirmatory tests.

In summary, VC is a classical procarcinogen, and is clearly a human carcinogen, causing ASL in a small percentage of highly exposed workers. There is suggestive evidence that it may be a weak general carcinogen at high concentrations, perhaps through an immunosuppressive mechanism, but more data are required to confirm this suspicion. Several studies of large populations have not shown a connection between general ambient exposure and increased incidence of cancer.

5. Reproductive Effects

Testing of vinyl chloride for mutagenicity has given mixed results, possibly because of the need for metabolic activation to an active species and because of its volatility. However, it is clear that it is a mutagen to several strains of bacteria and yeasts and in fruit flies under proper conditions (135).

Chromosome damage has been reported in workers with "VC illness" (136) but the changes do not appear to be permanent, and are repaired after exposure is stopped (137-8).

Picciano (139) concluded that any cytogenic observations were probably related to length and degree of exposure, and that any genetic risks were avoidable by adequate control of exposure. Basler and Rohrborn (140) found that this was true for the bone marrow cells of Chinese hamsters exposed to high levels of VC in vivo. Concurrent exposure to alcohol enhances the changes in rat mitochondria on exposure to VC (140A).

A test was made of the significance of the chromosomal damage to possible genetic risks by performing a dominant lethal study in male mice, which were mated with two untreated females for 8 successive weeks after exposure to 3-30,000 ppm of VC for 6 hrs/day for 5 days. There was no increase in the number of early deaths per implantation, and it was concluded that any expression of harm to the chromosomes of somatic cells was not carried over to stem cells (141). Short, et al., (142) performed a similar experiment with longer exposures to lower concentrations, and also found no effect on reproduction or survival. Himeno and coworkers also confirmed the lack of effect on male mice at 5,000 and 10,000 ppm, and reported that there was no change in sperm shape or mobility (141A).

Hehir, et al., (83) included a three-generation study in their program in which parent rats were exposed to 50 or 500 ppm VC 1 hr/day, 5 days/week for 10 weeks before mating and the subsequent three generations were examined for litter size, percent stillborn, growth, viability, and reproductive anomalies. No effect on the parents or the offspring from VC exposure was seen.

Studies by Schwetz, et al., (143) and by John, et al., (144) found no excess fetal wastage in mice, rats, or rabbits at VC exposures sufficient to cause maternal toxicity. The authors also found that VC, either alone or in combination with ethanol, was not teratogenic when dams were exposed on days 6-15 at 50-2,500 ppm VC. The combination of alcohol and VC did cause delayed development and a higher incidence of some skeletal variations.

Rice (145) concluded that there is no evidence that exposure to VC has produced increased tumors in the offspring of these animal tests.

Infante (146) has reported finding an excess of congenital birth malformations in three communities in Ohio that are near VC processing plants. However, the Center for Disease Control (CDC) performed a follow-up study and stated (147) that "it could not establish any association between cases and vinyl chloride exposure." Edmonds (148) has discussed the methodology of the follow-up study which was of the

case-control type, and stated that no relationship was found between the cases and their parents' employment or place of residence relative to the VC plants.

The CDC performed two other birth defect studies in areas possibly associated with vinyl chloride. In one (149) the hospital records for a city in Pennsylvania where a PVC plant is located were reviewed, and no increase in birth defects was seen. In another (148) hospital records for Kanawha County, West Virginia were reviewed for 1970-74 and all cases of birth defects were compared for residence and employment by case-control methodology. The study concluded that "no relationship between infants with malformations and parents' exposure to VC could be established."

Theriault and Goulet (150) reported a comparison of two cities in Canada, and found an increase in birth defects in the city which contained a VC processing plant. The increase was spread over a wide variety of types of defects, and only raw statistics were used. There was no attempt to compare exposures of the parents, nor were there controls for any other environmental factors. Thus, the significance of this finding cannot be evaluated, and the authors were careful not to ascribe excess significance to their data. A more detailed study of birth defects in Shawinigan, Canada led to the conclusion that stillbirths were not in excess. There was no relationship between the cases of defects and the parental occupation or residence, nor were the cases confined to any particular body system (151). Ambient concentrations up to 45 ppb were reported in this study.

Infante, et al., (152) have reported an increase in fetal wastage among the wives of workers in a PVC plant. This study has been criticized by Paddle (153), MacMahon (154), Downs, Stallones, and Frankowski (155), and by Monson (156) on the grounds of improper data gathering techniques, incorrect statistical treatment, and incomplete reporting. Many of the reported incidents occurred prior to the date of employment at that plant (157). In addition, the statistical significance of the reported excess of fetal wastage of exposed workers' wives disappears if those women subject to chronic spontaneous abortion are omitted. Hass and Schottenfeld (158) and Clemmesen (159) concluded that the inferences by Infante could not be sustained by the data.

Hatch (160) explored the statistical power of the various studies on reproductive effects. She found that the Ohio birth defect study (146) was deficient in power, but that the negative CDC recheck (147-8) of this report had adequate power to detect a significant effect, as did the CDC (149) study in West Virginia, which also was negative. Similarly, the worker study (152) on abortions and miscarriages had design deficiencies that prevented its results from being accurate.

Her conclusion was that "there are no data which point unambiguously to a relation between VC and reproductive outcome."

In summary, VC does not appear to be teratogenic, nor to cause excess fetal wastage in animals or humans. It can cause reversible chromosome damage in somatic cells, but apparently not in stem cells, and thus does not present a risk of reproductive effects.

B. Vinyl Acetate

Vinyl acetate (VAc) hydrolyzes readily in body fluids to acetic acid and acetaldehyde, both of which are normal metabolic products (161-2). The acetaldehyde is converted rapidly to acetic acid, also. Thus, there are only minor effects on mammals from moderate exposure to VAc. Both the acute and chronic toxicity of VAc have been reviewed extensively recently (162), and only the highlights will be summarized here. The EPA is in the process of developing a chemical information hazard profile (CHIP) for VAc and has requested that unpublished health studies be submitted for inclusion.

1. Acute Toxicity

The $LD_{50}$ doses in rodents by ingestion are reported as 2920 mg/kg for rats, 500 for guinea pigs, and 1613 for mice. The equivalent inhalation dose in 4 hours for rats is 4,000 ppm (163).

Humans experience eye irritation at 22 ppm. Rabbits suffer eye irritation from a 500 mg dose and skin irritation after 24 hours from 10 mg. Toxic effects in aquatic life are seen at 10-50 ppm in the standard 48-96 hour tests (163).

The current TLV is 10 ppm based on human eye irritation. NIOSH has recommended a maximum exposure of 250 $mg/m^3$, about 83 ppm, and states: "The irritations reported have all been reversible, and there are no known residual systemic effects" (162). Exposure above the TLV causes throat and bronchial irritation. The olfactory threshold is well below 1 ppm in air (162A) and about 0.25 ppm in water solution. It is probable that the ready hydrolysis to acetaldehyde is responsible for this low threshold, and is responsible for the sharp odor around most acetate copolymer plants. This, along with the irritant effect, serves as a sensitive warning to potentially harmful exposures. However, olfactory fatigue can occur on prolonged exposures.

A subchronic test (161) found that there was an 8% reduction in body weight in rats, but not mice, dosed with 5,000 ppm in the drinking water for three months. This result was not seen at 1,000 ppm or lower, and there were no other hematological or histopathologic effects. Inhalation exposure at 1,000 ppm for three months caused decreased weight gain in both species, and

in mice at 200 ppm. Irritation in the lungs also occurred, and mice developed hyperplasia and metaplasia in the bronchi at the higher dose. Similar effects were seen from 1,500 ppm for 4 weeks.

There was no evidence in the same study for teratological effects in rats from up to 5,000 ppm in the water during days 6-15 of gestation. Inhalation of 1,000 ppm was slightly fetotoxic; lower levels were not.

Metabolic conversion was found to be rapid with most being expired as carbon dioxide within two hours of exposure. There was no evidence of significant binding to tissues.

Vinyl acetate shares the property of most organic liquids of being an irritant to the skin by its defatting properties as a solvent for skin oils. Proper precautions should be taken to avoid direct skin contact during handling (164).

The sulfhydryl group appears to be involved in the detoxification of metabolized VAc, much as it is in VC. Sharply lower free non-protein thiol levels are found in rodents after vinyl acetate treatment (164A).

2. Chronic Toxicity

In the first chronic toxicity study reported, Maltoni exposed rats to 2,500 ppm VAc in air for one year. Survival was only 50%, and the results have not been reported in detail, but no neoplasms were found (165). It is understood, but not confirmed, that similar negative results and low survival was seen at 1,000 ppm in a later study.

A recent small lifetime feeding test of vinyl acetate in water (166A) resulted in an increase in neoplasms of the thyroid and uterus in female rats at the high dose rate (2,500 mg/l, or about 100 g/Kg lifetime dose) but no increase in neoplasms in the male high dose rats or in rats of either sex at 1,000 mg/l. The vinyl acetate solution was prepared twice a week, so the actual applied dose was smaller than indicated, and considerable acetaldehyde and acetic acid were ingested. The authors described the results as "not negative", and recommended a study with larger groups and fresh solutions.

This report has prompted a group of producers and users to sponsor through the Society of the Plastics Industry a large-scale bioassay program, and to conduct an epidemiological survey of industry workers. The latter study should be complete in 1984, and bioassay results in 1985.

The ACGIH quotes data showing no pathologic effects at exposures as hign as 630 ppm, or to repeated doses at 100 ppm in rats (166).

Study of a worker cohort with a mean service of 15 years at average exposures of 5-10 ppm, with excursions in the 50-300 ppm range, revealed no evidence to suggest chronic effects or serious residual injury from the excursions if treated promptly (164).

One recent report states that there is a slight elevation of abnormal chromosomes in exposed workers after 3 years as compared to controls (167).

Only negative mutagenicity tests have been reported for VAc (168-9) with or without activation. References to teratology studies other than the report cited above (167) were not found.

C. Trichloroethylene

Trichloroethylene (TCE) or other highly chlorinated aliphatic compounds are used as chain transfer agents in the manufacture of low molecular weight polymers, particularly the copolymers with vinyl acetate. This class of substances shares many toxicological features, so this discussion will center on TCE as the prototype for the class.

1. Toxicity

Exposure to TCE in the manufacture of PVC will be largely by inhalation, although skin absorption can occur also. The end effects, except for the skin irritation from contact with the liquid, are generally the same by either route, and occur primarily in the central nervous, cardiovascular, and biliary systems. The symptoms are related, and thus usually are seen together.

Some critical toxicity data for TCE are summarized in Table 2. More extensive information is available in references 178 and 179. Death has been reported in humans from inhalation of 2,900 ppm. The $LD_{50}$ in rats is 4,920 mg/kg. Oral doses of 6-7 g/kg causes death in humans and rodents, but death from injection occurs at doses as low as 0.1 g/kg.

TCE was used as an anesthetic for many years because of its strong narcotic effect on the central nervous system. Several patients developed trigeminal palsies following such treatment, possibly due to reaction products formed with the soda lime in the closed circuit anesthesia apparatus (170). Rapid, shallow breathing is a typical symptom. Industrial overexposures have been reported to cause headache, dizziness, nausea, and occasionally permanent nerve deficiencies (171-4). Death often involves ventricular fibrilation. Deliberate misuse, as in glue sniffing, results in respiratory and cardiac failure in extreme cases and liver and kidney damage in less extensive use (175-6).

Chronic low exposures (up to two or three hundred ppm) cause tremors, loss of motor function, insomnia, and cardiac disturbances (177-8). In general, these same symptoms have been reproduced in rodents.

Liver damage occurs infrequently in humans, but usually is massive and fatal, suggesting that some other complication has contributed to the event (179). The purity of the TCE may be important also (180), because of the various toxic corrosion inhibitors that may be present.

Mice are more sensitive than are rats to liver damage from exposure to TCE at low doses (181). Increased liver size, cell damage, and cell death are seen. This probably results from the higher ratio of metabolism in mice as compared to rats.

Alcohol has long been recognized as intensifying the toxicity of TCE (182) through a competition for the metabolism/ detoxification steps. The combination of TCE exposure and alcohol intake can result in development of red splotches on the skin that have been called "degreaser's blush".

TCE is metabolized by the same general process as is vinyl chloride, however, there is a major difference in the rates and in the detoxification stage. Little or no TCE is bound to the DNA, but is excreted as small metabolized molecules (183). The putative metabolites do not cause skin cancer in mice (183A) nor bind to glutathione or to DNA directly (183B). Theoretical considerations suggest that the chlorine-containing epoxide metabolites should decrease in reactivity as the chlorine content increases, and this has been confirmed experimentally (183C).

The principal metabolic product in humans is trichloroacetic acid, which can be detected in the urine, and used as an exposure monitor. Soleo and coworkers recently suggested that exposures in the 15-20 ppm range produce urine concentrations of this metabolic product which they consider safe (183D).

An equilibrium is established between the blood and expired breath contents of TCE, and breath analysis can be used, along with urine analysis, to estimate exposures (183E).

2. Carcinogenicity

The carcinogenicity of TCE is a very controversial subject. The regulatory agencies follow a general rule that any positive mutagenicity or bioassay tests requires classification of a substance as a potential human carcinogen, and thus TCE often is referred to in the public literature as a carcinogen. However, the data are less dogmatic.

