Richard Fleming Associates, Inc.

7661 Beryl Road
Zionsville, PA 18092

Phone (610) 966-2010
Fax (610) 966-2130

Invoice 95-1

Hanen, Alexander & Spalding
3850 Texas Commerce Tower
600 Travis
Houston, TX 77002

For services rendered from November 1994 through January 10, 1995 on behalf of Air Products in defense of allegations regarding vinyl chloride safety measures:

- Initial telephone interview with Harris and Hanen
- Search of personal files for pertinent material
- Submission of OSHA hearing testimony, June 1974, and two later speeches, with cover note
- Reading of complaints
- Preparation for and participation in meeting at APCI on 12/20 with Mr. Bruce Whitney
- Dinner meeting January 3
- Meeting at APCI January 4 with Whitney, Hansen, Harris et al

18 1/2 hours @ $225/hr =	$4,162.50
Out of Pocket Expenses	
• Auto mileage - 75 miles	22.50
• Two lunches	10.25
Total	$4,195.25

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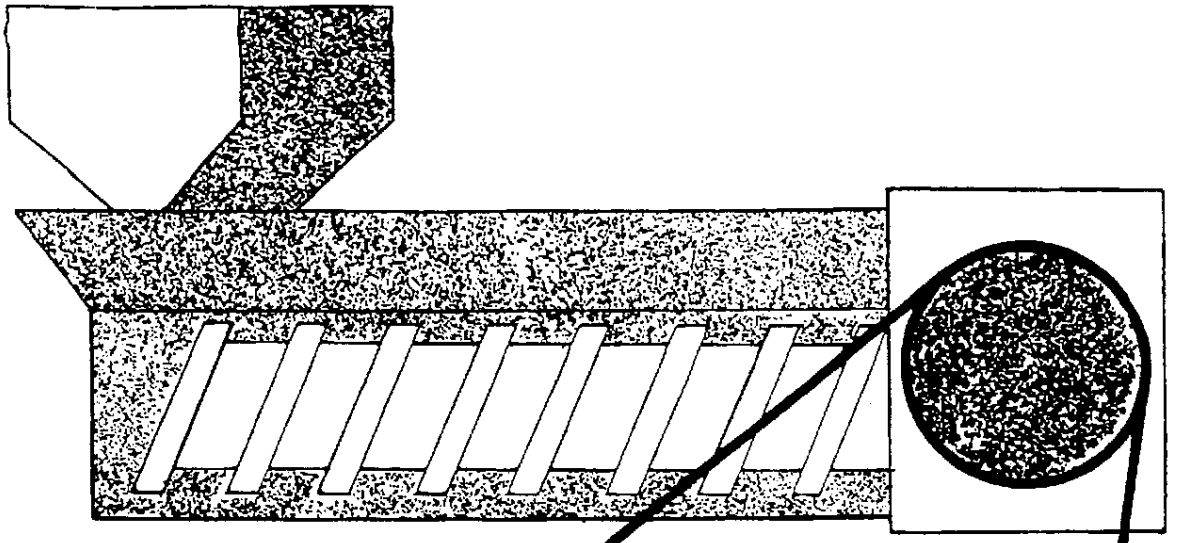

Encyclopedia of PVC

Second Edition,
Revised and Expanded

Volume 1:
Resin Manufacture and Properties

edited by
Leonard I. Nass
Charles A. Heiberger

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Second Edition, Revised and Expanded

Volume 1:
Resin Manufacture and Properties

edited by

LEONARD I. NASS
L. I. Nass Company
Warren, New Jersey

CHARLES A. HEIBERGER
Plastics Industry Consultant
Princeton, New Jersey

MARCEL DEKKER, INC. New York and Basel

Contents of Volume 1

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Safety and Environmental Concerns in Resin Manufacture

JOHN T. BARR

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

I. INTRODUCTION

Significant changes have occurred in polyvinyl chloride (PVC) manufacture in recent years because of developments in safety and environmental concerns in general and the concerns for vinyl chloride 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 1960s 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 Section 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 Section III. Similar regulatory actions have been enacted by many foreign governments. Extensive changes have been made in manufacturing practices and procedures to meet the challenge to reduce worker and environmental exposure, as well as because of technological advances. Some of these are presented in Section IV. Section 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 Section VII. A glossary of common acronyms is given in Section 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 paractices 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 1930s [1] and has been investigated by several workers [2-5]. Death occurs rapidly in animals at concentrations much above the anesthetic levels of 8 to 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.

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 at 57°F (Btu/lb)	158.4
Specific heat	
Liquid, 25°C (kcal/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 %	51.4
Vol %	33
Minimum oxygen content for ignition (%)	12
Flash point, open cup (°C)	-78
Autoignition temperature (°C)	472
Critical temperature (K)	431.4
Critical pressure (atm)	52.7
Critical density (g/cm^3)	0.370
Vapor cloud explosion yield (lb to yield the equivalent of 1 ton of TNT)	24,305
Vapor pressure (psia)	
-10°C	18
0°C	26
10°C	35
30°C	48
50°C	115
70°C	180

TABLE 1 (Continued)

Heat of combustion (kcal/mol)	2826
Latent heat (Btu/lb)	
0°C	147
50°C	126
Solubility in water, 30°C (wt %)	
Partial pressure	
0.5 atm	0.5
1.0 atm	1
Autogenous	2
Solubility of water in VC (%)	0.11

However, careful examination of liver effects in animals at 100 to 500 ppm for 4 to 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 Yale 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 to 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 [17], but the most reasonable figure seems to be either 1200 to 2000 ppm [18] or 500 to 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 to 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 to 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

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 (vol %)	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	100-1,000	100-1,000	10-100
Vapor pressure, 20°C (mmHg)	1,600	62	47	88
Solubility in water, 20°C (g/100 g)	1 (1 atm)	0.8	0.1	2.4

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 hr [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 hr/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. The 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 5000 ppm, 7 hr/day, 5 days/week for up to 1 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 has now become more closely associated with AOL than with 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 that 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 the USSR [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 significant 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 that had been exposed to VC for up to 25 years of 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 that include AOL or ASL disease. They find portal fibrosis and portal hypertension, thrombocytopenia, esophageal 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 Raynaud's disease, 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 United States. 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 reasons for predeliction to the disease in the four cases that 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 4777 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 et al. [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 gradation 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 effects observed 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 no definitive estimates have been 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 1600 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 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, p. 4-71] which showed that this reduced the residual content of the reactor vapor to 8000 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 3000 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 range of several thousand ppm. 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, sponsored by a group of European VC/PVC producers, used a 3% (30,000 ppm) concentration for 12 months. The attempt to cause AOL was not totally successful; instead, tumors developed at many sites,

especially in conjunction with the Zymbal gland, and in the lungs, skin, and bones. The Zymbal 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, 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 has 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 et al. [26] and Groth et al. [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 1964-1974 revealed 157 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 John Stafford of ICI, England [88]. His most recent compilation shows a total of 34 cases in the United States and 111 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 to 5, respectively.

The average latency period in the United States has been 25 years, but with a mode of about 22 years. The latency period in Europe, particularly in Germany, has been somewhat shorter. There is an unusual clustering of cases in relatively few plants (Table 4). All 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 is also 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 8384 men with at least 1 year of exposure before 1973 [91]. 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[a]

United States	34
West Germany	21
France	17
Canada	10
United Kingdom	9
Sweden	5
Yugoslavia	4
Italy	4
Czechoslovakia	2
Japan	2
Belgium	2
Norway	1
	111

[a]Includes 2 U.S. cases still alive.
Source: Adapted from Ref. 88.

Marsh [92a] followed 2490 workers who had been exposed for at least 1 year between 1949 and 1966 in a plastics-producing plant at 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].

TABLE 4 Angiosarcoma Cases in the United States by Company

Goodrich, Louisville, Ky.	14
Union Carbide, South Charleston, W. Va.	9
Goodyear, Niagara, N.Y.	4
Seven others	7
	34

TABLE 5 Chronology of U.S. Deaths from Angiosarcoma[a]

Year	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	3	1944, 1955, 1963
1984	1	1953
	32	

[a]Two cases living (first exposures 1954 and 1956).

Source: Data from Ref. 88.

Several studies have been conducted on smaller groups of workers which are also subjects of the larger study discussed above. Monson et al. [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 1151 workers who had at least 5 years of 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 show the transport of some metabolic intermediate from the hepatocyte to the adjacent sinusoidal lining to initiate the first stage of tumor development [87, 105-106]. 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 et al. [109] found no excess of mortality, including cancer, in British workers for 1948-1973, while following 2120 workers. Wagoner et al. [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 7000 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 et al. [32] reported on 1618 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 elevations 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 7736 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 et al. [30] studied 4341 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 107 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 that 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 who had lived the last 6 years of his life near a PVC plant and three cases where the men 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 that 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 compared to a similar nearby city. This difference was principally found in males aged 20 to 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 [127-128] 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 that was presumed to have been exposed to VC as children, but this project was not completed.

The disease ASL is difficult to diagnose [129-130], 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 [103-104], although the gammaglutamyl transpepsidase test is promising, together 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 an 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 [137-138]. 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 3000 to 30,000 ppm of VC for 6 hr/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 5000 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 to 15 at 50 to 2500 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 the animal tests.

Infante [146] has reported finding an excess of congeneital 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 defect was seen. In another [148], hospital records for Kanawha County, West Virginia, were reviewed for 1970-1974 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 et al. [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 et al. [160] explored the statistical power of the various studies on reproductive effects. They found that the Ohio birth defect study [146] was deficient in power, but that the negative CDC recheck [147-148] 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. Their 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 or 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 [161-162]. 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 hr for rats is 4000 ppm [163]. Humans experience eye irritation at 22 ppm. Rabbits suffer eye irritation from a 500-mg dose and skin irritation after 24 hr from 10 mg. Toxic effects in aquatic life are seen at 10 to 50 ppm in the standard 48 to 96 hr 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 responsible for this low threshold is responsible for the sharp odor around most acetate copolymer plants. This, together 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 5000 ppm in the drinking water for 3 months. This result was not seen at 1000 ppm or lower, and there were

no other hematological or histopathological effects. Inhalation exposure at 1000 ppm for 3 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 1500 ppm for 4 weeks.

The was no evidence in the same study for teratological effects in rats from up to 5000 ppm in the water during days 6 to 15 of gestation. Inhalation of 1000 ppm was slightly fetotoxic; lower levels were not. Metabolic conversion was found to be rapid, with most being expired as carbon dioxide within 2 hr 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 nonprotein 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 2500 ppm VAc in air for 1 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 1000 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 (2500 mg/liter, about a 100-g/kg lifetime dose) but no increase in neoplasms in the male high dose rats or in rats of either sex at 1000 mg/liter. 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. These studies should be complete in 1985.

The ACGIH quotes data showing no pathological effects at exposures as high 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 to 10 ppm, with excursions in the range 50 to 300 ppm, 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 [168-169] 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 focus 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 billary systems. The symptoms are related and thus are usually 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 2900 ppm. The LD_{50} in rats is 4920 mg/kg. Oral doses of 6 to 7 g/kg cause 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 [171-174]. Death often involves ventricular fibrilation. Deliberate misuse, as in glue sniffing, results in respiratory and cardiac failure in extreme cases and in liver and kidney damage in less extensive use [175-176].

Chronic low exposures (up to 200 or 300 ppm) cause tremors, loss of motor function, insomnia, and cardiac disturbances [177-178]. 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 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] or 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 range 15 to 20 ppm 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, together 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 mu-

tagenicity 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 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 [185-188]. It is of special 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 that 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 reference 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 doses, 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 that do not produce permanent organ damage [196]. A Committee of the National Academy of Science concluded that the low carcinogenic potency of TCE requires no special precautions 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 to 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 [201-202]. Skin absorption occurs readily and gives the same symptoms as inhalation or injection, in addition to the irritation effect of 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 [201-202]. Rats survive 200 to 300 ppm for 7 hr, but only 1 hr at 3000 ppm and 12 min 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 2000 ppm. The slightly sweet, typical chlorinated solvent odor at 100 to 200 ppm becomes unpleasant for most persons at 1000 to 2000 ppm and can cause drowsiness at 2000 ppm in as little as 5 min. Heparin has been used successfully in treatment of acute poisoning [205].