Mutagenicity test results have been mixed, with both positive and negative reports. Often, the positive results are from technical grade material containing a few percent of an inhibitor, and the pure material is very weakly positive, so it is not clear as to what substance is the cause of the results (179A). The putative metabolic intermediates are not mutagenic (184) and, as discussed above, there is considerable evidence that they do not bind to DNA, or possess any of the expected properties of a carcinogen.

Similar problems exist with the carcinogenic bioassays. Positive results have been obtained with mice at doses that clearly were toxic, using technical material (185). Rats and hamsters have been negative consistently, as have other tests with mice, using purified material (185-8). It is of especial interest that inhalation, as compared to gavage, produced a negative bioassay (188A).

Recent press reports (189) have stated that preliminary evaluation of a repeat bioassay by the NCI using pure TCE has shown elevated tumor incidence. This study, as were several previous ones, was conducted at doses causing extensive systemic toxicity. This latest series of studies used four different strains of male rats at the NTP, and preliminary results indicate that only one of these four has given a positive response. However, that bioassay program is under review because of procedural difficulties discussed during a quality audit (189A). Several authors (23A,183C,189B) have developed data which indicate that the intermediate oxide product from metabolism is not a carcinogen, as is the case for vinyl chloride. Thus the relationship of these results to the hazards to humans at current ambient level is not clear. Epidemiological studies have been uniformly negative, and place an upper limit on any risk which TCE may present to humans (190-194).

The EPA has performed an in-depth review of the health effects of TCE (179) and has concluded "that long-term exposure of humans to environmental (ambient) levels of (TCE) is not likely to represent a health concern -- signs of liver dysfunction have been observed only in experimental animals during exposure to excessively high levels (>1,000 ppm)." In regard to human carcinogenicity it was stated that "the more conservative scientific sentiment would regard (TCE) as a probable human carcinogen, but there is considerable scientific sentiment for regarding (TCE) as an agent that cannot be classified as to its carcinogenicity for humans."

No evidence of dominant lethal mutations was seen at 450 ppm, nor was there any loss of fertility or fetal development (194A).

Teratology studies, although unrelated directly to carcinogenicity, have also been negative in mice, rats, and rabbits, further reducing the concern for harm from exposure to TCE (195). See (179) for a review of several other earlier reports.

TCE appears to belong to that class of materials which do not cause direct harm to the genetic DNA, but may, if given in sufficient dose, produce tumor formation in animals by severe organ damage. This class of substances has been termed nongenetic or epigenetic carcinogens and it seems probable that they are not actually carcinogenic at doses which do not produce permanent organ damage (196). A Committee of the National Academy of Science concluded that the low carcinogenic potency of TCE requires that no special precautions are needed beyond normal good industrial hygiene practices (197). Another NAS review group stated (198) that "additional long-term studies -- should be conducted with purified TCE in order to determine if TCE is a toxicant, mutagen, or carcinogen, and the minimum times and doses that are required to produce adverse effects." Thus, TCE should be handled with respect, but it appears that it can be used with safety under proper conditions. Meanwhile, its human carcinogenicity remains controversial (197A). IARC places it in category 3, "cannot be classified as to its carcinogenicity to humans" (197B).

D. 1,2-Dichloroethane

Many of the toxic properties of 1,2-dichloroethane (EDC or DCE) are very similar to those of TCE, and the same general precautions should be taken for both substances.

1. Acute Toxicity

The $LD_{50}$ in rats for a single oral dose has been reported as 680 mg/kg (199) and 0.77 ml/kg (200). Deaths in humans have resulted from doses estimated to be in the range of 20-50 ml, and the ability of dogs and humans to regurgitate, which rodents do not have, appears to permit them to survive higher ingested doses than rodents (201-2). Skin absorption occurs readily, and gives the same symptoms as inhalation or injection, in addition to the irritation effect on the skin by defatting (178). Severe pain and irritation results from eye contact, and foxes and dogs, but not other species, develop an irreversible clouding of the cornea, apparently from the production of a secondary metabolic product (203).

Inhalation produces the typical halogenated solvent symptoms of drowsiness, nausea, dizziness, and other signs of central nervous system depression. Liver and kidney damage may also occur (201-2). Rats survive 2-300 ppm for 7 hours, but only 1 hour at 3,000 ppm and 12 minutes at 20,000 ppm (204). No $LC_{50}$ data as such have been reported for inhalation

exposures, but can be inferred from other data as about 2,000 ppm. The slightly sweet, typical chlorinated solvent odor at 100-200 ppm becomes unpleasant for most persons at 1-2,000 ppm and can cause drowsiness at 2,000 ppm in as little as 5 minutes. Heparin has been used successfully in treatment of acute poisoning (205).

2. Chronic Toxicity

Animal studies (204,207-9) show little effect on health at prolonged exposures of 100-200 ppm, but levels of 4-500 ppm or higher resulted in liver damage, and there was pulmonary congestion, kidney damage, and deaths at 1,000 ppm.

Review of human cases (210-211) shows kidney and liver damage. Many of the fatal cases were from accidental ingestion. Exposure data are uncertain for occupational inhalation. Studies collected by NIOSH (201) suggest toxic effects at exposures as low as 10-15 ppm, but this is not confirmed.

3. Carcinogenicity

The same controversy exists as to the carcinogenicity of DCE as for TCE. One NCI bioassay (212) gave increased tumor formation. The initial dose was stongly toxic and had to be reduced during the experiment to maintain the animals alive. Other studies (186,209,213) found no such effects. A National Academy of Science review group concluded that further tests are needed to settle the issue (198). Meanwhile, the regulatory agencies sometimes list DCE as a potential human carcinogen, but it is not included on the NTP list of carcinogens.

The mutagenicity data to support this conclusion are mixed. Several tests are available which report both positive and negative results. There is concern that the putative metabolites chloroethanol and chloroacetaldehyde may be the active species, but these also show mixed results. See references (198,205) for a review of these data.

A multigeneration reproductive study at doses up to 50 mg/kg/day showed no significant dominant lethal or teratogenetic effects on mice in either of the two generations of offspring, nor on survival or weight gain (206).

EDC also has been found not to be teratogenic in rats, chickens, or rabbits, nor does it affect reproductive capacity at doses high enough to show severe maternal toxicity (208-9, 214-15).

Thus, DCE appears to have well-established no-effect levels for its toxicological effects, and if it is a carcinogen, must act through a nongenetic process such as that discussed earlier for

TCE. See references (178,198,201-2,215) for more detailed discussion of these points.

E. Polyvinyl Chloride

PVC is an inert, indigestible material with no known direct toxic effects. There has been concern for problems which may be associated with residual monomers or polymerization adjuncts, but there are none which are associated with the polymer itself (216).

The principal health concern for PVC is from inhalation. PVC is regulated as an inert or "nuisance dust" by OSHA (29 CFR 1910.1000 table Z-3) which sets exposure limits at 5 $mg/m^3$ for the respirable portion and 15 $mg/m^3$ for total dust. The ACGIH recommendation is 5 and 10 $mg/m^3$, respectively.

Various reports have been issued concerning the effects of PVC dusts on animals and humans, most of them originating in Europe. Miller and coworkers (217) found diminished pulmonary function in long-term workers exposed to VC and PVC. Arnoud, et al., reported (218) that a bagger with 23 years' experience had PVC entrapped by the microphages of his lungs. Waxwieler, et al., speculated that his finding of no association between VC exposure and lung cancer in a plant cohort could throw suspicion on the PVC as a causative factor (95). However, this was shown later not to be the case (90,97,98). Mastrangelo, et al., studied 20 workers with high PVC dust exposure and found observable X-ray abnormalities and some respiratory impairment (219). Cordosco, et al., (220) found similar symptoms in three patients. These reports give very little detail on the degree of exposure or the type of resin or other materials which may have been present.

Two more detailed studies of workers at ICI plants in England have been reported. Chivers, et al., (221) examined the respiratory function of 509 workers, including 112 controls, and concluded that "PVC dust has not produced deleterious effects on ventilatory functions."

A more extensive study of 818 workers, many of whom had worked in older plants manufacturing plastisol resins, included X-rays and several lung function tests (222). Their conclusion was that there was evidence of a slight, nonspecific respiratory effect that was difficult to distinguish from the effects of aging and smoking. A follow-up study performed about a year later included the original 818 workers plus others in that plant for a total of 1,047 persons, and a group of 127 workers from a second plant which produced only suspension resins. The results of the first study were confirmed, with the exception that the men in the second plant appeared to have slightly less response than those in the first (222A).

OSHA issued a call for information on the occupational effects of PVC, and a symposium was held in March 1980 (223). The effects discussed above were reviewed, but no additional data were

presented. The proceedings of this symposium were published as Vol. 41 of Environmental Health Perspective, Dec. 1981.

Similar effects have been observed in animals after exposure to PVC dust as have been reported for humans (224-227). An unpublished NIOSH study exposed rats (12 months), monkeys (22 months), and guinea pigs (12 months) to more than 10 mg/m$^3$ of respirable PVC dust (plastisol grade) for 6 hrs/day, 5 days/week. Extensive biochemical, pathological, and respiratory tests (monkeys only) were performed on the animals. It was concluded that no liver damage was seen, some accumulation of dust in the microphages occurred, and for the monkeys, there was no impairment of respiratory function (228). In general, these authors remark on the mild effect of PVC dust, and compare it to other nontoxic substances.

Some PVC dusts show greater in vitro cytotoxicity and fibrogenicity than do others (229) and these two properties run in parallel. Richards and coworkers found (230-31) that the biological activity was due to the surface active agents present on plastisol resins, and that sodium dodecylbenzene sulfonate was the most active of those tested. Washing with ethanol or water reduced the activity greatly.

Wheeler has emphasized the need to distinguish between plastisol and suspension resins when considering health effects (223).

Chronic feeding studies of PVC, copolymers, or extracts of these to rats and dogs has not shown any serious effect (232-4). These resins are prior sanctioned by the FDA for food and cosmetic applications (21 CFR 121.106).

PVC is like other solids that it will induce local sarcomas when the proper size pieces are implanted in rodents. These results have been reviewed in several places (162,235-6) and are not considered relevant to risks for humans (195).

The difficulty of ignition of PVC dust is a function of its particle size. Very little yield is obtained from material 100 μm or larger, while 10 μm material is about as explosive as baking flour (237). The presence of small amounts of flammable gas increases the hazard. Solid PVC is nonsupportive of combustion, and most fabricated products earn the Underwriters rating of SE-0 unless sufficient modifier or plasticizer is added to offset the lack of flammability (238).

It is well known that PVC will produce hydrogen chloride upon heating, and this is the basis of the need for stabilizers during processing. This hydrogen chloride is the principal toxic hazard during fires that are large enough to force continued burning of PVC articles (239-40), along with the carbon monoxide that may be present in any combustion gases. This aspect of polymer toxicity will be discussed in more detail in Chapter 26 of Volume III of this Encyclopedia.

Some evolution of HCl occurs at any elevated temperature, but studies have shown (241-3) that this is not a significant risk to those who handle the hot materials, such as meat wrappers, when adequate ventilation is provided.

This is no depolymerization of PVC to the monomer, and the amount of vinyl chloride found in decomposition gases at processing temperatures is only that expected to be present as residual monomer (244).

## III. Regulatory Status

The current regulatory status of the materials discussed in Section II is summarized in Table 6 where an X indicates that there is a document or rule by that agency for the substance listed in the column heading. These rules are discussed in more detail in the following pages.

### A. The Food and Drug Administration

The first specific regulatory initiative toward vinyl chloride was in 1973, after it was found that up to 20 ppm of vinyl chloride could migrate into the contents of miniature liquor bottles. The Bureau of Alcohol, Tax, and Firearms of the Department of the Treasury (BATF) proposed (38FR12931, Sept. 1973) to withdraw the prior sanction status of PVC for use in these bottles. The proposal was based on adulteration of the bottle contents, and not on any specific health issue at that time. Bottlers stopped this use of PVC voluntarily, and no further action has been taken on this proposal.

The BATF has indicated to the FDA that it is willing to reconsider the use of PVC for liquor bottles if the FDA would clarify the status of PVC for that use. The FDA replied in a letter of January 13, 1981 from the Deputy Director of Foods to the Assistant Director of BATF that the FDA was still considering its policy in regard to indirect food additives. Two proposals concerning that policy were published for public comment at 47FR4972, February 2 and 47FR14464, April 2, 1982. Thus, this issue still is not resolved. The BATF has removed formal barriers to the manufacture of liquor bottles from plastics in general (47FR43944, October 5, 1982) but has not approved PVC specifically.

Earlier, the FDA published in September 7, 1975, at 40FR40529, notice of intent to withdraw its sanction for the use of rigid and semi-rigid PVC as food packaging material, while allowing the use of flexible materials to continue. This was based on the finding that residual vinyl chloride in flexible film was undetectable, but could be found to be present in rigid sheet, and therefore was presumed to migrate into foods. No action has been taken on this proposal, either. One of the reasons has been the strong activity by members of the Society of the Plastics Industry (SPI), who presented data to the FDA that the current very low residual vinyl chloride in PVC does not result in detectable quantities of vinyl chloride in the packaged food (245). In addition, the District of Columbia Circuit Court of Appeals ruled in Monsanto v. Kennedy [631F 2nd 947 (D.C.

Table 6

Regulatory Status of Various Substances

| | VC | VAC | TCE | EDC |
|---|---|---|---|---|
| OSHA | | | | |
| TLV ppm | 1/5 | | 100/300 | 50/200 |
| Standard | X | | (50/150) | |
| ACGIH | 5 | 10/20 | 100/150 | 10/15 |
| NIOSH | | | | |
| Crit. Doc. | | X | X | X |
| EPA | | | | |
| Standard | X | | | |
| Priority Pollutant | X | | X | X |
| Hazardous Substance | | X | X | X |
| RCRA | X | X | X | X |
| CERCLA (Superfund) | X | X | X | X |
| FIFRA | X | | | |
| FDA | X | | | |
| BATF | X | | | |
| DOT | X | X | | X |
| CPSC | X | | | |

Circuit 1979)] that risks cannot be inferred or assumed, but must be found by a reliable scientific process. The Second Annual Report on carcinogens (246) states that the FDA is reconsidering this proposal, and may withdraw it.

Meanwhile, the polymers and copolymers of vinyl chloride continue to be prior sanctioned for food and cosmetic packaging. Concern over possible action by the FDA has significantly affected this application, however. A recent industry survey by the SPI found that about 7.8% of the nations' food supply is now packaged in PVC, and estimated that this could rise to about 11% if the proposal were withdrawn (246A). No significant exposure to ingested VC can be expected at this level of use and the current low residual monomer levels.

Vinyl chloride was used as a propellant in a variety of pesticides and cosmetics up to 1973, when this use was withdrawn voluntarily. When the first reports of ASL issued, the three agencies having jurisdiction over these uses promulgated bans, the FDA at 39FR30830, the EPA at 39FR14753 and the Consumers Product Safety Commission (CPSC) at 39FR30112. The CPSC action was upset on procedural grounds and was later reinstated (43FR12308) without a by then useless recall provision. The FDA noted (39FR14215) in its proposal that a generally effective voluntary recall of unused packages had occurred in early 1974.

B. The Occupational Safety and Health Administration

OSHA adopted the recommendations of the American Conference of Governmental Industrial Hygienists (ACGIH) for occupational exposure to various substances as a part of its rulemaking by reference. These appear at 29CFR1910.100, tables Z-1 and Z-2. There is no listing for vinyl acetate. OSHA has not kept up with the subsequent revisions of this list by ACGIH, so that current ACGIH recommendations (shown in parenthesis in Table 6) differ from the official OSHA exposure limits. The ACGIH recommendation at the time of adoption by OSHA was 500 ppm. See the discussion of this point in Part II.A.1 above.

The allowable occupational exposure for vinyl chloride of 1 ppm is set by the OSHA workplace standard at 29CFR1910.1017. This was adopted in 1974, after extensive public hearings and became effective in April 1975. OSHA first set an emergency temporary standard of 50 ppm, and proposed a permanent limit of nondetectable exposure by a test sensitive to 1 ppm. Economic impact studies sponsored by both OSHA and industry showed that such a limit was not feasible (245A), and OSHA then promulgated a final standard of an 8-hour time-weighted average (TWA) of 1 ppm, and a 15-minute ceiling of 5 ppm, without regard to respirators.

In brief, the regulation sets:

1. An action level of 0.5 ppm below which no response is required. This generally exempts most fabrication plants and laboratories and many monomer plants.

2. A regulated area where exposures are above 0.5 ppm which restricts entry to authorized persons.

3. Medical examination schedules and exposure record retention for authorized employees.

4. A list of acceptable respirators for use at exposures over 1 ppm.

5. Monitoring and alarm systems for the workplace, and routine measurement of worker exposure.

6. Labeling and signs for regulated areas and containers of vinyl chloride and PVC.

7. Work procedures for hazardous operations, and

8. Training programs for employees.

OSHA described this as a "feasible" standard, and states that it was not derived from health considerations, therefore should not be considered a safe exposure limit.

It is difficult to determine the cost to the industry for compliance with this standard because of the work going on at the same time to respond to the expected EPA emission standard. In addition, some steps had been undertaken earlier by industry in response to the concern for AOL (63). The immediate effect was a sharp drop in productivity as new work practices were instituted and equipment was installed. Some of this productivity loss was recovered later, but there is a general industry consensus that there has been at least a permanent 5-10% loss (247-8). A few of the smaller older plants shut down, amounting to about a 5% loss of capacity and jobs (248A). Trade association estimates prepared a few years later indicate an overall capital expenditure of about $200 million that can be ascribed directly to OSHA, and added annual expenses of about $25 million.

Several authors have attempted to estimate the cost-effectiveness of this standard on a cost-per-life-saved basis. This is an especially difficult approach, because of the uncertainty of what exposures may have been in the absence of a standard, the inaccuracy of the risk assessments which were made from animal data, and the reluctance of most persons to accept a monetary value for a life. Nevertheless, Graham and Vaupel (249) estimated that the OSHA rule cost $7.5 million per life saved and $490 thousand per life-year saved over the option of leaving the limit at 50 ppm. Luken and Miller (250) arrive at an imputed value of $4 million per life, while Morrell (251) derived the higher cost of $200 million per life, assuming that the residual incidence rate would have been 0.1 cases per year without the standard. Northrup (252) calculated that the cost was $9 million per life, or $450,000 per year of life saved, based on no voluntary action by industry.

There are no specific OSHA standards for the other materials in this group except for the 8-hour exposure limits of 40CFR1910.1000 that are shown in Table 6.

C. The Environmental Protection Agency

1. Air Emissions

There are no recognized biological sources for the materials discussed in this chapter. Vinyl chloride is suspected to be formed by the photochemical decomposition of other halogenated materials, but this has not been confirmed. It is formed by the biological degradation of other chloroolefins (see below). Hoffman reported (253) that vinyl chloride was found in tobacco smoke, and speculated that it might be present in combustion gases from all chloride-contaminated organic materials, and therefore may be ubiquitous.

Grinard calculated (254) that the steady state, worldwide ambient concentration in 1973 was about 1.4 ppt based on emissions at that time. Vinyl chloride is active photochemically with a half-life in sunlight of about 5 or 6 hours (255-8). The reaction rates are slightly less than those of ethylene in the reaction with NO, and considerably less in the reactions with ozone. The residence time in the atmosphere was estimated as 1.8 days by Singh, et al. (259), with a 43% loss per 12 hours of sunlight, based on the rate of reaction with hydroxyl radical only. Smog chamber data were used to predict a consumption rate of 12% per hour, and the study showed a rate of about 18% (259A).

The EPA has conducted three ambient monitoring programs around VC handling plants (117,255). The first, in 1974, found measurable quantities at distances up to 0.5 km from a PVC plant. The third program failed to find significant quantities at the fence line of five large fabricating plants. The results of the second program have not been released formally, but an analysis of the data has shown that the average concentration in early 1975 at the plant tested was about 40 ppb at 500 meters from the plant center, 10 ppb at 1 km, and 2 ppb at 2 km. The EPA had calculated (75) an average exposure of 17 ppb to persons residing within five miles of a typical PVC plant, using emission data and modeling techniques which were strongly disputed by industry. The estimated 95% reduction of emissions by the current standard presumably reduces the current exposure to those within five miles of 0.4 ppb, by the EPA assumptions. The generally accepted field monitoring method for VC has a lower sensitivity of 10 ppb so that these estimates cannot be verified broadly, but recent tests in one plant suggest that the actual values are only 10-25% of this estimate (248).

Vinyl chloride, TCE, and DCE currently are found in the ppb range in the air around industrial locations, but generally not in detectable quantities at rural sites (179,259-262). There are diurnal and seasonal variations which link the emissions to human activity. A summary of an extensive EPA-sponsored survey is available in paper copy or on computer tape (262A).

The EPA formed a study group early in 1974 while OSHA was conducting its rulemaking. Several publications discussed the environmental aspects of VC (75,255,263-4) and the EPA ultimately concluded that there were nearly 5 million residents within 5 miles of VC/PVC production facilities that had been exposed to an average annual concentration of 17 ppb for 30-40 years, and that this led to the possibility of 10-20 deaths per year (127). This risk estimate has several serious flaws (265) and a more realistic estimate is several orders of magnitude lower. In any event, there have not been any cases of ASL which have been attributed to general ambient exposure. See the discussion in II.A.4 above. The final EPA standard was calculated by the EPA to reduce environmental exposure by 95%, and thus the projected death rate to less than 1 per year (266).

The final EPA standard (74) established the following conditions:

a. Fugitive emissions controls by leak patrols and design standards for pump and compressor seals, agitators, and loading devices.

b. Work practices for vessel openings and sampling.

c. Stripping requirements for residual monomer in resins and wastewater.

d. Abatement of all point source emissions to 10 ppm.

e. Prohibition of relief valve discharges, except for emergencies.

f. Extensive monitoring, reporting, and recordkeeping requirements, and

g. Specific analytical procedures.

The Agency prepared a model plant by choosing among the best control devices existent in the industry (75) and it now judges the compliance of a particular plant by the projected emissions from that model.

As was stated earlier, it is difficult to separate the compliance costs for this standard from those of the OSHA standard. An Agency report (267) estimated that the cost of compliance was $296 million through July 1981, and that an

additional $470 million would be spent in the next five years, all calculated in 1977 dollars. A more recent update of this report prepared for the Agency put the costs for 1981-1990 at $981 million. If the Agency estimate of 20 deaths per year is accepted, this would be a cost of about $5 million per life saved. However, there is no evidence that any lives have been saved by this standard and we do know that at least two workmen were killed during the compliance efforts of the industry. The industry position has been that the OSHA standard had provided adequate protection to the environment, and that the EPA-generated costs were unnecessary.

Environmental groups challenged the standard as being too lax, and as part of a settlement agreement EPA proposed additional restrictions on emissions (42FR28154, June 2, 1977). No further official action has been made on this proposal.

The Agency has stated more recently that it is again reviewing the emission standard for vinyl chloride, and plans to propose revisions in 1984 (48FR47914, October 17, 1983).

Meanwhile, the U.S. District Court for the Middle District of Louisiana dismissed cases brought by the EPA against Ethyl Corporation and Occidental Chemical Corporation for violations of the emergency discharge rule (40 CFR 61.65(a)) on the grounds that the standard is a work practice standard and not an emission standard, and as such was not authorized by the Clean Air Act as it existed in 1976 (267A). Work practices were authorized by 1977 and 1978 amendments to Sec. (112) of the Clean Air Act, but this was after promulgation of the standard, and thus the court noted that the present standard was subject to the Supreme Court ruling in Adamo Wrecking Co., United States 334 US 275 (1978), which held that work practices were not authorized at the time of promulgation.

At the same time, the District Court for Massachusetts has denied the petition by Borden, Inc., for dismissal of a similar suit. It ruled that the Adamo decision did not apply, and that Borden was barred from challenging the standard at this time.

The Agency has filed notice of appeal in the Louisiana rulings, and has continued to file additional cases against other facilities on an identical basis. It appears that this matter may be in litigation for some time.

Industry argued the same point that was made by the Louisiana court during the rulemaking procedures, but was not successful at that time. After promulgation, attempts to obtain a clarifying guideline from the Standards Setting Group in the Air Office were unproductive, and the Enforcement Office issued a series of memoranda which took a literal view of an "emergency" being little other than an "Act of God". The effort to attain relief here was complicated by the outstanding proposed amendments to the standard of June, 1977, published as

the result of the negotiated agreement with the National Resources Defense Council after their petition for review of the original standard, which would have made the standard more stringent. Neither these proposed amendments nor the requests for clarification of the definition of emergency were acted on.

The other materials discussed in this section are not regulated by specific emission standards, but all of them, including VC, are affected by general rules on volatile organic emissions, and thus come under the State Implementation Plans and New Source Performance Standards, which often require stricter control measures than does this standard. The oxychlorination reactor in particular has been subjected to additional controls (48FR40278, September 6, 1983), as have storage tanks. Most new volatile organic chemical manufacturing facilities are subject to a leak detection requirement similar to that for VC (48FR48328, October 18, 1983).

Vinyl chloride, TCE, and DCE are listed as priority pollutants under Sec. 307(a) of the Clean Water Act, and Water Quality Criteria Documents have been prepared for them (274). This subjects these materials to special considerations when discharge permits are issued. A Health Assessment Document has been prepared for TCE (179). These documents summarize the evaluation by the Agency of the health risks from these substances, and give some data on methods of waste treatment. Other sources of Agency data on VC, TCE, and EDC can be found in the "Treatability Manual" (262), the "Multimedia Environmental Goals for Environmental Assessment" (273), and "Fate of Priority Pollutants in Publicly Owned Treatment Works" (273A).

Vinyl acetate, DCE, and TCE also are subject to reporting requirements for spills as hazardous substances under Sec. 311(b) of the Water Pollution Control Act and Sec. 102 of CERCLA. See 40CFR116, 117, and 302.4. Reportable quantities (RQ) of spills are 5,000 lb. for DCE, and 1,000 lb. for vinyl acetate and TCE. Vinyl chloride has a temporary 1 lb. reportable quantity under CERCLA, pending designation of a permanent figure by the EPA. Reports are not necessary for releases at federally permitted facilities. The EPA has proposed to raise the RQ for vinyl acetate to 5,000 lb. (48FR23552, May 25, 1983).

The EPA issued a rule at 49FR5308 under which the distillation residues from the preparation of EDC and VC are to be listed specifically as hazardous wastes, rather than as the result of broader RCRA rules. This insures that all such wastes are to be disposed of only by RCRA-approved procedures.

2. Water

All of the substances discussed in the previous section also are controlled under general discharge provisions to the extent that they produce conventional pollutant properties, such as BOD.