2. Chronic Toxicity: Animal studies [204, 207-209] show little effect on health at prolonged exposures of 100 to 200 ppm, but levels of 400 to 500 ppm or higher resulted in liver damage, and there was pulmonary congestion, kidney damage, and deaths at 1000 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 to 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 strongly 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 and 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, 209, 214-215].

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, 202, and 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 that may be associated with residual monomers or polymerization adjuncts, but there are none 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. Arnaud 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]. Cordasco et al. [220] found similar symptoms in three patients. These reports gave very little detail on the degree of exposure or the type of resin or other materials that 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 1047 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/m³ of respirable PVC dust (plastisol grade) for 6 hr/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 [230-231] 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 [232-234]. 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, 235-236] 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' Laboratories 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 [239-240], together with the carbon monoxide that may be present in any combustion gases. This aspect of polymer toxicity is discussed in more detail in Chapter 26.

Some evolution of HCl occurs at any elevated temperature, but studies have shown [241-243] that this is not a significant risk to those who handle the hot materials, such as meat wrappers, when adequate ventilation is provided. There 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

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			

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, 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, 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 semirigid 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 packaged food [245]. In addition, the District of Columbia Circuit Court of Appeals ruled in *Monsanto* v. *Kennedy* [631F 2nd 947 (D.C. 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 39FR30112, and the Consumers Product Safety Commission (CPSC) at 39FR30112. The CPSC action was upset on precedural 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 parentheses 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 Section II.A.1.

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-hr time-weighted average (TWA) of 1 ppm, and a 15-min 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.
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 to 10% loss [247, 248]. 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 $490,000 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 case 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-hr exposure limits of 40CFR1910.1000 that are shown in Table 6.

C. The Environmental Protection Agency

1. Air Emissions: There are no recognized natural 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 hr [255-258]. 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 hr 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 m 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 5 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 5 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 to 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, 263-264] 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 to 40 years, and that this led to the possibility of 10 to 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 Section II.A.4. 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] establishes the following conditions:

1. Fugitive emissions controls by leak patrols and design standards for pump and compressor seals, agitators, and loading devices
2. Work practices for vessel openings and sampling
3. Stripping requirements for residual monomer in resins and wastewater

4. Abatement of all point-source emissions to 10 ppm
5. Prohibition of relief valve discharges, except for nonpreventable emergencies
6. Extensive monitoring, reporting, and recordkeeping requirements
7. 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 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 5 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 compiance 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). That proposal has now been withdrawn as part of a proposed revision of the standard which would set numerical limits on emergency relief device emissions rather than try to define "nonpreventable" (50 CFR 1182, January 9, 1985).

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 tht 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. v. 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 stand-

ard, 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], *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 5000 lb for DCE, and 1000 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 established a new RQ for vinyl acetate of 5000 lb (50FR13456, April 4, 1985). 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 ensures that all such wastes are to be disposed of only by RCRA-approved procedures.

2. *Water*: All the substances discussed in the preceding section are also controlled under general discharge provisions to the extent that they produce conventional pollutant properties, such as biological oxygen demand (BOD). As would be expected, vinyl chloride has low water solubility and is easily lost to the atmosphere from streams and discharges [268, 269]. Under one set of experimental conditions, the evaporative half-lives of VC, TCE, and EDC are less than ½ hr [269]. In another experiment, a stirred breaker lost 96% of its original 16 ppm of VC in 2 hr, 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/liter [268]. 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, 274; 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 ethylenes in groundwater has been established by recent work of 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 *Escherichia 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% per day at room temperature and 4% per 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 under way 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 to 100 ppb for VC and EDC, and 5 to 500 ppb for TCE. The Health Assessment Documents prepared as 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 a 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 noted earlier.

4. *New Product Manufacture*: The EPA also administers the Toxic Substances 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 filling 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 provided a very limited exemption for certain classes of polymers under 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 (49FR46066, November 21, 1984).

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, 276], 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 100 largest losses of the last 30 years [276b]. Table 8 contains a list 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 have been aided significantly by voluntary participation in trade associations. The Vinyl Chloride Safety Associa-

tion 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 Industry. 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 that may arise in plant operations. The PHR is in many ways an outgrowth of accidental 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 four to seven persons for all of the study, and others for portions. The initial phase may occupy 3 to 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 that 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 that 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 Figure 1, 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].

A second phase of the PHR is to attempt to quantify the probability of each contributing event, and of the postulated end result. This is usually 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 siruations 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 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 startup should include a further review of compliance with the PHR report.

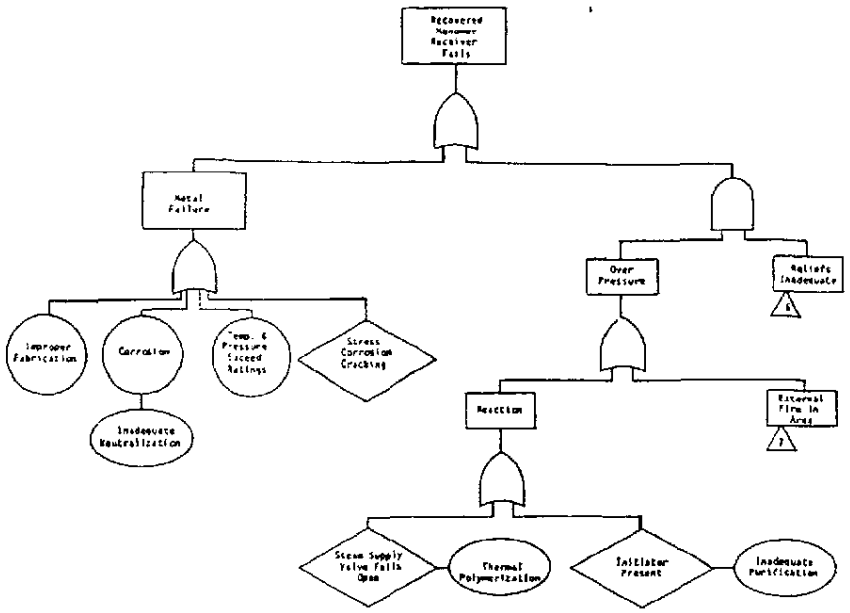

FIGURE 1 Fault tree for pressure failure of recovered monomer tank.

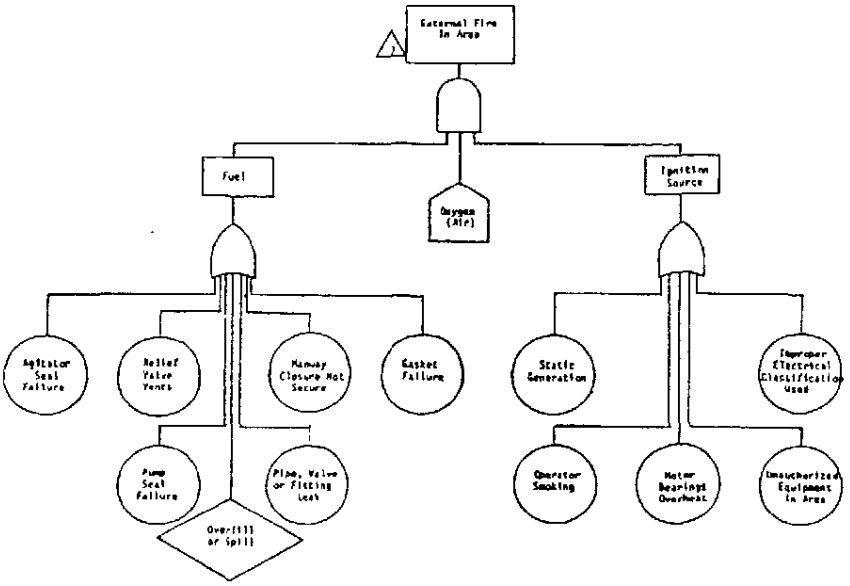

FIGURE 2 Fault tree for external fire in the process area.

A major uncertainty in the quantification analysis is the weight to be ascribed to operator error. This factor is often larger than the other factors that errors in estimation of its value override 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 influences 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 (46FR40.151) 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 gal. 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 are also 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 that 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 sharply reduced the severity of such incidents [276d].

The Society of the Plastics Industry, 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 build-

ing 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 by 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 that favor peroxide formation.

Oxygen reacts readily with VC to form a variety of cyclic and linear peroxides by simple addition [279-283]. 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 have caused serious damage in industrial accidents [283-284]. 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 to 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 that 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 on contact with the liquid, serving only to vaporize the liquid faster. Air-supplied respirators should be used by firefighters 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 type 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, 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 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. Inhibition with a few ppm of hydroquinone or an equivalent is still 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 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 [286-287]. Dilution

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
Diisopropyl peroxydicarbonate	30	0
α-Cumyl peroxyneodecanoate, 75%	59	0
Azobisisobutyronitrile	>70	60
Lauroyl peroxide	123	80

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 the thermostat. These are usually 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:

1. Mark each type of initiator with a distinctive label and store only one type in each location.
2. Remove only enough for immediate use from storage and keep it at the proper temperature on the operating floor.
3. Try to arrange the packaging so that only full shipping containers are used. Use extreme care in dividing packages, especially those that are solid at storage temperature.
4. Use only clean, dedicated containers if an intermediate container is necessary.
5. Never return material to a shipping container.
6. Remove empty containers promptly and dispose of separately, not with other trash.
7. 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 circulating 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 disks, 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 [288-290], 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 4000 gal to as much as 16 to 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 in. x 12 in. valves on 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 disk 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 disk has leaked pressure into the volume under the valve [290b]. Many other factors must also 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 high-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 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-gal 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 α-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 can sometimes 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 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 that 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 tailpipe. Insurance provisions and local codes establish relief valve inspection and test schedules, which should be no longer than 1 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. Dili-

TABLE 8 Major Vinyl Chloride Accidents

Year	Place	Cause	Result
1955	Massachusetts	Broken gauge glass on a storage tank, ignited by nearby boiler.	Major plant damage.
1964	Connecticut	Attempts to tighten a reactor sight glass while under pressure failed. Ignited by nearby extruder operation.	Seven killed, 22 injured. Plant destroyed.
1966	New Jersey	Operator opened wrong reactor bottom valve, discharging contents when handle failed. Ignited by static or other source.	One 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.	Four killed, 8 injured in plant, 2 outside. Major structural damage.
1970	Delaware	Head gasket failed. Ignited by nearby gas-fired drier.	One killed. Instrument and control systems destroyed by fire.
1973	Germany	Thermowell failure in bulk reactor. Ignited in the recovery section.	Five 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 bulk reactor due to instrument failure.	One 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.	One killed, 3 injured, major damage.
1978	Germany	Buildup of peroxides in recovery system exploded during steam purging.	Major equipment damage.
1980	Massachusetts	Operator opened wrong bottom valve, discharged fresh batch. Vapor cloud ignited above ground level.	Two 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.	Five injured. Destroyed laboratory and control room.

gent 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 nearly 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 or 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 290i.

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 are all interwoven with the efforts to protect workers and equipment from fire and explosion.

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 that 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, 292], 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 ensure 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 sometimes experience higher exposures than those performing routine tasks because they are more often at the site of unusual occurrences.

Personal monitoring using devices such as portable pumps with either gas collection bags or absorption tubes, or the more recent passive monitoring badges, is required by OSHA on a periodic basis. These devices were valuable in the regulatory learning process in assisting workers in determining which of their work habits were more likely to result in exposure.

and in convincing them that the area monitoring reports were accurate, even at those low levels.