As would be expected, vinyl chloride has low water solubility, and is easily lost to the atmosphere from streams and discharges (268-9). Under one set of experimental conditions, the evaporative half-life of VC, TCE, and EDC are less than a half hour (269). In another experiment, a stirred beaker lost 96% of its original 16 ppm of VC in two hours, while an unstirred beaker lost 25%, at 22°C. Plots of log concentration versus time gave straight lines, indicating volatility to be the only important loss mechanism. There was no difference in loss rates between distilled water, river water, or industrial effluent. It does not appear to be absorbed by microorganisms, as shown by tests with five mixed bacteria populations, three mixed fungal populations, two axenic bacterial cultures, and one algae. The mixed bacteria did not degrade the VC, nor was it toxic to the bacteria at concentrations up to 900 mg/l. It does not bioaccumulate in the food chain (270).

The EPA has reported (255) finding VC in the water supplies of some cities in the ppb range. The concentration was higher in the finished than in the raw water, indicating that it may be produced in the chlorination step. Dressman and McFarren (271) have found VC in the ppb range in water from distribution systems using PVC pipe. It is also present in the discharge of some VC-handling plants in the low ppm range (263). Banzer (272) states that no extraction of VC occurs from pipe containing less than 1 ppm residual by a test sensitive to 2 ppb.

The EPA and the FDA have entered into a memorandum of understanding which assigns the EPA the responsibility for regulating exposure for VC extracted from plastic water distribution pipe (274A). No specific action has been taken in this regard, possibly because of the rapid decline in detectable amounts in drinking water after new piping systems are put into use (274B). There is in place a voluntary industry standard limiting residual VC in the finished pipe to 10 ppmw.

This program appears to have been successful in eliminating the leaching of VC into water. Compliance is being monitored by the National Sanitation Foundation (NSF), whose stamp of approval is required by most codes before pipe can be sold or installed for potable water use. A recent report (274C) described a test for chlorinated organics in water extracts of plastic pipe which is sensitive to 2 ppb, and the President of NSF has stated (274D) that VC is not found in the extract at this limit of detection.

Similarly, TCE and DCE are found in streams and water supplies in low concentrations (179,262,273-4, see also 47FR9350). These seem to be present because of a combination of waste discharges, formation during chlorination of water supplies, and, in the case of TCE, use by individuals as a degreasing treatment for home sewer systems. Some state legislatures are considering a prohibition of this last use.

A relationship between vinyl chloride and chlorinated ethanes in groundwater has been established by recent work at Florida International University for the EPA (274E). Analyses in the outer perimeter of tri- or tetrachloroethylene-contaminated groundwater showed a larger than expected decrease in the original contaminants and the presence of vinyl and vinylidene chloride and 1,2-dichloroethylene. Experiments with anaerobic bacteria from Florida muck demonstrated that several classes of anaerobic bacteria, including the ubiquitous E. coli, can biodegrade the more highly chlorinated ethylenes to the mono- and dichlorinated derivatives.

Their work also confirmed the resistance of VC to further biodegradation, and reported a half-life of greater than 60 days under their experimental conditions, as compared to 43 and 34 days, respectively, for the tri- and tetra-substituted ethylenes. They developed a spray aeration system which attained greater than 95% efficiency for removal of VC per stage.

Vinyl acetate would not be expected to be persistent in water because of its rapid hydrolysis, which is reported to be 8.5%/day at room temperature and 4%/day at 4°C in tap water (166A).

The EPA has in progress two rulemakings which will regulate the allowable emission of VC, TCE, and EDC beyond that of the general emission standard. On March 4, 1982 the EPA published an advance notice of proposed rulemaking (47FR9350) requesting public input on work underway to limit volatile synthetic organic chemicals under authority of the Safe Drinking Water Act. It stated that it was considering establishing Maximum Concentration Limits of 1-100 ppb for VC and EDC, and 5-500 ppb for TCE. The Health Assessment Documents prepared as a part of this initiative still are undergoing scientific review.

On March 21, 1983 the EPA published a proposed regulation (48FR11828) containing effluent limitation guidelines for the organic chemicals and plastic industries which would place 50 ppb maximum for the VC content of plant effluents. The limit for TCE is proposed as 75 ppb maximum for any one day, and 50 ppb for the average of any four consecutive days. The EDC limits are 150 and 100 ppb, respectively. The standard for EDC would apply to both direct discharges and those whose effluent is treated further at public treatment works; those for TCE and VC apply only to direct discharges.

3. Solid Wastes

Vinyl chloride is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA), as toxic and ignitable. Vinyl acetate and EDC are ignitable wastes, and TCE is a toxic waste under these rules. See 40CFR261. Any disposal of these substances is subject to permits under RCRA. The EPA recently included the distillation wastes from the production of VC and EDC as hazardous wastes, as was noted earlier.

4. New Product Manufacture

The EPA also administers the Toxic Sustances Control Act (TSCA) which establishes health and environmental regulations for both new and existing substances. No one may manufacture or use a substance which is not on the Agency's official inventory, unless the EPA has accepted a Premanufacturing Notice (PMN). Polymers containing more than 2% of an incorporated substance are required to be on this inventory, in contrast to European rules which do not cover polymers. Incorporation of less than 2% of a substance is not deemed to be a new polymer, and a PMN is not required for manufacture. Producers have the choice of making these resins of low comonomer composition without a PMN, in which case they are not placed on the inventory and future variations are limited to less than 2%, or of filing a PMN, in which case future variations may contain any desired amount, but full disclosure of all processing ingredients and conditions are required. See 40CFR720, 48FR21722, May 13, and 41132, September 13, 1983, for more details on this regulation.

The EPA has proposed (47FR33924) procedures for exempting certain classes of polymers from the PMN rule, but the conditions for this exemption are so rigid that industry has opposed the proposal, and asked for a blanket exemption for all structural polymers similar to the European rules.

IV. General Safety Procedures

Extensive changes have occurred in the work practices and procedures in monomer and polymer plants in the last few years as the result of concern for the health effects of VC. These have been amplified by efforts to comply with the OSHA and EPA standards on vinyl chloride (248,252,275-6), and the broader volatile organic emission rules. There is no doubt that these compliance efforts have made the industry a safer place to work.

The VC/PVC industry always has been a relatively safe industry from the standpoint of major disasters and fatalities due to the inherent hazards of the processes, even when the ASL cases are considered. Nevertheless, there have been several major incidents that resulted in fire and loss of life (276A) one of which ranked among the hundred largest losses of the last thirty years (276B). Table 8 contains a listing of major

incidents in the past few years. Thus, the basic considerations of the flammability and the need for careful control of polymerization still remain the controlling factors in efforts to protect life and property.

Efforts to improve plant safety and to develop more effective means of compliance with health regulations has been aided signficantly by voluntary participation in trade associations. The Vinyl Chloride Safety Association has been especially productive, but substantial developments have come from the Compressed Gas Association, the Chemical Manufacturers Association, and the Vinyl Institute and its predecessor organization, which was an arm of the Society of the Plastics Industries. The industry has been very generous in exchanging nonproprietary information relating to safety and health.

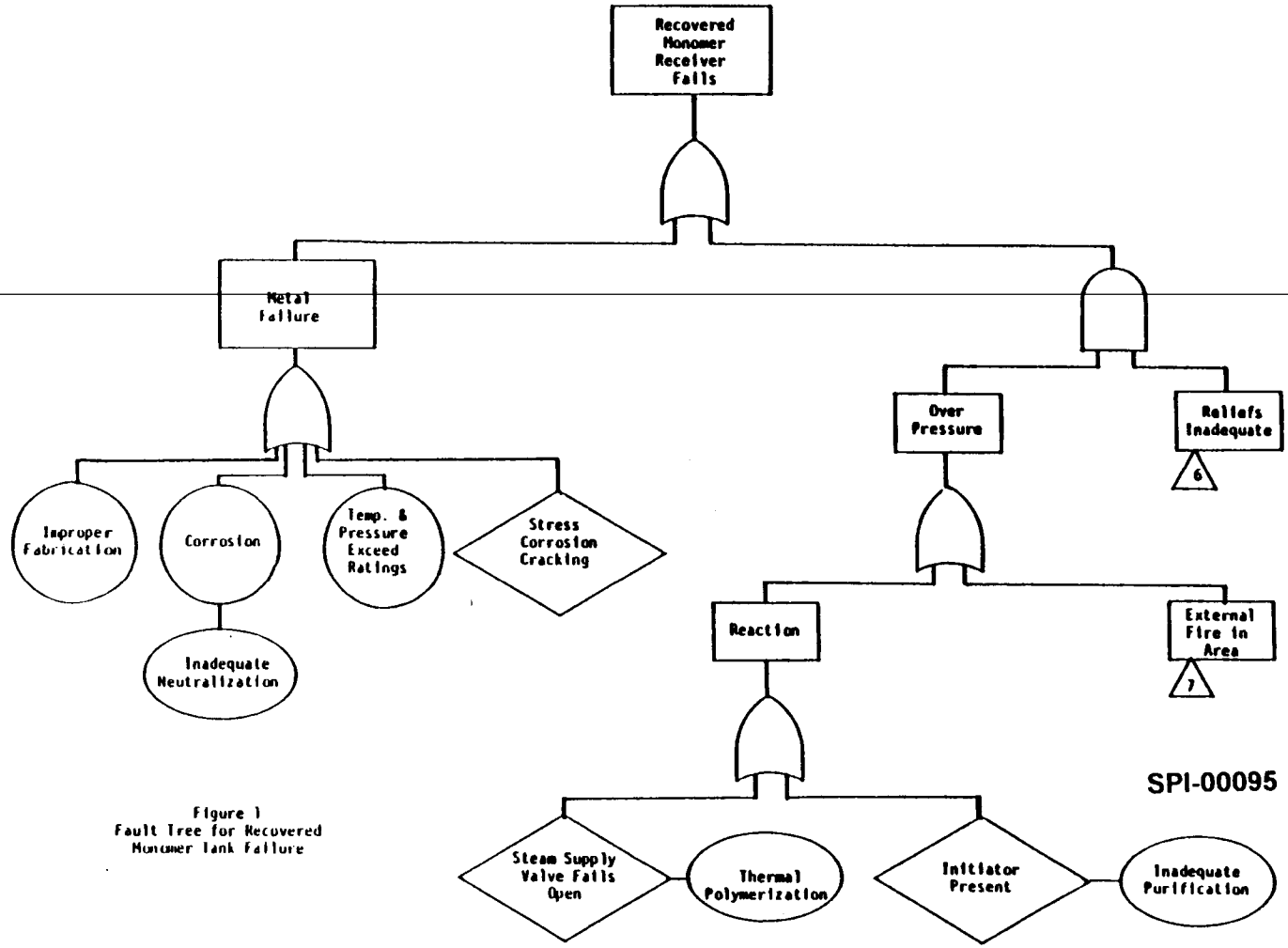
A formal Process Hazard Review (PHR) is used by many organizations to identify, evaluate, and plan remedial actions for potentially hazardous situations which may arise in plant operations. The PHR is in many ways an outgrowth of accident investigation, the difference being that the study is made before an event, with the intention of preventing it (287A,290E). Emphasis usually centers on the reactor and its attendant systems.

A team with broad experience conducts the PHR. The skills included should cover plant operations, safety engineering, environmental engineering, and experts in the process involved, and also any particular special problems posed by the process. This usually involves 4-7 persons for all of the study, and others for portions. The initial phase may occupy 3-10 days at the plant sites, after gathering the initial background documents and data which will help identify the concerns to be addressed.

Much of this first phase consists of a line-by-line examination of the process flow diagrams, but field inspections and interviews are important also. If the Review is for an operating plant, plant operating and support personnel should be interviewed. If the plant is in the design state, the designers and the future operators should be included.

Each section or unit operation is discussed by someone familiar with the design concept and operating philosophy. A person familiar with the fault tree concept then leads in an examination of each major piece of equipment for potential failure modes, determining (or speculating on) conditions which could cause, prevent, or modify such failures.

The results can be depicted in a fault tree, which show those conditions necessary to cause particular result as an "and" branch, and gathers those various groups which may cause the same result into "or" groups. Figure 1 is a generalized fault tree for the failure under pressure of a monomer storage tank, such as a recovered monomer vessel, and Figure 2 is a more detailed analysis of one of the branches of the previous figure, the probability of an external fire in the process area. The result is a description of the events necessary and sufficient to cause the potential incident (234).




SPI-00095

Figure 1
Fault Tree for Recovered Monomer Tank Failure

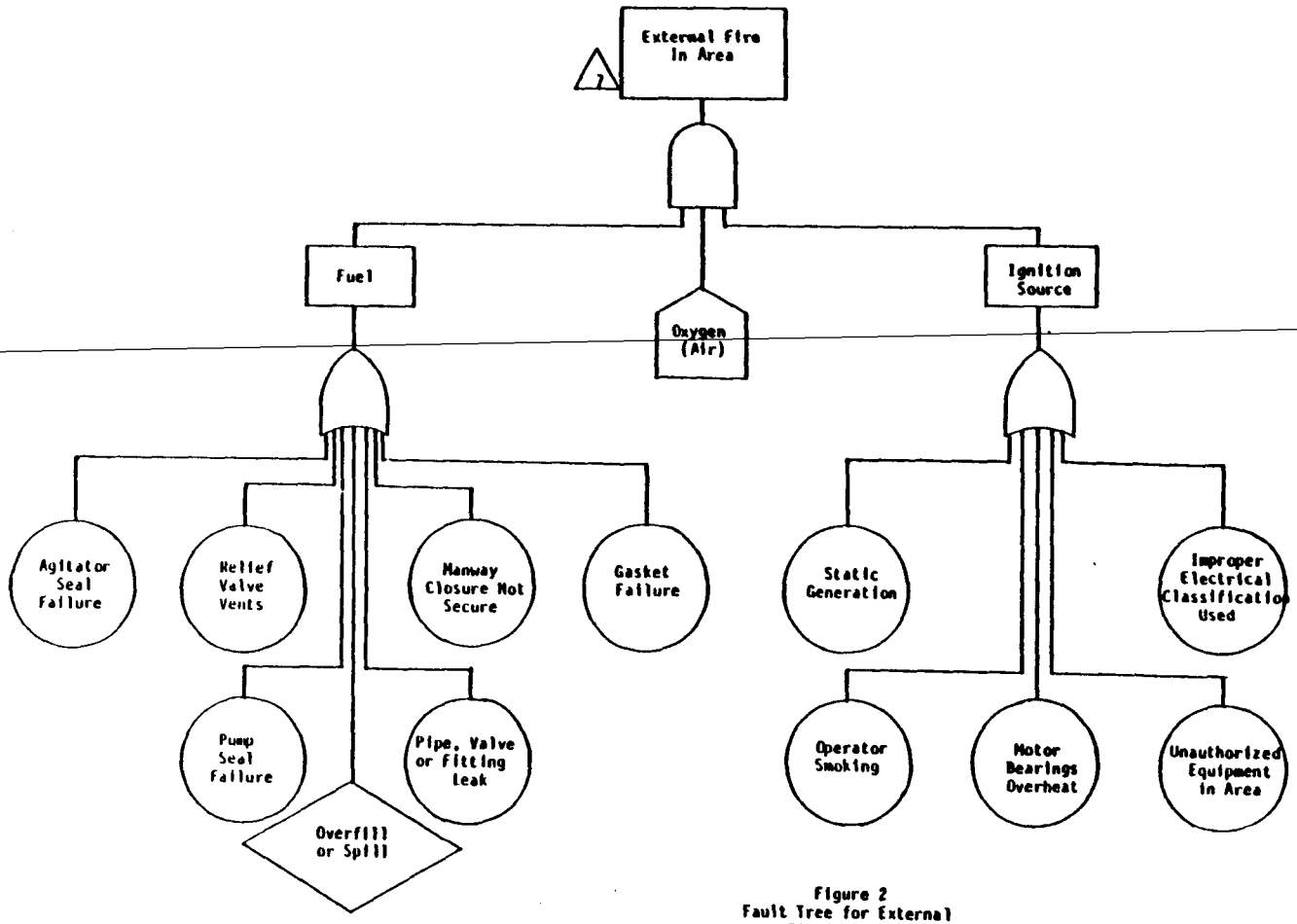



Figure 2
Fault Tree for External
Fire in Area

SPI-00096

A second phase of the PHR is to attempt to quantify the probability of each contributing event, and of the postulated end result. This usually is done by a specialist in risk assessment, who often is the leader of the team. Where available, actual experience for failure rates should be used, but publications giving predicted rates or rates for similar situations are available (290F,G). In this way those conditions or combinations of conditions which are unlikely to occur or to lead to a dangerous result can be identified and more attention paid to more probable scenarios.

The third phase consists of the preparation of the PHR report, which contains specific recommendations by the whole team, for preventative measures for the serious consequence conditions, with appropriate priorities and the assignment of responsibility for implementation of each action.

The final phase is a progress review of the implementation steps. Further change or revisions may be required as the result of new data or cost estimates, or further examination of the interaction of the changes made.

For new plants, the Operational Readiness Inspection (ORI) before start-up should include a further review of compliance with the PHR report.

A major uncertainty in the quantification analysis is the weight to be ascribed to operator error. This factor often is enough larger than the other factors that errors in estimation of its value overrides the other uncertainties in the estimate (290G). This emphasizes the value of the thorough operator training in the prevention of accidents.

Another fact apparent from such an experience is that an accident seldom results from a single event, but that a combination of failures and errors is necessary in most cases. This is because of the redundancy and diversity of design safety built in to most facilities. The use of the PHR to identify likely fault paths influence both design and operating philosophies so as to reduce the probability of undesirable combinations.

A. Raw Material Handling and Storage

1. Vinyl Chloride

The shipment of vinyl chloride is regulated by the Coast Guard (46CFR40.151) and the Department of Transportation (DOT) (49CFR172,-173). In addition, OSHA has specific rules for in-plant labeling of vinyl chloride containers (29CFR1910.1017), and requires that all shipping packages or containers of PVC carry a warning that PVC contains VC.

The principal method of shipment for vinyl chloride is by railcar, in Type 105A and 112J tankers, with capacity of up to 30,000 gallons. A few users are near enough to monomer suppliers to use pipeline transfer. Two suppliers can furnish

barge loads of monomer and one of these maintains a terminal in the Northeast from which tank truck or rail transhipments can be made. International shipments are made by specially equipped tankers.

Concern for the safe disposal of the contents of derailed tankers has led to the development of a technique to pierce the car shell with shaped explosive charges (276C,290H). The escaping material is then ignited. Leaking cars not already on fire also are ignited. This is a general rule for leaking vessels in which the leak cannot be stopped. The danger of an explosive vapor cloud is far greater than that of the combustion products, and point source flames should never be extinguished unless the source can be stopped. Reports of some recent transportation accidents involving VC can be found in the references listed under 276C.

The Compressed Gas Association, Arlington, VA 22202 has developed a field repair kit that can be applied to leaks which have developed in the loading dome in valves or at welds. Two sizes are available which will fit most of the cars now in service.

The Department of Transportation has required that all new cars put in vinyl chloride service be equipped with spade couplers, head shields, and has set minimum body insulation and relief valve specifications. A schedule has been set for retrofitting of all existing cars (49FR3468). An analysis of rail accidents since this change has been required indicates that it has reduced sharply the severity of such incidents (276D).

The Society of the Plastics Industries, New York, has organized a mutual assistance program between VC producers and users that can supply an Emergency Response Team for assistance from nearby participants in case of a transportation emergency. This is coordinated through the CHEMTREC emergency number, (800)-424-9300, which should be the first contact point.

A principal source of information on the safe handling of VC is in the data manuals provided by the manufacturers. The National Fire Protection Association (NFPA) codes specify the electrical and fire protection standards which are recommended (277). Insurance carrier requirements and local building codes vary, but generally require as a minimum the standards of the American Society of Mechanical Engineers (ASME) for pressure vessel construction. Many of these factors were summarized (278) a few years ago, and the following discussion is drawn from this source.

Vinyl chloride is stable in the absence of oxygen, water, and light and may be handled safely in iron, steel, or stainless steel if those substances are excluded. The use of phenol or other inhibitors to stabilize against spontaneous polymerization of the pure monomer was stopped more than 15

years ago. Inhibitors are still used in recovery systems to prevent polymerization of the recycle monomer under conditions which favor peroxide formation.

Oxygen reacts readily with VC to form a variety of cyclic and linear peroxides by simple addition (279-83). These peroxides are shock sensitive, decompose violently on heating, and can initiate polymerization in either the monomer or the water phase (268). They can be a major safety hazard in any manufacturing system which involves water and has the possibility of the entrance of air and has caused serious damage in industrial accidents (283-4). The peroxide formation is accelerated by the presence of acids and aldehydes, but can be prevented by the presence of a base (234,283). Careful warming with 5-10% sodium hydroxide in water, or preferably methanol if polymer residues are present, is adequate for removal from process vessels.

The EPA standard establishes specific rules for vinyl chloride unloading and handling (40CFR61.60). These are in addition to the general unloading rules prescribed by the Department of Transportation in 49CFR174.67(i). Unloading systems must be designed to minimize the release of vinyl chloride when the lines are disconnected, and "slip gauges" no longer are allowed. Pumps must be equipped with double mechanical seals, or the equivalent. Rupture disks are required under the relief valves on storage tanks to prevent leakage through the valve.

Storage tanks should be provided with adequate deluge systems to protect against local or adjacent fires. Efficient deluge systems which provide an effective water curtain sometimes can help prevent the spread of a vapor cloud, or the flame from its ignition. Saturation of the air with moisture also reduces the ignitability of the vapor. Drainage area within a dike is recommended which is sufficient to allow any spillage to run away from under the tank. The relatively high heat of vaporization of VC will cause large liquid spills to pool for several hours, thus increasing the potential for heat damage from fire. Fireproofing of supporting steel is required by most authorities. Critical valves in liquid service should have firesafe seats and automatic closing devices. Relief valves should be designed for at least the capacity required by a pool fire. Redundant level control systems are desirable to prevent overfilling. Insulation and/or reflective coatings are recommended to reduce heat input. All piping sections which can be isolated by valves should be provided with protection from thermal expansion damage.

Earlier prohibitions against the use of brass or copper instruments or tubing were due to the concern for formation of copper acetylide from the acetylenic impurities in monomer made by the addition of hydrogen chloride to acetylene. This does not seem to be a problem with VC from the oxychlorination process.

Consideration of the ignition temperature and energy of vinyl chloride suggests that "spark-proof" tools are not necessary, and this practice no longer is customary (284A).

Small fires can be extinguished with carbon dioxide or carbon dioxide-generating solid extinguishers, but care should be taken for reignition of the flame if vapor remains in the area of hot surfaces. Larger flames should be allowed to burn if the source cannot be closed off. Water is not effective on liquid fires because it is heavier than VC, and, of course, freezes upon contact with the liquid, and only serves to vaporize the liquid faster. Air-supplied respirators should be used by fire fighters that will protect against both the carbon monoxide and hydrogen chloride that are produced. Water spray or curtains should be used to protect adjacent equipment, reduce the spread of the fire, and, to some degree, absorb the combustion gases (278A).

Conventional gas dispersion models of the kind used by the EPA for studying diffusion effects (278B) can be helpful in preparing rough estimates of the size and concentration of vapor clouds for relatively small VC releases, particularly when no pool of liquid is involved. These small releases do not cause significant changes in the density of the gas volume. However, large releases, and especially those which involve evaporation from liquid pools, should be estimated by use of dispersion models designed especially for heavy gases. It is necessary to consider the effects of changes in gas density and the cooling which result from such large releases (278C).

All equipment should be properly bonded into a common grounding system to prevent static accumulation. This is especially important in flanged equipment, rail or truck unloading systems, and polymer air conveying systems. Continuity of the grounding system should be checked on a regular basis.

It should be noted that there are no cartridge-type respirators available for VC service which have effective end-of-service indicators. Therefore, as a general rule such respirators should not be reused and should be reserved for short-term service where the VC concentration is known to be low. Airline pressure-type respirators are used more widely than other types for this reason. All respirator programs must comply with OSHA regulation 29CFR1910.134.

2. Vinyl Acetate

Stainless steel construction should be used for storage and handling of vinyl acetate because of corrosion from the acetic acid potentially present from hydrolysis. Innibition with a few ppm of hydroquinone or an equivalent still is practiced. The flammability of the vapors requires exclusion of air in the headspace, and nitrogen padding is a usual practice. In

addition, fill and recycle lines should return to the bottom of the tank, and not generate a spray in the vessel. Hydrocarbon emission rules vary with the locality, but some type of emission control is required by most authorities. Coast Guard and DOT rules apply to shipping, and EPA spill control rules apply to storage.

3. DCE and TCE

Carbon steel equipment is satisfactory for dry pure material; stainless steel is needed for wet or recycle streams. The same general type of rules for vinyl acetate applies to transportation, emission controls, and storage. Aluminum is not a satisfactory material of construction.

4. Initiators

The search for greater productivity in the polymerization cycle has led to the use of more reactive peroxide initiators. Most of those in use now require storage well below ambient temperature. The oxygen content of these materials is such that they often need little external oxygen for combustion. This reactivity has led to the classification of initiators by their self-accelerating decomposition temperature (SADT), the temperature at which the decomposition is self-sustaining and becomes violent, usually with self-ignition (285). Table 7 presents the SADT and recommended storage temperatures for several commonly used materials (286-7). Dilution with inert solvents or making a suspension of the initiator in water decreases the danger of handling these materials, while storing in a reduced oxygen atmosphere lessens the danger of fire.

The most commonly used storage method is in commercial top-opening freezers which have been adapted to reduce the ignition hazard from the light and thermostat. These usually are arranged in an open shed with fire-resistant partitions between each unit and remote internal temperature alarms.

General safety rules for the use of initiators include:

- Mark each type of initiator with a distinctive label and store only one type in each location.
- Remove only enough for immediate use from storage and keep it at the proper temperature on the operating floor.
- Try to arrange the packaging so that only full shipping containers are used. Use extreme care in dividing packages, especially those which are solid at storage temperature.
- Use only clean, dedicated containers if an intermediate container is necessary.

Table 7

SADT and Recommended Storage Temperatures
for Typical PVC Initiators

| Name | SADT, °F | Recommended Storage Temperature, °F |
|---|---|---|
| t-Butyl Peroxypivalate | 80 | 40 |
| t-Butyl Peroxyneodecanate (pure) | 65 | 0 |
| 75% solution | 75 | 32 |
| bis (2-Ethylhexyl) Peroxydicarbonate | 34 | 0 |
| di-n-Propyl Peroxydicarbonate | 20 | -10 |
| di-iso-Propyl Peroxydicarbonate | 30 | 0 |
| alpha-Cumyl Peroxyneo-decanoate, 75% | 59 | 0 |
| Azobisisobutyronitrile | >70 | 60 |
| Lauroyl Peroxide | 123 | 80 |

- Never return material to a shipping container.
- Remove empty containers promptly and dispose of separately, not with other trash.
- Use proper protective clothing.