The efforts to reduce worker and environmental exposure have been successful. Workplace concentration had been reduced to below 5 ppm by mid-1975 [294], and by 1976 to less than 1 ppm. The general consensus among PVC producers is that compliance with the OSHA standard is greater than 95%, with the exceptions being due to malfunctions or process upsets. Vinyl chloride producers usually operate as deregulated areas except during maintenance turnarounds.

In the long term, however, the conscientious worker makes the greatest contribution to overall safety, including reduction of exposure. The employer's training program must be designed to motivate workers to safe work practices by helping them understand the need for such precautions, and by teaching safe habits and sound work practices. Firm enforcement of safety rules and ongoing retraining are fundamental to a successful program.

3. Other Considerations: The emphasis on reduction of worker and environmental exposure has decreased the probability of major accidents from the release of flammable vapors, but that possibility should not be forgotten. Electrical construction should be grounded properly and in conformance with NFPA Class I Group D specifications [277]. Structural steel and tank and reactor supports should have adequate fire protection. Major valves should be fire-safe and fail-safe on loss of power. Damage to instrument and power lines often is a major cause of production loss from fires, and adequate protection should be provided for those services.

Walk surfaces should be of a type which provide sure footing when wet or covered with PVC powder. There should be adequate access platforms for elevated areas such as around relief valves, where prompt and frequent service may be required.

Many employers have utilized the action-level concept to establish a policy for casual visitors and others who are not "authorized employees" under the OSHA rule. As an example of its application, visitors are allowed to be inside regulated areas for no longer than 45 min per day as long as the area monitors indicate that the ambient levels are below 5.0 ppm, or 3.5 hr at 1 ppm. It is impossible to accumulate more than 4 ppm-hr under this policy, and thus the OSHA program is not invoked.

Some employers have taken conservative positions regarding the potential teratogenicity or transplacental carcinogenicity of VC, and have established rules that do not permit women with childbearing capacity to work in regulated areas. At least one such policy has withstood legal challenge [294a].

Sight glasses are useful devices on reactors and other vessels. They allow monitoring of the contents to assure that reactors actually are emptied between batches, and serve as a check on the charging system to prevent overfilling, or excessive foaming during venting or evacuation. They also allow some degree of evaluation of the degree of fouling on the walls and thus help prevent the loss of temperature control of the batch.

After the 1964 explosion and fire in Connecticut, manufacturers reevaluated their use of sight glasses. Many decided to stop their use of them on reactors, and others changed to a different type. The glasses in most general use before 1964 were simple disks of thick glass, sealed in place by gaskets above and below, and tightened by a conventional flange. The type in most common use today consists of a laminated disk sealed by compression on the circumference from pressure by a lantern ring or packing. Even if cracked,

these will not fail catastrophically, and major releases will not occur. It still remains good practice, however, not to attempt to adjust these devices under operating conditions.

Care should be taken to install an air gap between the sight glass mount and any permanent light source so that excessive heat buildup will not occur. See the discussion on chloride-induced stress corrosion in the following section. Localized high temperatures can accelerate the decomposition of any polymer deposits, and thus the corrosion rates also.

Similarly, gauge glasses are useful manual checks on level devices for storage or process tanks. These are subject to fouling, either internally at the connection ports or from sunlight through the glass. Adequate attention to inhibitor level and an aggressive preventative maintenance program can reduce these problems. A special glass is now available that transmits fewer ultraviolet rays and thus reduces the glass coating by polymer. Magnetic indicator devices are available that eliminate the glass sections altogether. Any glass units that are used should have excess flow systems in the isolation valves.

A major reason for the trend toward more computer-controlled large reactor operations is the increased safety that 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 min to 1 hr) at temperatures of 160 to 195°F, depending on the residual heat stability of the product. This procedure left upward 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 1000 to 2000 ppm of VC at the time of shipment [294c].

The EPA standard set a limit of 400 ppm VC in suspension resin (2000 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. Low-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 2000 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 (T_g) 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 that 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 T_g 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 that approach 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 that 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 that 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 1 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 extensive 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, in 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 can sometimes 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 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 in the past that 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 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 Dandliker [269] suggest that all these substances should air strip easily. However, all 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 feasible 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 5 g steam per kilogram of feed. Under the same conditions, TCE needed seven trays and 3 g/kg of steam, and VC only six trays and 2 g/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 prevaporation 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 concentrate 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 permit substantial recovery of the chlorine values [302-304]. 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 to 75 ppm, but as it is concentrated about 10-fold 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 [306-307].

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 to 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 is 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 constituents are well known, it is necessary to use a combined gas chromatograph/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 [260-261]. 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 constituents in water which are useful to 0.2 µg/liter and claims a detection limit of 0.01 µg/liter. 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 [314-317]. Reference 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/liter, 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 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 absorbant 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-min 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 "setup." 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. Setups occur very rarely in homopolymer systems, and usually occur in copolymer

batches after the density of the organic phase has increased to more than 1.0. This is well into the polymerization cycle, at about 60 to 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, 282] and polymeric sludges in the recovery equipment. It is usually 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 also becomes more important. 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 in design and proper operation of the reactor and recovery system, in particular, are necessary in the manufacture of copolymers in order to offset the additional hazards present.

GLOSSARY OF ACRONYMS

ACIGH	American Conference of Government and Industrial Hygienists, Cincinnati, OH 45211
AOL	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 and Human Services Department, Atlanta, Ga.
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
DNA	deoxyribonucleic acid, the constituent of chromosomes
DOT	Department of Transportation
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 gives the volume, the following numbers are the page; Volume 48 was published in 1983
GGT	same as GGTP
GGTP	gamma glutanyl transpepsidase, a liver enzyme
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
NCI	National Cancer Institute
NFPA	National Fire Protection Association, Quincy, Massachusetts
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 copolymer
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 hr
VAc	vinyl acetate
VC	vinyl chloride

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about the editors . . .

LEONARD I. NASS is head of Technical Information Exchange (TIE), a worldwide network of polymer industry consultants involved in marketing and multidisciplinary developmental projects. Mr. Nass is a veteran of the chemical and plastics industries with more than 35 years' experience in plastics additives and PVC. He is a Fellow of the Society of Plastics Engineers and member of the Plastics Institute of America, American Chemical Society, and American Society for Testing and Materials. He is the author of numerous publications and holds patents in areas such as polymer stabilization, catalysis, compounding, processing, testing, and instrumentation. Mr. Nass has been an instructor and guest lecturer for the Society of Plastics Engineers, Plastics Institute of America, and various colleges. He received the B.S. degree in chemistry from Syracuse University, and has pursued graduate studies in organic chemistry at Polytechnic Institute of New York.

CHARLES A. HEIBERGER served, until his untimely death in 1985, as a consultant to the plastics industry and was associated with the Princeton Polymer Laboratories, a general consulting group in polymer technology, as well as with Technical Information Exchange (TIE), a specialized consulting firm for PVC technology. Dr. Heiberger was a veteran in the polymer sciences with more than 45 years' experience in the fields of PVC resins and compounds, PVC homopolymers and copolymers with vinyl acetate, propylene and other olefins, and grafts and postchlorinated vinyl chloride polymers. He held more than 25 U.S. patents and authored many technical publications. Dr. Heiberger was an emeritus member of the American Chemical Society and member of the Society of Plastics Engineers, Society of the Plastics Industry, Plastics Institute (London), and Technical Association of the Paper and Pulp Industry. He received the B.S. and M.S. degrees in chemical engineering and Ph.D. degree in organic chemistry from Lehigh University.

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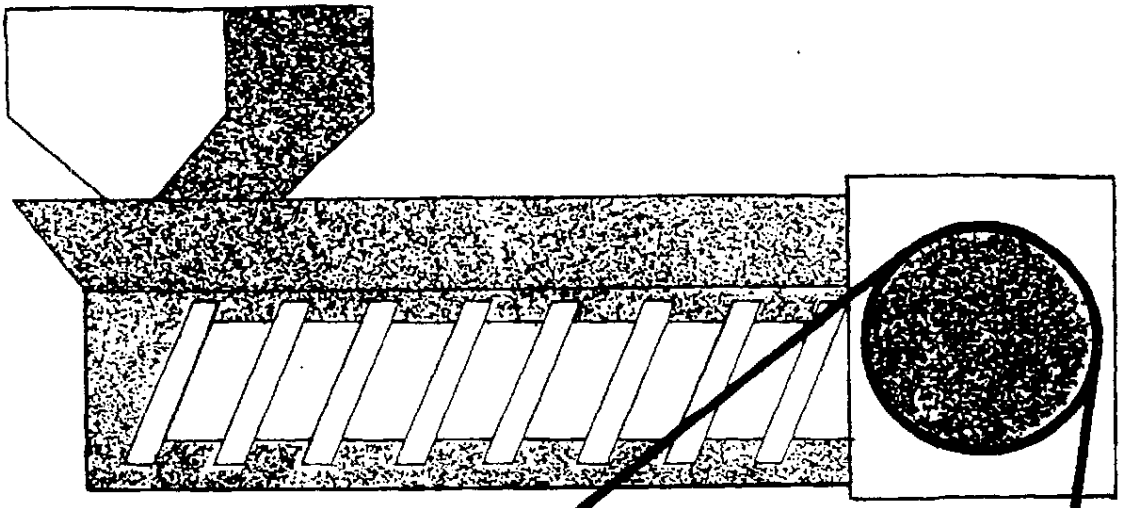

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about the editors . . .

LEONARD I. NASS is head of Technical Information Exchange (TIE), a worldwide network of polymer industry consultants involved in marketing and multidisciplinary engineering and developmental projects. Mr. Nass is a veteran of the chemical and plastics industries with more than 35 years' experience in plastics additives and PVC. He is a Fellow of the Society of Plastics Engineers and a member of the American Chemical Society and American Society for Testing and Materials. He is the author of numerous publications and holds patents in areas such as polymer stabilization, catalysis, compounding, processing, testing, and instrumentation. Mr. Nass has been an instructor and guest lecturer for the Society of Plastics Engineers, Plastics Institute of America, and various colleges. He received the B.S. degree in chemistry from Syracuse University and pursued graduate studies in organic chemistry at Polytechnic Institute of Brooklyn.

CHARLES A. HEIBERGER served, until his death in 1985, as a consultant to the plastics industry and was associated with the Princeton Polymer Laboratories, a general consulting group in polymer technology, as well as with Technical Information Exchange (TIE). Dr. Heiberger was a veteran in polymer sciences with more than 45 years' experience in the fields of PVC resins and compounds, PVC homopolymers and copolymers with vinyl acetate, propylene and other olefins, and grafts and postchlorinated vinyl chloride polymers. He held more than 25 U.S. patents and authored many technical publications. Dr. Heiberger was an emeritus member of the American Chemical Society and member of the Society of Plastics Engineers, Plastics Institute (London), and Technical Association of the Pulp and Paper Industry. He received the B.S. and M.S. degrees in chemical engineering and Ph.D. degree in organic chemistry from Lehigh University.