The most critical period in initiator handling is when the proper charge for a batch has been weighed and is placed into the charging device. Any delay in the batch, or leakage of vinyl chloride or other materials into the charge device, can initiate a violent reaction. Cooling of the charge device with a jacket or by addition of cold water can be of some assistance, but only if the SADT is above 32°F.

Decomposition is catalyzed by any organic reducing substance and many metal ions such as iron. Thus dust, rust, concrete, and many such common contaminants have caused problems. Leaking containers may be the single most prevalent problem, and care should be taken to see that all containers are stored upright and that the caps are tight. Any spilled material should be absorbed in an inert solid such as vermiculite and destroyed immediately.

Manufacturers provide proper disposal directions for each product (287), but in the absence of specific instructions the material can be added cautiously to glowing charcoal embers in a ditch or hole at a safe distance from any flammable material.

B. Monomer Production

In addition to the general hazards of handling, storing, and shipping large quantities of VC, the production plant must deal with a potential explosive mixture in the oxychlorination reactor. Flow control failure for any of the three major streams ethylene, hydrogen chloride, or air (oxygen) can produce a reaction mixture in the explosive range (287A). In addition to being a necessary reactant, the hydrogen chloride serves to dilute the oxygen content of the mixture below the explosive range. Therefore, considerable effort must be made to assure that flammable concentrations cannot occur.

Another hazard is the danger of overheating the reaction vessel by loss of the cooling system flow or excessive rates of reaction. This is particularly true when fresh, active catalyst is in use, and is a greater problem for fixed tube reactors than for fluid beds.

C. Polymerization

The major safety and health hazards in the polymerization section have been from the danger of uncontrolled reactions and the exposure to vinyl chloride, especially from reactor cleaning. Methods to control these hazards and others are discussed in this section. An

EPA report is available which presents the results of a brief industry survey by a contractor concerning some of the causes of emergency releases (248), one of the contributors to safety problems in this area.

1. Reactor Control

The heat of polymerization of vinyl chloride is about 660 Btu/lb (Table 1) and this heat is not released uniformly during the batch unless special initiator blends are used. The heat release tends to be less at the beginning of the cycle, and accelerates until just before the pressure drop begins in the case of homopolymers (282). There is a tendency to design the reactor batch charge so that there is a small but adequate margin of control left at the time of the peak exotherm. However, because all of the batch is charged at the beginning, there is no easy method for making adjustments during the cycle for unforeseen conditions.

The standard method of temperature control is to add cooled water to the jacket circulation system. The heat transfer values of a clean system (Q value) range from 50 to 110, with the lower figure obtained with glassed steel, and the higher with polished stainless steel. The value decreases during the cycle as the viscosity of the batch increases (234), and also can be decreased drastically by fouling on either the water or process sides. If that should happen unexpectedly during a batch, or if the cooling water supply or the agitation is lost, a runaway batch can result.

Control of a runaway batch depends on the successful removal of the heat of polymerization. This can be done by several means such as additional cooling, addition of a chemical to stop the polymerization, removal of the unreacted monomer, or in the last resort, relief of the pressure by manual venting or by activation of the pressure relief devices.

Most facilities use mechanical pressure relief valves on reactors and VC storage and handling vessels, preceded by a rupture disk, as is required by the EPA standard. A few facilities, however, use only rupture discs, usually two in series, as the protective device on reactors. Mass polymerization systems must use rupture disks rather than relief valves.

There are no really satisfactory means of calculating the required venting area of a polymerizing system. Theoretical calculations have been made (288-90), but the situation is complicated severely by the mixed flow regime which occurs, the plugging tendency of the spongy, partially polymerized mass, and the fact that the rate of increase of the reaction with temperature is a function of the slope of the initiator half-life. Neither the amount of initiator left at a particular point nor the slope of the decomposition rate at very high temperatures is known with any degree of certainty.

This has resulted in an empirical approach to relief valve sizing. Nozzles on which the relief valves are placed range from 4 in. on the smaller vessels up to about 4,000 gals. to as much as 16-18 in. on 25,000 gal. reactors. Relief valve sizes range from a single 4 x 6 in. valve on the smaller reactors to multiple 8 x 12 in. valves on the larger sizes.

This appears to have been a satisfactory approach, for there are no known reports of reactors having exploded because of relief capacity design. One case is known where a reactor exploded after an enormous overcharge of initiator, perhaps as much as 30 times normal, was pumped in as the result of an instrument failure, but this can hardly be ascribed to the relief valve design. Also, there are anecdotal reports of one glass-lined reactor having been stretched sufficiently to spall off much of the lining, but not failing. The size of the relief system for that reactor is not reported.

The American Institute of Chemical Engineers has formed a Design Institute for Emergency Relief Systems which has been working for several years to improve the design basis for relief systems. The results of this effort are expected to be released in 1985 (290A).

Installation of a rupture disc below a relief valve requires reduction of the valve capacity to 80% of its original rating, unless that specific combination has been tested for capacity. There must be a pressure gauge, vent, or other suitable telltale device between the valve and disk to indicate if the disc has leaked pressure into the volume under the valve (290B). Many other factors also must be considered in rupture disk design and installation, and final choices of materials and type should be made only after consultation with suppliers (290C).

Both redundancy and diversity in control instruments are used to assure proper information on the internal temperature of the reactor. Dual temperature probes plus at least one pressure check are the most common forms.

Reflux condensers can be used on some types of processes. These can offer a significant reserve cooling capacity, and often are connected to the emergency cooling circuit that is activated by high temperature or pressure alarms on the reactor.

One company has described an emergency monomer removal-cooling system which connects the reactor to a large external condenser and tank. In the case of an emergency the monomer is then condensed outside of the reactor, both cooling the reactor and removing the source of any further heat. This has been used successfully on reactors up to 50,000 gallon capacity (290D).

Agitation failure usually results in a relief valve discharge because of the reduced heat transfer in an unagitated vessel. Current flow or torque monitors can be used to confirm proper agitator action, but greater assurance results from detectors which measure the rotation of the agitator shaft itself. Routine vibration measurements and visual inspection of the drive motor, gear box, coupling, and seal are important preventative maintenance items.

A polymerization inhibitor (short-stop) is effective in controlling or slowing overheated batches if enough is added before the reactor is truly out of control, and there is adequate agitation to assure good mixing. Organic monomers which do not copolymerize well with vinyl chloride, such as butadiene, styrene, or alpha-methyl styrene, have been used, as well as straight inhibitors such as phenol, t-butyl catechol or similar substances. Sodium nitrite is effective if the pH is low enough to assure formation of nitrogen oxides from decomposition of the nitrous acid. This requires a pH of about 5 or below. Nitrogen or steam sparging through the bottom valve can sometimes supply the needed mixing action if the agitator is not operating, and if sufficient monomer venting rates cannot be achieved.

Short-stop addition systems should have a means of injection that is independent of the plant utility systems. A dedicated nitrogen pressure system or manual charge pot systems can be used. All nozzles on the reactor head should be inspected frequently to be sure that they are not plugged with polymer. This is especially true, of course, for those leading to the emergency relief and short-stop systems.

Where there is room in the reactor, such as near the end of a batch, the injection of cold water sometimes can provide sufficient time for other systems to overcome an incipient runaway reaction.

The EPA has accepted manual venting to the atmosphere as a last resort step to avoid the usually irreversible action of the relief valve system [40CFR61.64(a)(3)]. Venting to the recovery system, flare, or a gasholder may be helpful in marginal cases, but great care should be taken that foam and polymer are not carried over and plug the system.

It is not feasible to build a gasholder large enough to hold all of the vapor from a large reactor, or more than one small reactor. Limitations on the rate of movement of the piston control the speed with which vapor can be added. Thus, gasholders are not to be considered emergency devices except to a limited extent. Improper attempts to control or delay emergency releases may cause more total release than if not used, if there is a general plantwide emergency.

Relief valve assemblies should be anchored firmly to resist the thrust which develops on activation. Tail pipes should be short, and if curved upward for better dispersal, a weep hole or easily removable plastic cap should be used to prevent ice blockage in the winter. An effective rain shield can be made from a short length of larger size pipe supported by standoffs on the tail pipe.

Insurance provisions and local codes establish relief valve inspection and test schedules, which should be no longer than one year, and after every activation.

Instrument failure during charging can result in overfilling of the reactor (or other vessels) and cause hydrostatic pressure on the rupture disk as the temperature increases. Level control instruments inside the reactor have not proven effective because of the fouling problems, and external devices such as radiation meters are not sufficiently sensitive or reliable. Diligent instrument maintenance, redundant metering, and visual inspection are the most reliable means of prevention for overfilling.

Premature rupture disk failure has been a problem in compliance with EPA rules (248). Fatigue from pressure-vacuum cycling during the batch or from vibration or swaying of the vent system, mechanical damage during installation, corrosion, and distortion by polymer formation are among the most frequent causes of this failure. Careful installation, frequent inspection, and routine replacement are necessary.

Insurance and corporate safety codes usually forbid manifolding of reactor relief valve discharge systems. On the few occasions where this has been tried, it was abandoned quickly because of the near instantaneous plugging of the system. The greatest safety in the long run is obtained by rapid dispersion of any vapors released by a discharge. Other relief valves not in polymer service may, however, be manifolded to flares or other abatement devices (248).

A survey of the major accidents involving the production and polymerization of VC is presented in Table 8. This table does not include transportation accidents, for none of those have been reported to have caused any loss of life, nor major property damage beyond the accident scene. Also not included are VC releases which did not result in serious injury or major damage. Two recent events of major proportion which did not cause loss of life are described in references 290H and I.

2. Worker Exposure

Plant design, process procedures, work practices, surveillance equipment, and personal protective devices all play a part in reducing worker exposures to potentially harmful concentrations of vapors. These methods all are interwoven with the efforts to protect the workers and equipment from fire and explosion.

## Table 8

### Major Vinyl Chloride Accidents

| Year | Place | Cause | Result |
|---|---|---|---|
| 1955 | Mass. | Broken gauge glass on a storage tank, ignited by nearby boiler. | Major plant damage |
| 1964 | Conn. | Attempts to tighten a reactor sight glass while under pressure. Failed. Ignited by nearly extruder operation. | 7 killed, 22 injured. Plant destroyed. |
| 1966 | N. Jersey | Operator opened wrong reactor bottom valve, discharging contents where handle failed. Ignited by static or other source. | 1 killed. Plant destroyed. |
| 1967 | Louisiana | Pump failure. Ignition course unknown. | $830,000 damage |
| 1968 | Rhode Island | Manway gasket failed. Ignited by static? | Extensive reactor damage from falling roof members. |
| 1970? | Japan | Discharged contents of wrong reactor. | 4 killed, 8 injured in plant, 2 outside. Major structural damage. |
| 1970 | Delaware | Head gasket failed. Ignited by nearby gas-fired drier. | 1 killed. Instrument and control systems destroyed by fire. |
| 1973 | Germany | Thermowell failure in bulk reactor. Ignited in the recovery section. | 5 killed outside structure by flame front. Plant badly damaged. |
| 1973 | Japan | Broken valve yoke | unknown |
| 1974 | New Jersey | Manway not secured properly, ignition from static discharge. | Several weeks production lost from wiring damage. |
| 1977 | Texas | Initiator overcharge to buik reactor due to instrument failure. | 1 killed, 1 injured. Plant destroyed. |

Table 8

(continued)

| Year | Place | Cause | Result |
|---|---|---|---|
| 1977 | Mexico | Workman serviced valve on storage tank improperly, discharged contents, ignited at adjacent plant. | 1 killed, 3 injured, major damage. |
| 1978 | Germany | Buildup of peroxides in recovery system exploded during steam purging. | Major equipment damage |
| 1980 | Mass. | Operator opened wrong bottom valve, discharged fresh batch. Vapor cloud ignited above ground level. | 2 injured, damage over $1 million. |
| 1980 | California | Use of improper valve type allowed a bottom valve to remain partially open. Ignition at nearby switch box. | Major damage |
| 1981 | Canada | Buildup of vapor in a sewer line entered laboratory building. | 5 injured. Destroyed laboratory and control room. |

The production and polymerization of vinyl chloride are, of course, closed processes. Outdoor-type construction is used to the greatest extent possible, but the severe winters of 1979, 1980, and 1983 illustrated the limits to this feature, with even facilities in the Gulf Region suffering damage and production interruptions. Area and local ventilation are used for those parts of the plant which must be enclosed.

Reactor cleaning operations were associated with most of the AOL and ASL cases, and thus this procedure has been limited sharply. Additional impetus came from the introduction of large polymerization vessels, which are not practical to clean by hand. Antifouling treatments (291-2), solvent cleaning procedures (293), and improved suspension recipes have allowed closed reactor operation for many polymerization cycles. High-pressure water cleaning is a useful supplementary tool, and massive buildups can be loosened by dynamiting rather than by hand cutting as in the past.

The development of effective spray rinse valves has assisted in reducing worker exposure by reducing the frequency of reactor opening for inspection and cleaning (293A). These valves can be used to improve the efficiency of application of antifouling agents or rinsing solutions, and for better distribution of short-stop solutions.

When vessel entry is necessary, careful adherence to detailed vessel entry and lockout procedures, the use of mechanical or human standby systems, the wearing of a proper safety harness, forced ventilation of the vessel, and proper monitoring of vapors and oxygen concentrations can help insure the safety of the worker. The OSHA regulation for VC requires the use of respirators and protective clothing and prescribes the type to be worn under various circumstances such as monomer loading/unloading or mechanical repairs, as well as vessel entry.

Extensive stripping of the unreacted monomer from the polymer slurry has made a major contribution to reduced worker exposure. Emissions from the slurry vessels, centrifuge raffinate, and dryer outlets are controlled to less than 10 ppm by the EPA standard, either by direct emission controls, or by stripping of the slurry before transfer to these systems. This is an example where an expenditure for EPA rules has assisted in meeting the OSHA standard. Another example is the requirement for pressurized double mechanical seals on pumps, compressors, and agitators.

The OSHA requirement for an area monitoring system to warn operators of concentrations requiring the use of respirators was adopted by the EPA as a leak detection device. Overall correlation between area concentrations and personnel exposure can be shown if adequate attention is put on a time-motion study, but short-term conformance is poor (234, 293B). It has been observed that mechanics and senior operators - foremen

A major reason for the trend toward rising computer-controlled large reactor operations is the increased safety which comes from fewer units, and thus fewer connections and fewer systems to control. This improvement has been realized, but brings with it some hazards of its own. It has added another level of interface, and it requires a higher level of technical sophistication for maintenance. In addition, if total reliance is placed on electronic systems, manual recovery from disaster conditions is lost. It is normal to install sufficient analog systems to allow at least an orderly shutdown in case of necessity. Tunkel (322) has reviewed the design criteria to be considered in protecting vital equipment from blast damage.

Computers with dual, automatic switchover processing units have demonstrated on-line service of well over 99%. However, operators have reported rare, unexplainable "GREMLINS" that either cause loss of control or issue random uncontrollable signals. Thus, special attention should be paid to the computer installation and its maintenance program (323).

Careful attention should be paid to the failure mode of critical valves not only for loss of operating power, but also for loss of operating signal. In addition to emergency analog control, the most critical valves should have an independent hardwired signal to the control room.

D. Stripping

Prior to 1974 unreacted monomer was recovered from the PVC batch on an optimized economical basis. The reaction mass was transferred from the reactor to a blowdown tank, or the pressure was reduced on the reactor by venting, at the point where conversion rates no longer justified utilization of reactor time, and further conversion was likely to reduce desirable properties of the resin such as porosity (282,294B). The slurry was then subjected to a short vacuum exposure (30 minutes-1 hour) at temperatures of 160-195°F, depending on the residual heat stability of the product. This procedure left upwards of 2% by weight of vinyl chloride dissolved in the resin. Much of this was lost during subsequent transfer and drying operations, but the finished product usually contained 1,000-2,000 ppm of VC at the time of shipment (294C).

The EPA standard set a limit of 400 ppm VC in suspension resin (2,000 ppm for emulsion products) at the time the slurry was released from a closed system as an alternative to placing abatement controls on the VC in the dryer discharge air stream. The time to achieve this level by the conventional means is excessive, and puts the resin through a harmful heat history, resulting in yellowing.

Most producers of suspension resins have adopted some variation of a continuous stripping system in which the slurry is passed down a tray tower against a countercurrent stream of steam. Short residence time at elevated temperature and good agitation results in lower final VC content, and less heat stress than did the older method (294D).

General purpose resins of average porosity generally exit the column at a few ppm residual VC, which is reduced to well under 5 ppm by time of shipment. Lower molecular weight resins, which generally have lower porosity, give somewhat higher figures, and very low molecular weight resins (bottle grade) and copolymers have difficulty meeting this standard on a 100% basis, although the long-term average is well within the requirement (248).

Emulsion resins are more difficult to strip because of their strong foaming tendency and sensitivity to coagulation with heat. A variety of falling film or spray devices have been developed which allow meeting the 2,000 ppm standard (294E). These and other less useful devices are discussed by Burgess (294F).

The theory of VC migration in PVC has been developed by several workers. The monomer is quite soluble in the polymer, although the contrary is not true. The final solubility depends on the pressure and the temperature, and the rate of equilibration is a function of temperature, particle size, and morphology (294G). The rate is diffusion-controlled, and can be described by classical thermodynamic equations (294C,H). Diffusion rate is more important than temperature at higher concentrations, but temperature is the controlling parameter for the final interphase partition coefficient (294I). There is a discontinuity in the controlling constants at the glass transition temperature (Tg) of the resin (294C,J), and above this temperature the rate of diffusion increases sharply.

In practical terms, these basic data show that stripping consists of movement of the monomer molecule through the body of the resin and across the solid/liquid or solid/gas interface, through the pores of the resin into the larger body of the suspending water, through the water to the liquid/gas interface, and eventually out of the vessel. Any condition which can shorten or speed this movement assists in the stripping rate. Smaller particle size, greater porosity, absence of a pericellular membrane on the resin, good agitation, and temperatures above the Tg all assist the progress of the monomer. Lack of porosity and especially the presence of glassy beads or gels hinder the rate greatly, and even a small amount of such particles can prevent proper stripping. Low molecular weight resins tend to be less porous, and this offsets any advantage of the greater mobility that might be expected within shorter molecules.

Application of these concepts has resulted in successful equipment design for the stripping step, and allows prediction of the migration of monomer under many conditions (294K,L). The latter reference contains a procedure for estimating the potential exposure to workers in warehouses and other storage areas, for example.

Even further reduction in residual monomer can be achieved by applying these principles in the processing and compounding steps also (294M), and levels can be obtained which near the limits of detection. It has been proposed on both theoretical and experimental bases that a residual level can be reached beyond which no further diffusion will occur (294N,O).

Each mechanical stage of air transfer, unloading, or processing represents a disturbance of the established equilibrium between the dissolved VC in the polymer and its surroundings, and thus will cause some release of VC, and the beginning of a faster rate of release of the monomer until equilibrium is reestablished. Therefore, caution should be exercised in opening and entering railcars, storage silos, or other closed storage areas unless it has been established that the free space is below the allowable concentration. Even moderate ventilation will assure that this has been achieved.

E. Downstream Operations

The PVC process changes from a pressurized batch operation to a generally open, continuous system after the blowdown/stripping step, and the safety hazards change to those related to material handling procedures.

The exception to this generalization is in the monomer recovery section, which is of necessity closed, and is pressurized after the compressors. Partial vacuum can occur upstream of the compressors in the blowdown/stripping section, and provides the opportunity for air to enter the system. The oxygen can react with vinyl chloride and other olefins at the temperatures encountered in the compressor to produce peroxides, as discussed above. These peroxides can cause extensive fouling and plugging of the recovery system, and are shock sensitive. Dilute caustic can be used to control the formation or to remove these products. However, careful maintenance to prevent leaks in vacuum lines, together with proper inhibitors and pH control, can prevent their formation.

Entry and cleaning of blowdown tanks, stripper vessels or towers, and recovered monomer tanks present the same potential hazards as does reactor cleaning and the same precautions should be observed. There are anecdotal reports of workers being asphyxiated by the inert atmospheres which may be maintained in these vessels. Thorough work entry procedures, including oxygen monitoring, and the use of color-coded air and nitrogen hoses with noninterchangeable fittings can reduce these dangers.

The more thorough stripping required by the EPA standard and by commercial considerations has reduced greatly the exposure to VC which occurred in the past in this section of the plant. Many of the manufacturers have found that the drying and shipping areas can be deregulated under the OSHA standard. Fabricators and processors generally find their operations are below the action level for the OSHA standard if they have even rudimentary ventilation systems.

The "half-life" of residual VC in bagged resin is about one week, so there is some possibility of exposure in large unventilated warehouses for bagged resin. Bulk storage presents a higher probability of monomer accumulation in the air space, so that silos and bulk cars should be ventilated and tested before entry.

This extended stripping has caused an additional hazard, however. The higher operating temperature at longer times has accelerated the formation of hydrogen chloride in the slurry, which has resulted in accelerated chloride-induced stress corrosion near the welds in stainless steel equipment. This appears to be caused by chromium depletion in areas near carbide precipitates, and is especially pronounced at pH below 5 (294P). Cracking has been seen in reactors, especially those also used for stripping, and particularly near nozzles which may have some polymer deposition, in blowdown tanks, continuous stripping towers on the trays and support rings, and occasionally on centrifuge scrolls.

Routine removal of polymer deposits, additional buffering of the treated slurry to avoid the autoacceleration of decomposition by acid, and avoidance of excessive localized temperatures can help alleviate this situation. Clad vessels will be less prone to catastrophic disintegration than will solid stainless vessels. The use of proper grades of construction materials, such as low-carbon 316 stainless steel or high nickel alloys (295), and careful adherence to good welding practices also are of assistance. Dye tests of suspect areas sometimes can reveal the problem before it becomes a serious threat to safety.

Dust exposure is a common problem in the bagging and shipping areas, more so with the fine emulsion and dispersion resins than with the coarser suspension resins (296). Also, the problem exists more with the total dust levels than with the respirable fraction. Operators are reluctant to wear respirators or masks in these work areas because of the greater exertion necessary, and the higher ambient temperatures often are encountered, so careful equipment design and good local ventilation are required.

Slips and falls from bulk cars and trucks can be a hazard, especially in wet or icy weather. Safety harnesses have been designed for this purpose, and access platforms can be provided to avoid much of the climbing that would otherwise be necessary.

Strong static charges can develop during the air conveying of PVC, especially during dry, cool weather. Static discharge in a conveying system is suspected as being the source of ignition for at least one major explosion following a vinyl chloride release. Various methods have been tried to prevent or dissipate this static buildup, but the most effective seems to be controlled humidification of the conveying air.

V. Waste Streams

A. Water

The EPA standard requires that water streams which have been in contact with vinyl chloride be stripped to below 10 ppm before they are released or mixed with other streams. This is because vinyl chloride degasses readily from water at atmospheric pressure, and would therefore become an air contaminant. It has been observed

that in the past the centrifuge waste streams provided a significant contribution to worker exposure if they were transported in open trenches. This is no longer true for slurries which are stripped in accordance with EPA rules.

All of the substances discussed here undergo biodegradation or removal in biological effluent treatment systems (262,297-301). Somewhat surprisingly, one EPA report states that EDC is said to be removed more readily in some cases by air stripping than by biodegradation in comparison to the other substances (301A). Another EPA report (301B) states that EDC is relatively difficult to air strip, and that performance can be predicted by the Henry's Law constant of the substances. The values stated are 180 for VC, 0.5 for TCE, and less than 0.1 for EDC. The data of Dilling and of Roberts and Dandlicker (269) suggest that all these substances should air strip easily. However, all of these substances showed ready biodegradation in activated sludges, as they did in 24-hr. batch tests (301C).

Air stripping and steam stripping are reported to be economically viable alternatives to biodegradation. The EPA has calculated that six theoretical trays are required to reduce EDC to 50 ppb from a saturated feed when using reflux, while only four are needed for TCE or VC (301A). Without reflux eight trays gave the same results for EDC and required 5g steam per kg of feed. Under the same conditions, TCE needed seven trays and 3g/kg of steam, and VC only six trays and 2g/kg, to obtain 100% efficiency.

This same document gave examples of activated carbon removal efficiencies of 99% for TCE from very dilute streams, but did not show examples of the application of this technology to the other substances.

The Dade County water system found air stripping to be effective in removing VC from contaminated groundwater (274G).

A recent paper by Zhu, et al. (301D), describes a pervaporation technique for removal of EDC and other chlorinated hydrocarbons from dilute aqueous solution by permeation through a polymeric membrane against a vacuum. The organic solutes permeate preferentially and may be collected in a concentrated form.

Some success has been seen in reuse of wastewater, especially as makeup to cooling towers, provided that adequate filtration of residual solids is performed. There has been limited success in reuse of centrate in the polymerization batch because of potential cross-contamination by residual suspending agents. It has been shown to be feasible in pilot runs, however, and could be possible in a single-product plant. Very thorough filtration is necessary, and a blowdown stream may be required to purge dissolved salts (234,298).

B. Liquids and Gases

There are few nonaqueous liquid streams from polymer production, but still bottoms and by-products are formed in monomer production. These can be incinerated, provided that the chlorine formation is minimized by careful combustion air control and the hydrogen chloride is removed from the stack gas. Processes have been developed for redistillation or catalytic decomposition of these substances which permits substantial recovery of the chlorine values (302-4). The EPA has listed the liquid wastes from the production of VC and EDC as hazardous wastes, which will restrict the disposal of these by-products to RCRA-permitted facilities.

The EPA also classifies spent TCE from degreasing operations, and bottoms from TCE manufacture, as hazardous wastes (40CFR261.31 and .32). The commercial substances vinyl chloride, EDC, and TCE are themselves hazardous wastes (40CFR261.33) and may not be discarded without following RCRA regulations.

Incineration has become the process of choice for abatement of the collected vent and purge gases from polymerization operations. Carbon absorption processes have been developed which recapture the vinyl chloride, but various operating problems have prevented widespread adoption of this process. One problem with copolymer operations is the difficulty experienced with desorbing the vinyl acetate. In addition, there is a need for a purge stream to remove the nonreactive methyl chloride from the recycle stream (304A). This occurs in monomer at 25-75 ppm, but as it is concentrated about tenfold each cycle, it can soon build up to an unacceptable level as an inert diluent. It is necessary to have a small incinerator to destroy the purge stream containing this contaminant, and economics often do not justify any additional equipment.