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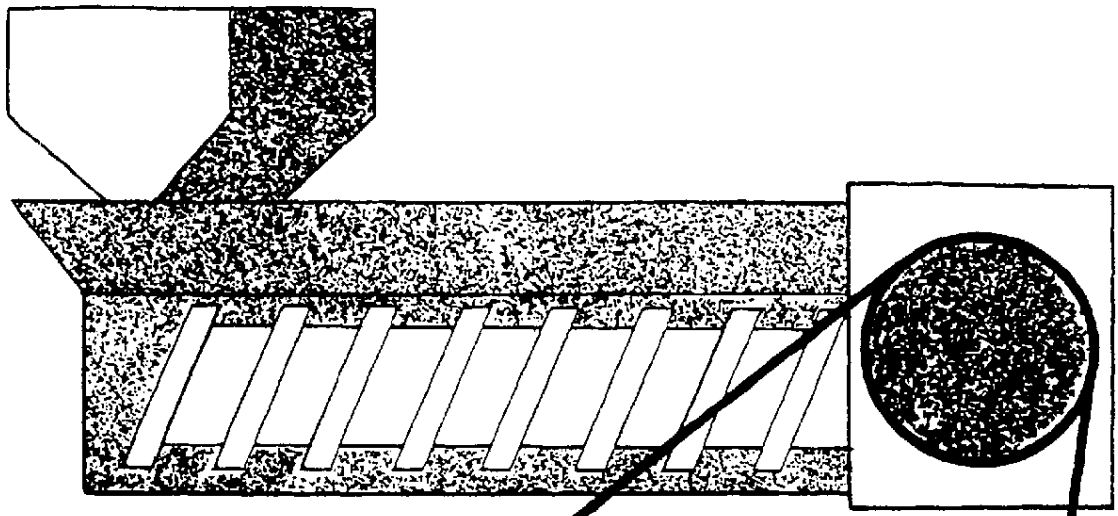

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Second Edition,
Revised and Expanded

Volume 3:
Compounding Processes,
Product Design, and Specifications

edited by
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Contributors to Volume 3

John T. Barr* *Air Products and Chemicals, Inc., Allentown, Pennsylvania*

Robert S. Brookman *Colorite Plastics Co., Ridgefield, New Jersey*

Zenas Crocker *Synergistics Industries Limited, Mississauga, Ontario, Canada*

Luis Gomez *Monsanto Company, Indian Orchard, Massachusetts*

Ved P. Gupta *Synergistics Industries Limited, Mississauga, Ontario, Canada*

Paul O. Hong *Occidental Chemical Corporation, Pottstown, Pennsylvania*

Peter Lloyd *BF Goodrich Company, Avon Lake, Ohio*

Russell A. Park* *Occidental Chemical Corporation, Pottstown, Pennsylvania*

David W. Riley *Extrusion Engineers, Branchburg, New Jersey*

Fred Roesler *Consultant, New Brunswick, New Jersey*

Richard A. Ronczka† *USS Chemicals,‡ Pittsburgh, Pennsylvania*

Ashok C. Shah *BF Goodrich Company, Avon Lake, Ohio*

Lewis B. Weisfeld *Consulting Chemist, Philadelphia, Pennsylvania*

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*Retired.
†Deceased.
‡Now Aristech Chemicals.

Contents

8

Safety and Environmental Concerns for Vinyl Compounds and Products

JOHN T. BARR

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

I. INTRODUCTION

This chapter addresses the safety and environmental concerns in the PVC fabrication industry. The major and minor ingredients are discussed first, followed by comments on the processing steps; then the products are reviewed in the context of their applications.

The PVC industry has played an important role in achieving our current standard of living. Literally everything that we eat, drink, or use is affected by the increasing versatility of synthetic materials. The PVC industry, as one of the largest of the suppliers to this market, has made a major contribution in this development, and the growth in this area is one measure of the safety and acceptability of the products.

Nevertheless, careless or incorrect use of any material can lead to problems. This chapter discusses the potential causes for concern and reviews briefly the data relating to that concern; it also outlines the

(generally stringent) regulatory status of the materials and attempts to place these concerns in the proper perspective.

A glossary of acronyms and abbreviations is provided at the end of the text for convenience in following the regulations and codes involved in this industry.

Continuing activity by governmental and regulatory agencies during the preparation of this chapter has resulted in several recent significant standard changes.

The two most significant legislative actions were the reauthorizations for the Superfund and the Clean Air Acts. Both actions expanded the power of the Environmental Protection Agency (EPA) in these areas and mandated many specific rulemakings.

The Occupational Safety and Health Administration (OSHA) hazard communications rules were expanded, demanding more information on more substances, and the EPA added environmental data to the requirements. Under Superfund activities, communities must now be informed of the amounts present or processed in local facilities for a prescribed list of raw materials and products. In addition, quantities released into the environment must be reported, and cooperative emergency response procedures must be developed.

Water quality criteria have been made much more restrictive and expanded to a longer list of substances, similar to the expanded list of hazardous wastes. One result has been that the permissible residual vinyl chloride levels in PVC, fabricated products and waste streams has been reduced by more than an order of magnitude.

These stricter standards do not change any of the facts discussed in this chapter, but reflect the greater concern for and participation in environmental affairs by the public. Complete and open cooperation with neighbors and authorities is a necessary way of conducting business.

II. COMPOUNDING PROCESSES

All PVC must be mixed with other materials (compounded) before it is suitable for use. The reasons for this, and the methods for accomplishing it, are covered in detail in Volumes I and II and the earlier chapters of this volume of this encyclopedia. The Vinyl Institute provides a booklet, "Facts About Working with PVC," which processors may find helpful.

Producers of end products who handle more than a few million pounds per year of materials usually find it more economical to combine the compounding and fabrication steps in the same facility. Smaller fabricators, and those who produce small amounts of specialized products, may purchase their supply in ready-to-use form, usually as processed pellets but sometimes as a dry powder blend. This chapter discusses the compounding and fabrication steps as separate operations because of the differences in hazards and risks that are seen in those areas. Product application is treated as a third area.

A. Raw Materials

Fabrication operations range in size from small operations that receive the raw materials in bags, drums, and other small packages, to operations large enough to use bulk storage for most or all ingredients. The opportunity for worker exposure or release to the environment therefore covers

a wide spectrum, with the manual handling at small operations usually providing a higher probability of spillage, but also having more limited opportunity for a significant release. In any case, the hazard of the substance is the same; it is the risk that changes. The discussion that follows centers on these hazards.

1. PVC and CPVC Resins: The basic polymer of vinyl chloride and its copolymers with vinyl acetate have prior sanction under rules of the U.S. Food and Drug Administration (FDA) for use in food-contacting surfaces. Specific approval has been granted for the use of copolymers of VC with ethylene, propylene, hexene-1, and lauryl vinyl ether (see 21 CFR 177.1950-1980). The FDA reaffirmed the prior sanction status of PVC food packaging (51 FR 4173, 3 February 1986) and has established residual vinyl chloride concentrations that are considered safe for consumers.

The EPA controls the components of pesticides under FIFRA, and has approved the use of PVC as an insert component of various formulations (40 CFR 180).

No other application of PVC requires specific regulatory approval of the resin. The basic point of importance is that PVC is nontoxic to humans because it is not absorbed if ingested [1]. Many local regulatory agencies do require that products conform to their rules or to the voluntary consensus standards of various trade associations in regard to the physical properties of the products. Some examples are the National Sanitation Foundation (NSF) codes for potable water pipe, National Fire Protection Association (NFPA) codes for electrical fittings, Consumers Product Safety Commission (CPSC) rules (16 CFR 1500.45), and various architectural codes for the flammability of interior furnishings. These, and others, are more fully discussed in Chapter 7.

The toxic properties of PVC were discussed in Chapter 5 of Volume I of this encyclopedia and are not repeated here. Chlorinated PVC (CPVC) has very similar gross properties and should be handled in the same manner. At one time, chloroform was used as a swelling agent to assist in the chlorination step, but that practice was stopped several years ago. Thus the production of CPVC is no longer a source for even the minimal release of chloroform that may have been possible earlier. A further result of the chlorination step is that essentially all of any residual VC has been removed.

Concentrations of VC above the action level prescribed by the U.S. Occupational Safety and Health Administration (OSHA), namely 0.5 ppm, can develop in the free space after extended storage of PVC in closed containers. Provisions for ventilation or respiratory protection should be provided if workers enter silos or railcars that have been used for PVC storage or transport. To a lesser degree, some buildup can occur in warehouses or transportation vehicles used for bagged product. Generally, there is enough natural ventilation to prevent exposures over the action level, but the possibility of such levels exists in tightly closed areas where a large volume of bagged material is present.

Similarly, some VC can be expected to escape during the compounding step, especially at the first heating or fluxing stage. The quantities are small, and even rudimentary ventilation can prevent overexposure. About one-third to two-thirds of the residual VC in the resin will be lost through this process step; losses will be greater if plasticizer is present and the compounding operation involves several steps at elevated temperature, and lower if rigid pellets are formed by a single-stage operation.

The industry has adopted a voluntary standard of no more than 10 ppm VC in potable water fittings. This usually is met by having the supplier provide resin below 10 ppm to avoid the necessity for further testing after compounding. In practice, the actual level for pipe and general-purpose resin usually is well below 5 ppm at the time of delivery. Thus only minor amounts are available for release in the compounding step. Ventilation that is adequate to control dust and plasticizer and stabilizer odors from heated operations should be adequate to control the releases. For example, an extruder processing 1000 lb/h of 2 ppm resin will release about 0.001 lb/h of VC. A ventilation rate of only 200 ft^3/min (assuming good mixing and no point ventilation) would be adequate.

Nonporous resins, such as some very low molecular weight homopolymers and many of the copolymers, are more difficult to strip than the general-purpose resins and thus may contain higher VC residuals. The processing of these resins calls for more attention to ventilation. Some resins with high residual VC may become hazardous wastes under RCRA if the proposed limits for defining hazardous wastes are approved. The EPA has proposed that any waste that develops a concentration of 50 ppb VC in water after an overnight extraction test be declared hazardous (see 51 FR 21648, 13 June 1986, for details).

After liquid stabilizer or plasticizer has been added to PVC, the mixture no longer is dusty. Before that stage, adequate ventilation should be provided to hold the amount of dust in the air to less than 15 mg/m^3 of total dust for a time-weighted average (TWA) over 8 hours, or 5 mg/m^3 of respirable dust (particle size <10 μm), to meet the OSHA standard [29 CFR 1910.1000(a)]. The American Conference of Governmental and Industrial Hygienists (ACGIH) recommends 10 mg/m^3 for total dust, rather than the value of 15 listed by OSHA. Neither organization lists PVC as a specific substance controlled by these limits, but prudence dictates that these values be observed. Suspension PVC ordinarily does not contain a significant respirable fraction.

Any PVC that has been spilled on concrete or steel walkways can create a very unsafe walking condition and should be removed at once. This is especially true of stairs and catwalks around silos and railcar unloading stations.

2. Stabilizers: Stabilizers may be divided conveniently into two major categories for the purpose of this discussion: FDA-approved and non-FDA-approved. Table 1 lists classes of substances that are in common use for this purpose.

The Food and Drug Administration is responsible for the implementation of the Food, Drug, and Cosmetic Act, which includes the setting of regulations for food additives. Polymers and other substances that come into contact with food are classed as indirect food additives, because of the presumption that some component of the package can migrate into the food and thus become an additive under the terms of the regulations. Rules for controlling food additives are codified at 21 CFR 170-189, with polymers being grouped under Part 177, and most stabilizers under Part 178. Antioxidants, plasticizers, and such can be found at Part 175 and other locations.

Packaging materials or containers intended for aseptic conditions, such as in meat or poultry packaging plants, must meet several FDA standards for approval, but the actual compliance is monitored by the Department of Agriculture under rules published in the Code of Federal Regulation (9 CFR 300 et seq.).

TABLE 1 Generally Used Stabilizers for PVC and CPVC

Metallic compounds	FDA approval	Usual organic components	Inorganic components
Lead	No	Stearates, phthalates	Sulfate, carbonate
Barium	No	Stearates, naphthenates, alkylphenylates	
Calcium	Some	Stearates, naphthenate	
Zinc	Some	Stearates, octoates, naphthenates	
Cadmium	No	Stearates, octoates, naphthenates	
Antimony	No	Mercaptoacid esters or mercaptoalcohol esters	
Tin	Some	Mono- and dimethyl, -butyl, or -octyl maleates, or mercaptides, and mercaptoesters, sulfides	
None	Some	Epoxidized oils and fatty monoesters	
	No	Amines	
	Some	Phosphite esters	

Plus other organic adjuvants including polyhydric alcohols, ß-diketones, plasticizers, solvents, carriers, etc.

It is necessary for a producer to obtain specific approval from the FDA to use any substance in a food-contact use that is not on the approved lists. Approved substances are those specifically listed in the rules named above, those on the Generally Recognized as Safe (GRAS) list, and those with prior sanction because of broad general use before 1958. In addition, any substance approved as a direct food additive is acceptable also as an indirect additive.

The metallic component of FDA-approved stabilizers is limited to salts of calcium, zinc, or tin, all of which have limited toxicity to humans. The nonmetallic component may be from a wide list of naturally occurring fatty acids or several synthetic organic groups. Stearate esters are a favorite choice because of the lubricating property of the salt and because stearic acid itself is considered to be GRAS by the FDA (29 CFR 84.1090). Mercaptides are used widely for their excellent stabilizing actions [2].

Calcium, tin, and zinc all are normal components of the diet and the body, and although any dietary component can exhibit toxicity from overconsumption, little concern has been expressed by their use as constituents in food-contact products because of the very small amount that may be added to the diet through migration.

Tin is a metal of moderate toxicity, and oral rodent LD_{50} doses for its salts usually fall into the range of 50–200 mg/kg. Stannous chloride was

found negative in a rodent bioassay [3], and dibutyltin dichloride has been found to reduce the incidence of cancer caused by treatment with a nitroso compound [4]. Dibutyltin compounds are used as antihelmintics for poultry.

Tributyltin fluoride and a variety of dialkyltin difluorides reduced the tumor growth rates in cancerous mice [5].

Tin is a component of all human tissue [6] and is present in many foods, but because it is not a normal dietary component at substantial levels, it has been subjected to more rigorous controls. The FDA has approved several mono- and dialkyltin salts for use in food applications, after reviewing test results (21 CFR 178). Nevertheless, the Interagency Testing Committee (ITC) recommended a group of alkyltin stabilizers to EPA for further testing (47 FR 54626, 3 December 1982). The EPA has concluded that a proposed test program by a group of manufacturers will be adequate to answer the questions raised by the ITC, and this program will explore the chemical and environmental fate of this class of substance.

The EPA stated (48 FR 51361) that the tin stabilizers are not expected to be released rapidly into the environment and that the material that is released is the reaction product formed during the stabilization step, such as dibutyltin dichloride, rather than the intact alkyltin [7]. Total tin release to the environment from either compounding operations or use in pipe was estimated to be very low by the EPA. Migration rates from new PVC pipe were projected to be about 10^{-8} mg/m²/s. EPA calculated that the added tin concentration for an average receiving stream resulting from plastic pipe use would approximate 7×10^{-6} ppb. This is well below background in most areas.

Alkyltins decompose slowly in the environment by hydrolysis, photolysis, and biodegradation, with a half-life in the range of a few weeks. The bioconcentration factor (BCF) for the organosalts are in the range of 3–16, suggesting the possibility of some concentration in the food chain. After reduction to the alkyltin halides, the BCF drops below 2, outside a range for concern. The leaching rate also is far below the biodecomposition rate, further reducing the opportunity for concentration in the biota.

Epoxidized fatty esters frequently are used in conjunction with barium/cadmium or calcium/zinc salts as an aid to removal of the hydrogen chloride and polymer radicals generated during processing. Those made from epoxidized soybean or linseed oil are approved by the FDA. Synthetic octyl esters of stearic acid or the tallates are not. These have low oral toxicity and are not absorbed readily by the skin.

Some of the phosphite esters used to chelate the metal halides formed from the stabilizer system also are FDA-approved (see 21 CFR 178). These esters biodegrade readily through hydrolysis and actually must be protected from moisture in storage.

Organic amines sometimes are added as acid scavengers in a stabilizer system. These substances have mild toxicity, are absorbed through the skin, and may not generally be used in food or potable water applications. They offer no significant hazard at the concentrations present in commercial formulations, nor in the final product, but the usual good personal hygiene practices should be followed as a precautionary step during the compounding stages.

The non-FDA-approved stabilizers in common use include salts of antimony, barium, cadmium, and lead, all of which are toxic heavy metals. Lead stabilizers are approved for use in potable water pipe in many parts of the world but not in North America. These materials are used widely

for nonfood (or drinking water) applications because of their greater price efficiency as compared to the approved stabilizers.

Each of these metals is listed in Appendix VIII of the Resource Conservation and Recovery Act (RCRA) rules (40 CFR 261), which makes them potentially subject to the hazardous waste rules of RCRA. In general, if the extraction procedure toxicity test (the EP test) of Appendix II, 40 CFR 261, applied to a substance produces an extract containing more than a specified concentration of the metal, the hazardous waste rules apply to any waste of that composition that is discarded. The test consists of contacting approximately 1/3 in. particles with 16 times their weight of dilute acetic acid solution and measuring for the extracted substances after 24 hours. The specified maximum concentrations for barium, cadmium, and lead are:

Barium	100 mg/L
Cadmium	1 mg/L
Lead	5 mg/L

Thus, waste stabilizer is a hazardous waste and scrap compound may be, depending on its extractability. However, very few compounds will fail the EP test, especially when formed into the finished article.

As an illustration of the effect of particle size (surface area) on extractability, a child's teething ring mold was used to prepare plasticized rings weighing about 13 g from a conventional barium/cadmium formula. Extraction of 50 g of the ring, the original pellets, and the chopped ring into 100 mL of simulated gastric juice for 4 hours at 99°F gave the following results:

	Amount (ppm) in liquid	
Sample	Cd	Ba
Original pellets	0.75	1.1
Whole ring	0.03	<0.3
Chopped rings	0.20	<0.3

Repeat extractions on the same sample gave less than 10% of the original concentrations. Thus, each of these forms would have passed the EP test described above [8].

Gross and co-workers have reported [9] that the amount of lead extracted from several lead-containing rigid PVC formulations increases up to 3 phr in the mixture. Addition of filler or impact modifiers decreases the amount of lead extracted. Extraction drops off rapidly as the surface layer concentration is reduced. Recalculation of the data presented in that report indicates that those formulations also would have passed the EP test.

It has been proposed in some localities to designate waste that *contains* these metals as hazardous waste, regardless of the extractability. This proposal would classify many consumer products as hazardous wastes when discarded but not when in use. California has such a rule and is issuing broad variances to avoid the obvious impossible situations that would result from its strict enforcement.

There is no question as to the cumulative toxicity of many of these metals to humans, and workers should receive full training, and protective

equipment as appropriate, to prevent overexposure. OSHA and the ACGIH have set (29 CFR 1910.1000 et seq.) the following exposure limits, in milligrams per cubic meter:

	OSHA		
	8-hour TWA	Ceiling	ACGIH
Calcium	—	—	5
Cadmium (dust)	0.2	0.6	0.05
Barium	0.5		0.5
Lead	0.05		0.15
Tin	0.1	—	0.1
Zinc chloride (fume)	1	—	1

As in many other cases, the ACGIH recommends lower values for some of these metals than does OSHA.

Current OSHA hazard communication rules (48 FR 53280, 25 Nov. 1983; new section 29 CFR 1910.1200), as well as many local community "right to know" laws, require extensive disclosure by the supplier of the composition and hazards of all commercial substances and require that workers be informed of these hazards and be supplied with a Material Safety Data Sheet discussing the properties of the substance.

These materials have been handled safely for many years, and with the exception of lead, there has been little evidence that workers have been overexposed. The introduction of "nondusting" forms of lead formulas [10], enforcement of good personal hygiene, and the present regulatory status should prevent problems in the future.

OSHA also requires a quantitative respirator fitting program for employees exposed to dusts containing more than 50 mg/m³ of lead, and removal of an employee from exposure if the blood lead level is above 60 mg/100 g until the value has returned to below 40 mg/100 g (20 CFR 1910.1025). Careful attention to personal hygiene, segregated eating and dressing facilities, and good ventilation are necessary to meet these standards, as well as close attention to sound work practices [10, 11].

3. *Plasticizers*: The development of the procedure for plasticizing PVC was a key to the current widespread commercialization of the polymer. It was not until the later development of equipment and stabilizers adequate for the successful processing of rigid PVC that rigid products became a dominant part of the industry and overtook plasticized products in volume.

Phthalates: The principal phthalate ester in use in PVC traditionally has been di(2-ethylhexyl) phthalate (DEHP, sometimes termed DOP). It amounts to about a third of total plasticizer use, primarily because of its high efficiency and good properties at normal use temperatures. In recent years, it has begun to be replaced by diisononyl phthalate (DiNP) and by other mixed alcohol phthalates.

DEHP has very low acute toxicity, with rodent LD_{50} values (dose necessary to kill half the animals in 14 days) in the 30 g/kg range (about the same as sugar) and mild irritation properties [12]. OSHA has set an

8-hour threshold limit value (TLV) of 5 mg/m³. The ACGIH recommends the same value, with a short-term exposure limit (STEL) of 10 mg/m³. The EPA recommends a water quality criteria of 15 mg/L in human drinking water, based on animal feeding studies [13], but the solubility in fresh water is only 0.34 mg/L, and it is about half that soluble in seawater [14].

Esters with alcohol chain lengths of four carbons or greater are not sufficiently soluble in water to present significant acute toxicity symptoms in a variety of aquatic species [15, 16].

DEHP does not hydrolyze as rapidly in water as do some of the shorter chain analogues [17]. It has the potential to bioaccumulate in the food chain because of its low ratio of water to oil solubility, but it also is absorbed strongly by sediments, and biota have been reported to contain less DEHP than the sediments above which they live [18, 19]. In addition, it is metabolized readily by the host. The ubiquitous nature of DEHP, even in laboratory equipment, has led to a number of erroneous reports of its distribution in the environment. Extreme care is necessary at the very low levels of detection possible today to be certain that analytical findings are not due to some artifact of the sampling or testing procedure [20, 21].

DEHP is removed readily from waste streams by conventional biological methods, after acclimitization of the biomass. Primary biodegradation of 90% or higher is seen in all members of the class, with ultimate biodegradation reaching over 99%. The half-life in biological systems increases with the ester chain length, as expected. There is no apparent toxicity to natural microorganisms [22, 23]. Destruction is much more rapid in aerobic systems than in anaerobic processes. The EPA has proposed a new source effluent standard of 150 µg/L (48 CFR 11828) and classified it as a material that does "not pass through or interfere with the operation of" public water treatment systems. It also is removed readily by carbon adsorption and flocculation–precipitation treatment methods [24–27].

The National Toxicology Program (NTP) reported [28] a positive bioassay for DEHP, as the result of an increase in hepatocellular carcinomas in both rats and mice. It has been suggested that this is the result of liver damage, rather than direct genotoxicity, because this result was seen only at the highest of the two doses, up to 1.2% in the diet, and had not been seen in earlier studies at lower doses. Furthermore, neither the alcohol, nor DEHP, nor its principal metabolites are positive in a variety of teratogenicity and in vitro mutagenicity tests [29–31]. That concept is supported by the fact that DEHP is a promoter of mouse liver tumors but not of skin cancer, and is not an initiator of either liver or skin cancer [32]. One study reported inhibition of the development of neoplastic indications in rats treated with diethylnitrosoamine [33], while another reported promotion of this effect [34].

Scientists at the NTP have reviewed the evidence for the carcinogenicity of DEHP and have concluded "that DEHP has been shown to be carcinogenic to rodents in a valid chronic test. Further experimental inquiry will be required, however, to accurately assess the potential health risks posed to humans by exposure to small amounts of this plasticizer" [35]. The NTP has included DEHP in the Third Annual Report on Carcinogens [36]. The International Agency for Research on Cancer (IARC) has concluded that there is "sufficient evidence" for animal carcinogenicity, but that the evidence to evaluate the carcinogenicity of DEHP in humans is inadequate [37].