Incinerators must be equipped with scrubbers to meet local and federal limits on hydrogen chloride and particulates (47FR27520). Incinerator design is based on the requirement for less than 10 ppm in the stack gas; actual performance is much better, with concentrations usually below 1 ppm. Vinyl chloride is readily combustible, and the calculated combustion chamber temperature for 99.99% destruction at 1 sec. residence time is 1371°F (305). Vinyl acetate requires a temperature of 1223°F under the same conditions.

Studies have shown (305A,B) that flares and industrial boilers can give greater than 99% destruction of organic wastes, but the EPA will not permit these to be used for routine removal of hazardous air pollutants without further demonstration of their efficiency.

C. Solids

Polyvinyl chloride is biologically inert, and is suitable for disposal in any properly maintained landfill. There was a statement by the EPA (45FR33118, May 19, 1980) that it intended to promulgate RCRA rules for "batch residues from the batch polymerization of chlorinated polymers" but no further action has been taken.

Presumably, this was to have been done because of reports that vinyl chloride had been detected in very low concentration around some pre-1975 landfills. Current operating procedures preclude the probability that any significant amount of vinyl chloride will find its way to a landfill.

Water from the centrifuge in suspension processes contains a small amount of fine polymer. This settles rapidly in clarifiers or sedimentation ponds. In fact, it is a good substrate on which other suspended materials gather. Together with the larger particles resulting from the cleanup of spills and from washdown operations, this material, or sludges in which it may be present, may be disposed of in any convenient fashion.

Solids recovered from solvent cleaning operations are free of vinyl chloride and thus also are not restricted for disposal.

The only problem concerns large unstripped particles, such as those from "BB" batches, filters ahead of the stripper, and equipment cleaning. These are not now regulated by RCRA, but prudence would dictate that the residual monomer content should be reduced to prevent either employee or environmental exposure. This can best be done by weathering in some isolated locale.

Solid PVC wastes can be incinerated if mixed with an adequate quantity of a combustible material. There is little reason to do this, except for the disposal of used consumer items. The generation of hydrogen chloride from household trash containing PVC articles has been a matter of controversy in the past, but several studies have shown that the present consumption rates of PVC in consumer goods add little to the normal chloride content of wastes (306-7).

## VI. Analytical Methods

The EPA prescribes the analytical methods 106 and 107 of 40CFR61, Appendix B, for the analysis of gases and of water or solids, respectively. Method 106 uses a 2 m. Chromosorb 102 chromatographic column followed by a flame ionizing detector to analyze an integrated gas bag sample. A secondary column of Chromosorb B is required if acetaldehyde is present. The method is said to have an absolute sensitivity of 1-4 x $10^{-7}$ mg. of vinyl chloride. Collaborative tests indicate that the repeatability is about ±1 ppm at 10 ppm concentrations and ±10 ppm at 50 ppm (308).

Method 107 uses the headspace method (309), in which an equilibrium is established in the free space above the sample in a vial, and an aliquot is injected onto a 2 m. column of Carbowax 1500 on Carbopak A. Poropak Q is used if methanol or acetaldehyde are present. This is stated to have the same absolute sensitivity as method 106. Equipment is available which performs the entire analysis automatically once the sample vials are filled (309A).

Revisions to test methods 106 and 107 were published at 47FR39168, September 7, 1982 and 47FR39485, September 8, 1982, which permit alternate columns to be used, and impose certain quality assurance requirements.

OSHA requires that an analytical method be used for personal monitoring that has a 95% confidence level of ±35% at 1 ppm of VC. A procedure generally based on NIOSH Methods 127 and 178 has come into broad use for this application. Air is drawn over granular carbon at a known rate for a known time. The carbon is extracted with carbon disulfide and an aliquot is analyzed by gas chromatography (310). A variation on this procedure involves the use of other commercial absorbents (Tenax or Spherocarb) and/or desorption by heat rather than by a solvent (311). These procedures have been developed so that under ideal conditions they are capable of detecting as little as 0.2 ppb, (312) but under average field conditions are reliable at about 10 ppb (41FR46560).

Instrumental procedures such as infrared or ultraviolet absorption, or decomposition of the vinyl chloride followed by measurement of water conductance caused by those products, have been used in the past (276). These are limited generally to the ppm range, and are not as versatile or portable as the carbon tube or bag collection methods.

The absorption/desorption method also is applicable to a wide range of substances, and can be used to determine the concentration of many different substances from the same sample. Unless the constitutents are well known, it is necessary to use a combined GC/mass spectrometer to identify the peaks with certainty. This combination has been used to measure the ambient concentrations of vinyl chloride, trichloroethylene, ethylene dichloride, and many other substances in several areas of the country (260-1).

If this method is used for vinyl acetate analyses, special precautions must be taken to avoid hydrolysis or polymerization of the absorbed acetate. Kimble (313) has described a procedure which answers these requirements.

The EPA has developed "purge-and-trap" methods for determining trace constitutents in water which are useful to 0.2 µg/l, and claims a detection limit of 0.01 µg/l. The same problems of interference exist in this system or any chromatographic method (313A).

Several helpful manuals have been published describing practical application of the analytical procedure described above (314-17). Ref. 317 contains an extended discussion of interferences and alternate column packing.

Bromination of VC in water samples, followed by extraction into hexane and analysis with an electron capture chromatograph, is reported to have a limit of detection of 0.3 µg/l, or 0.3 ppb. This method has been used to analyze surface and drinking water supplies (317A).

Portable vapor detectors have come into general use as "leak detectors". They are used in conjunction with the fixed-point or area detectors for vinyl chloride, which are required by the OSHA standard, to locate the sources of excursions, and they are used for patrolling areas outside the area detector coverage. The EPA has promulgated a requirement that all new "volatile organics" processing facilities use these as a part of an emission control program (40CFR60, Appendix A, Method 21), thus extending their application to all of the substances discussed in this chapter. These may have short chromatographic columns attached to provide some selectivity for various materials, but most often they are used in the nonselective mode as simple combustible vapor detectors. They have a wide range of sensitivity for different substances, and usually come calibrated for methane. The EPA has published tables of response factors for other compounds (318). Numerous problems have been described in the actual field use of these instruments (319) and they are not suitable for precise work, but they are a useful adjunct to a leak detection and preventative maintenance program.

One additional type of device has come into limited use in Great Britain as a fence-line monitor (320). Based on the reaction of vinyl chloride with potassium permanganate-impregnated paper, it is not sensitive to concentrations much below 1 ppm, and is subject to a number of interferences. Similar limitations apply to the Drager tube procedure. For these reasons, these devices are not particularly valuable at present conditions.

Passive personal monitors have come into wider use because of the bulk of the electric pumps, and the cost of maintaining them in operation. These have exposed absorbent cartridges which can be "developed" and analyzed by a variety of means, and can sometimes be regenerated for reuse. The accuracy of such devices is adequate to meet regulatory needs (320A) for long-term samples, but generally do not have sufficiently rapid response times for 15-minute tests.

Experience has shown that process sampling and analysis of VC can result in high personnel exposure if adequate precautions are not taken (117). One of the European ASL cases is reported to have received his primary exposure as the result of sampling activity, by what must have been a very unsatisfactory procedure. Laboratory analysts must guard against inadvertent direct or indirect exposure, especially when conducting some of the evaporative tests on the monomer.

Sampling systems have been developed which use essentially closed piping loops (320B). A double-ended sample tank is placed in a bypass system at the sample point and a flow-through process allows purging and filling the container with a minimum of release. This procedure also disposes of the unused sample safely. The EPA requires that all VC samples be taken with a system equivalent to the one described.

## VII. Vinyl Acetate Copolymers

The manufacture of VC/VAc copolymers is more difficult than that of homopolymers, or of some other copolymers. This increased difficulty results in additional hazards not seen in other processes.

One spectacular hazard is that of agglomeration of the reactor charge, or a "set-up". This results from failure of the suspending system, and its effects are enhanced by the plasticizing effect of the unreacted VAc. The reacting mixture shrinks in volume (increases in density) as the polymerization progresses, and at the same time the unpolymerized monomers are enriched in VAc because of the relative reactivity ratios of the two monomers (321). The unreacted VAc swells and softens the precipitated PVC in each droplet, increasing the tendency toward agglomeration if the suspending system is not performing correctly. Set-ups occur very rarely in homopolymer systems, and usually occur in copolymer batches after the density of the organic phase has increased to more than one. This is well into the polymerization cycle, at about 60-75% conversion. Severe mechanical damage can occur to the agitator, shaft, baffle, and drive units. Release of VC is not usual, because of the relatively low amount of unreacted monomers at that stage.

The primary hazards result from the difficulty of removing the rubbery mass from the reactor in the presence of VC and VAc. The most satisfactory method appears to be to cook the mass under vacuum to remove as much monomer as possible, then reduce the mass to workable size by many small explosive charges (234). This has been found to be both quicker and safer than manual removal, and results in less damage to the equipment.

The residual unreacted VAc also causes problems in the stripping step because of its plasticizing action. Copolymer is inherently less heat stable than homopolymer, and the greater tendency to adhere to vessel walls adds to the probability of producing burned resin. This results in more potential worker exposure from cleaning operations.

The presence of VAc in the recovered monomer stream presents several potential hazards. Acetaldehyde, which is formed readily by hydrolysis, accelerates the formation of VC peroxides (234,283) and polymeric sludges in the recovery equipment. It usually is necessary to add more inhibitor in the recovery systems for copolymers and to maintain better control over the pH of the system in an attempt to control both the hydrolysis and peroxidation reactions and to reduce corrosion of the equipment. Limitation of the oxygen content of the recovery streams becomes more important, also. Careful design is necessary to avoid polymer buildup on instruments, relief valves, and outlet lines.

Liquid and solid waste problems increase with copolymer production. There will be increased BOD loads on the waste treatment system from the vinyl acetate and its hydrolysis products. Solid wastes increase and are more likely to have entrapped organic materials.

The recycle streams are more corrosive than those in homopolymer systems because of the presence of higher chloride levels and acetic acid. Type 316L stainless steel is recommended for use here, and attention should be given to prevention of corrosion at welds.

Thus, considerably more attention to design and proper operation of the reactor and recovery systems, in particular, are necessary in the manufacture of copolymers in order to offset the additional hazards present.

## VIII. Acknowledgement

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## IX. Glossary of Acronyms

| | | |
|---|---|---|
| ACGIH | - | American Conference of Government and Industrial Hygienists, Cincinnati, OH 45211 |
| ACL | - | Acroosteolysis |
| ASL | - | Angiosarcoma of the liver |
| ASME | - | American Society of Mechanical Engineers, New York |
| BATF | - | Bureau of Alcohol, Tax, and Firearms, a section of the Treasury Department |
| CDC | - | Center for Disease Control, a part of the Health, Education, and Welfare Department |
| CEFIC | - | European Council of Chemical Manufacturers' Federations |
| CERCLA | - | Comprehensive Environmental Responses, Compensation, and Liability Act of 1980 (Superfund) |
| CFR | - | Code of Federal Regulations, a compilation of promulgated rules. OSHA rules are in Chapter 29, those for the EPA in Chapter 40. |
| COC | - | Cleveland Open Cup, one method of testing for flammability |
| CPSC | - | Consumer Product Safety Commission |
| DOT | - | Department of Transportation |
| DNA | - | Deoxyribonucleic acid, the constituent of chromosomes |
| EDC | - | 1,2-dichloroethane |
| EPA | - | Environmental Protection Agency |
| FDA | - | Food and Drug Administration |
| FR | - | Federal Register. The official daily publication of the federal government. The number before the letters give the volume, the following numbers are the page. Volume 48 was published in 1983. |
| GGTP | - | gamma glutanyl transpepsidase - a liver enzyme |
| GGT | - | same as GGTP |
| IARC | - | International Agency for Research on Cancer, Lyon, France |
| IGC | - | Indocyanine Green Clearance - a test of liver function |

| | | |
|---|---|---|
| $LD_{50}$ | - | Lethal dose for 50% death of the experimental animals within 14 days |
| NAS | - | National Academy of Science |
| NFPA | - | Nation Fire Protection Association, Quincy, Massachusetts |
| NCI | - | National Cancer Institute |
| NIOSH | - | National Institute of Occupational Safety and Health |
| NSF | - | National Sanitation Foundation, Ann Arbor, Michigan |
| NTIS | - | National Technical Information Service, Springfield, VA 22161 |
| NTP | - | National Toxicology Program |
| OSHA | - | Occupational Safety and Health Administration |
| PB number | - | Document identification number used in ordering from NTIS |
| PHR | - | Process hazard review |
| ppb | - | Parts per billion. Units are per volume for gases, by weight for solids or liquids. |
| ppm | - | Parts per million. See ppb for units. |
| ppt | - | Parts per trillion. |
| PVC | - | Polyvinyl chloride, homo- or co-polymer |
| RCRA | - | Resource Conservation and Recovery Act |
| SADT | - | Self-accelerating decomposition temperature, at which peroxygen compounds decompose violently |
| TCE | - | Trichloroethylene |
| TLV | - | Threshold limit value - a guide to allowable exposure, set by the ACGIH |
| TWA | - | Time-weighted average of exposure to substances in air, usually for 8 hours |
| VAc | - | Vinyl acetate |
| VC | - | Vinyl chloride |

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