Metabolism occurs after absorption in the gastrointestinal tract following hydrolysis to the monoester [38]. The alcohol metabolites appear to be the primary toxic substances, as concluded from specific studies on members of the series and the fact that the esters of lower alcohols are even less toxic and are not carcinogenic in bioassays. In addition, phthalic anhydride itself [39], and of course, its immediate hydrolysis product, phthalic acid, is not carcinogenic in either rats or mice. The Science Advisory Board has notified EPA that its grouping of all phthalate esters into a single carcinogenic class is not justified.

The carcinogenic effects of DEHP, the alcohol, and the half-ester metabolite are believed to be due to the damage to hepatocytes as the result of induction in these cells, in the presence of high levels of fatty materials, of high levels of peroxisomes [40a]. DEHP is not directly genetoxic in rat or human hepatocytes [41], does not cause direct DNA damage on rat hepatocytes [40a], and is not a conventional promotor or initiator [40b].

It has been found that esters of straight-chain alcohols are less potent in this peroxisome induction than are branched chains [42]. Inhaled dibutyl phthalate will be oxidized in the lungs of rats as well as in the liver [43]. The short-chain alcohol esters are essentially nontoxic to humans [40a].

The low toxicity of these esters results in very high doses being administered to rodents. Under such circumstances the difference in metabolism of straight- and branched-chain substances in rodents and humans, and the relatively high concentration of minor metabolites or of the metabolites of impurities, call in to question the relevance of rodent bioassays to human hazard at low ambient concentrations [44]. This is especially true in view of the failure of either DEHP or DEHA to bind to DNA in the liver or to accumulate in blood cells. Any body storage is in the lipoproteins of the plasma, not in the cells. These facts suggest that a no-effect level exists which is below normally expected ambient exposures [61].

The monoethylhexyl phthalate ester, the primary metabolite, has a no-effect level of 50 mg/kg as a teratogen in rats; above that dose, maternal toxicity and weight loss of the embryos were seen [45, 46]. The parent ester increased fetus malformations when fed at the maternally toxic doses of 1% or more in the diet [47].

DEHP causes testicular atrophy in rats and is positive in the dominant lethal assay at 1 mL/kg dosage [48–50].

An insufficiency of toxicity data in 1980 [13, 51] led to listing of the substance by the Interagency Testing Commission for consideration for further testing to determine whether regulations should be imposed by the EPA. That agency established a multitier testing program to be performed by a group of manufacturers. The results were reported in 1984 [15]. The EPA had concluded earlier [52] that, prior to obtaining data indicative of more serious consequences, the ester presents risks below a level at which regulation normally would be taken. The NTP is exploring the question of genotoxicity and other related factors [53]. The Consumer Product Safety Commission (CPSC) established a Chronic Hazard Advisory Panel to advise it on hazards for consumer products containing DEHP (48 FR 6628, Dec. 22, 1983). The panel released its report in September 1985, concluding that DEHP is a nongenotoxic animal carcinogen and that more research is needed to determine whether there is in

fact a threshold for carcinogenicity in humans. The Chemical Manufacturers Association (CMA) Phthalates Panel sponsored a study [54a] that concluded that if no threshold exists, the maximum risk to the most exposed humans is well below one in a million, and is zero if a threshold does exist, as seems probable. Strongly nonlinear dose–response results have been reported [54b]. The metabolic process seems to be saturated quickly, and excess ester is excreted without accumulation in the body [54c].

This substance is included on the hazardous waste list by the EPA, and thus disposal of wastes is regulated under the RCRA rules. The statutory reportable quantity for a spill for all phthalate esters is one pound, under the current Superfund rule. Both these listings are the result of including phthalates on the priority pollutant list. The EPA has proposed a 5000 lb reportable quantity for spills of DEHP under Superfund (48 FR 23552), and lower quantities for other alkyl phthalates.

Other phthalate esters have similar properties. For example, the butyl benzyl ester has a half-life of about 6 hours in all tissues and is completely cleared from the body without adipoise storage in 2 or 3 days, just as is DEHP [54e]. Water solubility and rate of biochemical degradation increase as the size of the alcohol group decreases, as does the acute oral toxicity to rodents [15]. The dimethyl and butyl benzyl esters gave negative results in NTP bioassays [55], whereas diallyl phthalate showed "equivocal" evidence of carcinogenicity in female rats only [56]. A branched dinonyl phthalate showed carcinogenic liver response in rats at 5000 and 10,000 ppm in the diet, but not at 500 [57]. Table 2 summarizes some of the environmental characteristics of DEHP and some other commonly used plasticizers. Several reviews of the toxicity of phthalates are available [54, 54c, 58–60].

Mellitates: Esters of trimellitic acid are used for high temperature applications, and the 2-ethylhexyl triester (TOTM) is a common component of high temperature wire compounds. It has been added to the ITC testing list (47 FR 54624) primarily because of concern for the toxicity of the alcohol components. Its toxicological and environmental characteristics are very similar to those of the phthalates, and it is approved by the FDA for use in medical products. Further testing is underway by industry and the NTP (48 FR 51842). Preliminary results suggest that TOTM is a less potent toxin than DEHP [60b].

Adipates: The esters of adipic acid often are used to plasticize PVC because of the improved low temperature properties obtained, and the 2-ethylhexyl ester is the most widely used. This substance also has been found positive in an NTP bioassay, but only in mice and not rats, where it caused an increase in liver adenomas and carcinomas when fed at up to 2.5% in the diet [59]. The IARC has concluded that there is "limited evidence" for carcinogenicity in animals and "inadequate evidence" to assess its carcinogenicity in humans [37].

The oral LD_{50} in rats is 9 g/kg [12]. This series of esters otherwise resembles the corresponding phthalates in general toxic properties, including failure to show genotoxicity in short-term tests. It is not on the EPA "priority pollutant" or hazardous waste (RCRA) lists and therefore is not subject to the same stringency of regulation as are the phthalates.

Sebacates: The esters of sebacic acid can be considered to be homologues of the adipates. DEHS has an LD_{50} in rats of 1.3 g/kg, and

TABLE 2 Environmental Data for Some Commonly Used Plasticizers

Plasticizer	Rat oral Toxicity LD_{50}, g/kg	Solubility in water, mg/L	Biode-gradability	Bioconcentration factor	In vitro tests	Terato-genicity
DEHP	31	0.34	Good	Metabolized	Negative	Negative
Chlorinated paraffin	>10	Insol.	Nil	High	Positive	Negative
DEHA	9.2	—	Good	Metabolzied	Negative	Negative
TCP	—	—	Slow	Low	Negative	Negative
TOTM	>3.1	—	Slow	Metabolized, excreted	Negative	—

like the adipates, is negative in the short-term mutagenicity tests [12]. The NTP has recommended against further testing of this ester (51 FR 21020).

Citrates: Acetyl tributyl citrate is an FDA-approved component in some food wrap and other food application compounds. It has low acute toxicity and is not a mutagen in the short-term Ames tests [12, 60a].

The Belgian Plastics Association issued a summary [34] of data relating to human exposure to plasticizers. It was estimated that the maximum exposure was less than 200 mg/day under extreme conditions. Studies were discussed which indicate that at doses higher than those necessary to induce liver damage in rodents, primates detoxify DEHP metabolites by combination with glucuronic acid through a procedure not found in rodents. This detoxification avoids the induction of excess peroxisomes in liver cells, which is thought to be the base cause of rodent tumor development.

Fire-Retardent Plasticizers: The addition of organic substances such as plasticizers to PVC reduces its inherent nonflammability. For example, DEHP has a flash point of 325°F (open cup), which places it in flammability hazard group 1 ("must be heated to ignite") of the National Fire Protection Association (NFPA). It and compositions with PVC will burn if exposed to a sufficiently strong ignition source. Appropriate fire protection should be provided for storage areas containing plasticizers and plasticized products [62].

This situation has led to the use of fire-retardant plasticizers in some products [63]. Aryl phosphates, esters of chlorinated acids, and chlorinated paraffins are used and, although effective for the intended purpose, each of these carries with it a hazard that must be understood for safe application.

Tricresylphosphate is an example of a substance that has found use as a fire-retardant plasticizer and hydraulic fluid. A total of 36 million pounds of all the aryl phosphates was used as plasticizer in 1977, but 1980 data from the EPA suggest that a significant drop has occurred since that time. About 90% of this total was used in PVC formulations. Lack of adequate toxicity data to evaluate the hazard to the public led the Interagency Testing Commission to designate the aryl phosphate category for consideration by the EPA for further testing rules (see 43 FR 16684). The EPA has accepted some proposals by the manufacturers for tests to supply the needed data, but has proposed (48 FR 57452) additional tests. These include 90-day mammalian tests for specific organ toxicity, needed to supplement the preliminary results in rats, which found liver and kidney toxicity at 1000 ppm in feed; additional short-term mutagenicity tests to confirm the negative Ames tests, and further reproductive tests. The EPA concluded that the data are sufficient not to require teratogenicity or carcinogenicity tests at this time. Also proposed are tests to define further the neurotoxicity of the ortho-TCP isomer and its chronic toxicity in lower aquatic life forms. In the proposal, the EPA noted that because of the generally low toxicity of TCP and its strong tendency to remain in the finished article or absorbed on soil, it was not likely to present significant environmental exposure as the result of waste disposal. Tris(2-ethylhexyl) phosphate has been reported by the NTP to show "equivocal" evidence of increasing adrenal tumors in male rats, liver cancer in female mice, and thyroid tumors in male and female mice [64]. The reports noted

that no mutagenic effects were seen in bacteria. The phosphates as a class are delayed neurotoxins, and ingestion should be avoided.

Chlorinated paraffins with chain length of 10–30 carbon atoms and 40–70% chlorine are useful in many higher temperature applications. These are semiviscous oils at room temperature with insignificant vapor pressure or water solubility. They have very low acute toxicity, do not biodegrade, and are not mutagenic or teratogenic. They also induce increased activity by liver enzymes, as do the other plasticizers discussed here [65a].

Because of their persistence in the environment and tendency to bioaccumulate in the aquatic environment, the ITC placed this class on the recommended testing list in 1977, and the EPA accepted the testing proposal of an industry group in 1982 (47 FR 1017). Partial results of the phase 1 program were reported in 1984 (49 FR 5187). In general, little aquatic or rodent toxicity was found, and the EPA has concluded that these materials "will not pose an unreasonable risk to terrestrial ecosystems." These substances are not regulated under any specific rules, nor are they cleared for food applications.

The NTP recently concluded that there was no evidence of carcinogenicity in male rats and only equivocal evidence in female rats in a lifetime bioassay assay in which the females ate the equivalent of their own weight of chlorinated paraffins containing 43% chlorine and an average carbon chain length of 23. Mice, which consumed three times their own weight during the test, were said to show clear evidence of carcinogenicity in males and equivocal evidence in females [65b].

In contrast, C-12, 60% chlorinated paraffins were said to show clear evidence of carcinogenicity in both sexes of both species, and the shorter chain product was, in general, more toxic to rodents than the longer chain material [65b].

4. *Other Ingredients:*

Fillers: Fillers seldom are used in food applications, if for no other reason than the general requirement for clear products in such uses. Concern for FDA approval therefore usually is not relevant, but some natural materials such as calcium carbonate do have GRAS status (21 CFR 184.1191). Most fillers originally were natural minerals such as calcium carbonate, clays, or some types of silicate, but synthetic equivalents or replacements are also encountered now. These are of low toxicological concern to either the processor or user, except for the necessity to avoid excessive dust levels during processing and handling.

Asbestos fibers were an integral part of much vinyl floor tile made in the past, but concern for its health effects has eliminated this use.

As is discussed in more detail later in this chapter, the inorganic fillers reduce the combustibility of the final product and often make it more sturdy. Therefore, the net environmental effect is positive, as well as having a desirable economic impact.

Colorants: Several different terms have been used in the past for materials used to impart color to or mask color development in plastics. Some of the most common are dyes, pigments, and colors. A more general term is "colorants" (48 FR 46773), and this includes both dyes (generally thought of as chromophoric organic molecules) and pigments (mostly inorganic materials). Colorants may range from colorless materials designed

to improve whiteness by their reflectant capacity or by obscuring the yellowing that may occur during processing, to substances that possess strong color values.

Here, again, if food, drug, or cosmetic contact is intended, and the material may be expected to become a component of the product, the FDA must approve the substance, and this has led to a series of numbered "FD and C" dyes. Recently several of these have been restricted in use or banned because of the carcinogenicity of the dye, or one of its precursors. Those that are approved are listed in 21 CFR, Parts 74, 81, and 82.

Colorants that are intended for use in packaging and may not reasonably be expected to become a part of the food contents are not subject to FDA regulations (see 40 CFR 18.3297). The FDA no longer will provide letters of approval for this use, and customers may rely on assurance of the suppliers that a substance is not to be considered a food additive, or that it is an appropriate material for the intended use (see 49 FR 2230 for the regulations on this point). Considerable confusion may result from the significant changes in practice that these revised rules have entailed. This policy applies to both FDA-regulated packaging and meat packaging operations controlled by the Department of Agriculture.

The FDA no longer lists as approved for use as indirect additives substances that are approved as direct additives (see 48 FR 48456). Thus, all substances listed at 21 CFR 184 are presumed to be listed under Part 186 also.

Some of the more intensely colored materials are salts of heavy metals such as cadmium, and these may not be used in food applications. Cadmium is listed on the RCRA hazardous waste lists and as a priority pollutant. Any colorants containing cadmium salts will become hazardous wastes if discarded and may be classed as controllable wastes in wastewater. Whether the products containing these colorants are hazardous wastes when discarded depends on the degree to which the colorant is extracted by the EP toxicity test of EPA (48 CFR 261, Appendix II), described earlier.

Substances that yield extractable concentrations greater than that allowed are classed as hazardous and must follow RCRA rules if discarded from a commercial operation. This rule does not apply to household or retail trash. Most commercial applications of heavy metal colorants can pass this test, and therefore there is little concern for leaching of the colorant from discarded products.

There is the usual problem of controlling exposures from dusts of these heavy metal salts. One method in common use is to prepare a master blend of the color or dye with a part of the resin and some liquid component, such as a stabilizer, for charging to the blender or mixer. This often is done away from the general work area and by persons of greater technical training. This procedure helps avoid cross-contamination of colors and conserves expensive materials, as well as reducing the dust exposure.

The same stringent rules of personal hygiene that were discussed under lead stabilizers should be applied here. A useful booklet containing guidelines for the safe handling of dyestuffs is available from the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (1330 Connecticut Avenue, Washington, DC).

Light Stabilizers: These materials are added in small proportions to some formulations. The usual FDA regulations apply to food contact uses.

Many of the light stabilizers belong to the class of substituted benzophenones. These have very low toxicity, are nonirritating, and are approved as direct food additives; therefore, they present no significant hazard as a polymer additive [66].

These stabilizers function by absorbing preferentially the shorter light rays in the ultraviolet or near ultraviolet regions that have sufficient energy to cause bond breakage or radical formation in the polymer. Any light-blocking agent, such as dark pigments or fillers, or some metals that may already be present in the stabilizer, such as zinc, can assist in this protection.

Sometimes alkylated phenols of the resorcinol groups are used. These form benzophenones upon oxidative-induced rearrangement and therefore can serve both as antioxidants and as light stabilizers. They have the same acceptable toxicity properties as the benzophenones.

B. Compounding Operations

A variety of safety hazards can arise during the processing of chemicals in heated rotating equipment. None of these hazards is unique to this industry, and a satisfactory solution appears to have been found for most problems, as reflected in the 1982 OSHA safety statistics for this industry, which compare favorably with those for the private sector as a whole and with other manufacturing groups [67]. This section discusses sources of some of these hazards and how they may be controlled.

1. Storage and Handling: Some of the hazards connected with the raw materials have been discussed earlier. These hazards usually become apparent only if the materials are spilled or otherwise mishandled. Good housekeeping in a workplace is a reflection of good safety practices also, and efforts spent in reducing spillage are rewarded in reduced accident rates. Good lighting, open aisles, proper storage, and segregation of materials all are necessary for an efficient operation and contribute significantly to safety as well.

Pallets of bags or drums should never be stacked more than three high, and preferably only two high, to avoid tilting and spillage. Adequate maneuvering space for forklift trucks must be available, and operation on slopes or ramps should be avoided. Glued or strapped pallets add to the protection from falling containers, but an excess of glue can sometimes cause the bags to rip, increasing spillage. Care should be taken in cutting strapping to avoid a whipping effect, or bags falling when the tension is released, and all strapping materials should be removed to avoid a tripping hazard.

Workers should enter silos, transport vessels, or process vessels only under the control of an effective confined-space entry program and only after all electrical equipment has been locked and tagged out of service. A rescue harness and an outside observer are required by many safety programs. The National Institute for Occupational Safety and Health (NIOSH) recently announced plans for developing a lockout/tagout standard (48 FR 9374) and OSHA earlier published its intentions to prepare a standard for work in confined spaces (44 FR 60333), but neither of these has been finalized. Various insurance companies and trade associations

do provide guidance in this area. The American National Standard Institute (ANSI) issued Standard Z244.1 in 1982 for guidance in situations requiring lockout or tagout. Standard Z117.1 for work in confined spaces was issued in 1977. Consensus standards such as these should be followed in the absence of other codes.

Plasticizers, some stabilizers, lubricants, and the paper and wood used in pelletizing PVC or other raw materials are combustible items. Storage of these materials should conform to local and insurance requirements and should follow the guidelines of the NFPA National Fire Codes in Volume 3 of that series.

Dust masks should be available to employees who may have to clean up solid or powder spills. This is especially true if a silo or railcar of PVC is being emptied completely. There is a tendency for electrostatic attraction to hold fines on the walls of these vessels, and the last material forced out can be much more dusty than the bulk of the material.

2. *Equipment Hazards:* Numerous potentials for accidents are present in the compounding operation workplace, where heavy rotating equipment is operated at elevated temperatures, often with electrical heating units located near cooling water troughs. The operation is principally a materials handling unit process, and thus a variety of physical hazards is present.

Proper mechanical guards and electrical safety devices have been the key to maintaining safe conditions. Equipment should have, as a minimum, the mechanical protection required by the OSHA standards of 29 CFR 1910.216 and should conform to the electrical standards of Subpart S of that rule (Sections 303–304). Equipment manufacturers often design to higher standards, and insurance or local codes may require these improved levels of protection. For example, ground fault protection, especially in areas subject to wet floors, is highly desirable and frequently mandatory.

Walking areas should be designed to prevent slips and falls in the event of spillage of water or plasticizer/stabilizer oils (or both combined — particularly) and also from resin or pellets on the dry floors. Sturdy outdoor grade carpets are useful in nonmanufacturing areas because of the better protection they provide against slips and falls as compared to tile, concrete, or steel walking surfaces.

Equipment and walkways must be arranged so that workers cannot fall into or onto heated or moving equipment or product. In addition to the requisite guardrails, triplines and similar protective devices are useful here.

The comments made in the preceding section regarding lockout and entry work practices are equally applicable here. No repair or cleaning work should be allowed on any heated or moving equipment until the mechanic and the supervisor have inspected the device for safe status and the workman has attached his own effective lockout device. These steps should be performed in reverse order and the equipment tested for proper working condition before it is returned to operational status.

Excessive noise is a normal problem in compounding plants, particularly in the cutting of strip or strands into pellets. Insulation or isolation of cutting and grinding equipment is only partially successful, and noise levels usually exceed the 90 dB allowance at considerable distances from the machines.

The OSHA enforcement policy for its hearing conservation rule [29 CFR 1910.95(c)] allows the use of personal protective equipment when engineering standards are unable to reduce noise levels to 90 dB in a cost-effective manner, as long as the ambient level is below 100 dB. This standard provides an extensive monitoring program for the employee and sets specific departures from the baseline hearing activity that must be reported and investigated to see whether they are related to occupational exposure. Hearing protection that is reliable and effective is available, but some care must be exercised in the choice for each situation [68, 69].

3. Wastes and Emissions: Empty containers should be collected and removed from the operation promptly, as should all scrap and waste. Whether this waste will be regulated under RCRA depends on the type and the results of the EP test discussed earlier and whether the total amount of "hazardous" waste exceeds the RCRA small generator exemption. In any event, current social (and legal) policy places the ultimate responsibility for the future on the generator of the waste, regardless of who actually hauled the waste away or disposed of it. It is far easier to take the necessary steps to assure proper disposal at the time of generation than it is to try to convince local politicians (or the EPA) or concerned neighbors years later that the red color or the oil seeping from a landfill is FDA-approved and therefore is not a health hazard.

The EPA promulgated effluent limitation standards for the plastics molding and forming industries, except for phthalate wastes, on December 17, 1984. See 49 FR 49026, for the rules that are codified at 40 CFR 463.

The molding and forming industries are defined by EPA to include "processes that blend, mold, form, or otherwise process plastic materials into intermediate or final products." The regulations apply to both existing and new facilities and are divided into three categories of effluents. Only direct discharges are affected. Facilities sending their wastes to public treatment systems are not limited to any specific concentrations of pollutants but must follow certain general rules for that class of discharges.

Contact cooling and heating water is limited to maximum average daily concentrations of the 5-day biological oxygen demand (BOD_5), 26 mg/L; oil and grease, 29 mg/L; total suspended solids (TSS), 19 mg/L: and a pH not outside the range of 6.0–9.0 at any time.

Waste cleaning water (water used to clean either the product surfaces or the equipment processing surfaces, including detergent cycles) must not exceed 22 BOD_5, 17 oil and grease, 36 TSS, or 6–9 pH at any time.

The finishing water used in deflashing or machining is limited to a daily average of 37 TSS and a 6–9 pH only. The EPA reserved regulations on phthalate esters, pending further determination of the most appropriate control technology and general effluent guidelines for this class of substances. Vinyl chloride was listed as a pollutant not found in the wastewater.

These regulations are substantially different from those first proposed in February 1984 (49 FR 5862) and represent a successful effort by the industry to demonstrate with convincing data that the original EPA data base on pollutant releases was incorrect. EPA also concluded that public treatment works (POTWs) were not harmed by the wastes for these operations and that the POTWs successfully removed the major portion of the incoming wastes.

The EPA has not scheduled the plastics forming industry for a specific air emissions rule under a new source performance standard (NSPS). Some associated operations that are controlled include storage of volatile liquids, and vinyl coating and printing. Under this rule, if printing inks contain more than 50% volatile solvent, abatement equipment must be installed that reduces emissions by 85%. Final rules for pressure-sensitive tapes and adhesives were promulgated at 48 FR 48368. These rules set allowable limits for quantities of volatile organic solvents released in the air per unit of production. The general trend is to phase out organic solvents and replace them at least partially with water-based coatings.

The EPA has commenced study of the application of polymeric coatings to substrates (docket no. A-83-42) and has issued a source category survey for comment.

Existing plants in these process categories will not be covered by these new source performance rules. However, they, and all existing plants in nonspecified categories, are covered by other sections of the Clean Air Act that require the states to produce rules to reduce the same classes of emissions. The states must develop a state implementation plan (SIP) that sets rules at various levels of stringency that all facility operations must meet by at least 1987. Depending on whether the local air quality district has attained the national ambient air quality standards, the SIP can invoke emission standards that may be even more stringent than the NSPS rules. If the area is nonattainment, an offset of similar emissions at another source is required for any new source or expansion. If the area is in attainment, the nondegradation rules can place very tight limits on any incremental emissions. In these cases, the best available abatement technology of the NSPS rules usually is applied to existing plants. The phthalate esters are classed as volatile substances by the EPA (48 FR 48328), so almost any organic substance is covered. General statements cannot be made on the specifics of these local rules; rather, the local air pollution authority should be consulted for details.

The EPA has promulgated many of the reportable quantities (RQs) that it is required to set under CERCLA (Superfund). Any spills or releases outside the immediate work environment greater than an RQ for that substance is required to be reported by telephone within 24 hours to the National Reponse Center, at (800) 424-8802. The present RQs for substances of interest to the plastics industry are generally in the 10—1000 lb range for the heavy metals such as cadmium, chromate salts, lead, zinc, and for many phthalate esters. Chlorinated solvents are generally in the 1000 lb range. These quantities are listed at 40 CFR 302.4.

The EPA has under consideration revisions for the RQs based on its reevaluation of the chronic health effects of these materials, and many of the salts of the heavy metals will be assigned RQs in the 10—100 lb range. Users of these salts as stabilizers should be alert for issuance of these revised values. See 50 FR 13514, 4 April 1985 for a discussion of this reevaluation process.

The discussion in this section applies equally to both the compounding and the processing industries. The Vinyl Institute provides a booklet, "Facts About the Disposal of Solid Wastes Containing PVC," that processors may find useful.

C. Fabrication Processes

1. General: Fabrication of final or intermediate products may begin with the basic raw materials (in which case the discussions in Section II of this chapter apply), or it may use preprocessed compounds and have to deal only with situations specific to the final stages. In either case there are many similarities in the hazards and potential risks that may be present. The larger the operation, the more likely it is that both processes will be located in the same facility.

One significant difference between the two processes is that the wastes from the fabrication step are likely to be innocuous as far as having significant health and environmental hazards. The absence of risk from exposure to fabricated products has been recognized by OSHA, which has exempted "articles" from its hazard communication policy (29 CFR 1910.1200).

Process or product wastes that cannot be recycled or converted into by-products usually can be discarded at conventional sanitary waste sites, subjected only in some instances to the EP test described in Section II. Wastewater is unlikely to be contaminated beyond what can occur in any manufacturing operation from accidental releases of lubricating fluids or cleaning materials. Specific wastewater regulations were discussed in the preceding section. Air emissions and worker exposures usually are negligible as long as adequate precautions are taken [70, 71]. If coatings or adhesives are involved in the process, emission controls of the solvents may be required by local authorities.

2. Equipment Hazards: Final fabrication of products uses a wider range of machinery and operations than are needed in compound preparation. It is not surprising that an SPI analysis of injury reports to OSHA shows higher incidence and severity rates in processes that involve presses, stampers, and similar heavy-duty moving equipment than for continuous processes not requiring individual operator intervention.

Guards and shielding are required for all such machinery by OSHA rule 29 CFR 1910.216 and aggressive preventive maintenance programs are necessary to assure proper operation and integrity of these devices.

Many of these operations are on a large scale, using high speed, automatic equipment that feeds conveying lines and packaging machinery in complex arrangements. Operators and maintenance workers must act promptly in case of a malfunction to prevent expensive losses of material and product. Adequate care is necessary in both equipment design and supervisory instructions to avoid accidents in such situations.

Accident report analyses show that the great majority of disabling accidents in the plastics industry, as in the other manufacturing groups, is caused by slips, falls, striking against or by, or the various other categories that cover hitting or being hit by solid objects. Some of the causes that might be expected to be related to the plastic materials being processed, such as burns or toxic effects, represent a surprisingly small proportion of such causes.

Table 3 compares Bureau of Labor Statistics data for 1982 injuries with similar data collected by the SPI in a survey of 437 companies with 589 facilities employing 77,344 workers. Both the resin producers and the processors exceeded the safety record of the total private sector in all categories. Within these groups, the larger companies and the larger facilities generally had better records than the smaller ones. The entire

TABLE 3 1982 Injury Statistics for Plastic Producers and Processors

National data	Incidence per 100 employees		
	All injuries/ illnesses	Lost work days	Severity
Private sector	7.7	3.5	58.7
Manufacturing	10.2	5.4	75.0
Plastics industry			
Resin/material suppliers (113)[a]	5.01	1.97	49.5
Processors (223)	6.05	2.16	35.7
Machinery, equipment (68)	13.0	3.92	50.5
Moldmakers (40)	13.1	2.51	40.4
Total (437)	8.7	3.28	60.5

[a]Number of facilities reporting.

industry as a group exceeded the record of the national manufacturing sector. These data reflect a substantial commitment to safety by both the employees and the employers, but also present a challenge for further reductions through better training, improvement of equipment, and closer supervision.

III. PRODUCT APPLICATIONS

A. General

This section discusses several major areas in which PVC products are used. Considerable emphasis is placed on the regulatory status in each area because, in many cases, regulations have become at least as important as economics or customer preference in controlling the growth or breadth of many applications. The perceptions of the lawmakers and the rulemakers, and the political influence of various interest groups, have played a major role in the recent history of this industry. An effort is made to discuss the bases for these concerns and to present the salient data relative to them. Technology has, unfortunately, played a less important part than have these other factors. Future growth will depend in great part on how responsive the industry becomes to these concerns, and how effective that response is.

B. Food Packaging

A survey [72] by the SPI of its members in 1983 disclosed that about 7.8% of the American food supply is packaged in PVC materials and that this segment was expected to grow more than 11% in the next 5 years if the FDA took positive action in regard to the regulatory status of PVC in this area.

It is recognized that PVC has GRAS status at the FDA because of its widespread use for food packaging before 1958. In 1975 the FDA proposed (40 FR 40529), however, to withdraw this status for rigid formulations because of concern for migration of residual VC into the package contents. That proposal was withdrawn (51 FR 4173) in 1986, and the safety of PVC food packaging was reaffirmed as long as it met the FDA limits for residual VC.

The miniature liquor bottle market had been denied to PVC in 1973 when it was found that the contents were "adulterated" with ppm levels of VC. The Bureau of Alcohol, Tobacco, and Firearms (BATF) has asked the FDA whether it would be suitable to reinstitute this use, and the SPI survey referred to above is one step that the FDA required before it would respond to the BATF request for advice. However, plastic bottles as a class now are permitted for liquor use (47 FR 43944, codified at 27 CFR 19.11), and PVC has become acceptable now that the FDA has withdrawn the 1975 proposal.

Most of the foods packaged in PVC are contacted by flexible materials. The SPI survey showed 5.35% packaged at least partially in flexible films, and 1.95% in packages with PVC-containing coatings. The safety of these classes of packages never was questioned by the FDA, but nevertheless, a "cloud" was placed over all forms of PVC for food contact use by the 1975 proposal. That "cloud" has now been dispelled.

Rigid bottles and jars currently provide protection for only about 0.8% of the food supply, and rigid film is used in about 0.44%. These uses are expected to expand to 0.7 and 0.9%, respectively, if the FDA does proceed to restate the GRAS status formally.

The Supreme Court issued a ruling of major importance in 1982 in the case of *Kennedy* v. *Monsanto* [613 F. 2d 947 (DC Cir. 1979)] in which it ruled that the FDA may not suppose that a material in a package wall will migrate into the package contents, but must demonstrate its presence by scientifically sound procedures. The court also stated that there is a de minimus level of concern for health effects below which the FDA need not regulate nor consider the Delaney clause of the Food Act to be applicable. The FDA has been struggling for nearly 10 years to find a way to set a practical limit on trace components of foods, but has as yet been unsuccessful. It has reproposed (47 FR 14464) a "sensitivity of the method" procedure that would ignore a material not found to be present by an analytical procedure that is sensitive enough to show its presence at any concentration thought to be of significant risk, and it has practiced this procedure in some recent rulemakings that have been upheld in the courts, but it has not promulgated the rule.

Taken with the Supreme Court decision in the benzene case (*Industrial Union Dept.* v. *Am. Petrol. Inst.*, No. 78-911) in which OSHA was told that it must find a significant risk at prevailing levels before a regulation may be promulgated, the Monsanto case places a much greater burden of proof on the regulatory agencies. At the same time, the continually increasing sensitivity of analytical methods reveals a growing number of trace contaminants, both natural and man-made, in all our foodstuff. It will be necessary for both Congress and the agencies to adopt a more realistic and scientifically based attitude toward minor components before this situation can be resolved in an acceptable manner.

The issue in the case of PVC packaging or potable water pipe revolves around the question of whether the components of the package, and in

some cases the impurities in these components, can migrate into the package contents in sufficient quantity to present a significant, or even a detectable risk to human health. Before the Monsanto decision, the FDA has assumed that all the potential migrations would occur into the package, ignoring the loss from the wall in the opposite direction or the retention of a portion of the migrant within the polymer matrix.

The diffusion of small molecules from and through plastic matrices follows a Fickian process involving a relaxation process of the localized swollen polymer [73–75]. A concentration gradient is established in the wall of a pipe or food container that provides the driving force for solute movement, and at equilibrium the migration rate is a function of the square of time, the temperature, and the residual concentration. The principal limiting factor is the original concentration but theoretical and practical considerations also set a lower limit of concentration below which little significant migration occurs [76–78]. Experience has confirmed the theoretical prediction that at VC concentrations in rigid PVC of 1 ppm or less, the concentrations in water will be below the practical detection limit of 1 or 2 ppb [79]. The detection limits in nonaqueous food-simulating solvents is about 1 ppb, and under exaggerated conditions of storage some migration can be seen at fractional ppm residual VC levels [80].

The FDA requires a series of simulated storage tests on food packaging for any indirect additive petition. A review of these protocols by A. D. Little [81] has found several problems, including requirements for testing temperature and periods that are not representative of realistic use conditions, effects on the package wall by swelling of the test solvent, and inappropriate solvents. The consultants concluded that in the prescribed tests "the variability of the degree of exaggeration is such that prediction of behavior in untested systems will have a high degree of uncertainty." In other words, the tests are so severe that they do not relate adequately to real use conditions.

Once the degree of migration has been estimated, the next step is a judgment of the risk to the consumer from this degree of exposure. The use of quantitative risk assessment has grown rapidly in the last few years [82–84]. An effort is made to interpret existing data, which usually consist of animal toxicity results, in a manner that measures the human risk. Properly done, this should result in an evaluation of all relevant existing data [83], including the significance of the animal test data to the postulated human exposure [85]. In reality, however, the application has centered on carcinogenicity concerns and has utilized primarily bioassay data from the National Cancer Institute or its successor, the National Toxicology Program [86, 87]. The standard practice has been to accept any positive study in animals as indicative of human hazard, and to equate the human risk as being equal to that of the most sensitive test species. Quantitative risk is estimated by a series of "prudent" conservative assumptions, ignoring all comparative pharmacokinetics or other relevant data, to give a result that may be several orders of magnitude too high [88], if indeed it has any applicability to humans [89].

The National Academy of Science has urged that a better scientific foundation be laid for this process [82], and this is one of the problems with which the FDA is struggling in its effort to develop a carcinogen policy (44 FR 17070, 47 FR 4792).

The FDA has indicated, however, that it will apply its so-called constituent policy, which it has been using on an informal basis for direct

food additives such as dyes, to indirect additives also (see 49 FR 13018). Under this policy, additives that themselves are not carcinogenic but contain impurities that are suspected of carcinogenicity will be evaluated by a conservative risk assessment procedure. If the resulting risk is found to be sufficiently small, the additive may be deemed to be safe. This policy allows the FDA to avoid strict application of the Delaney clause to this particular application.

A much wider variety of foods is packaged in PVC in Europe [61, 90], including butter and butter substitutes, cooking oil, wine, and carbonated beverages including beer. In the United States many nonconsumptive products, such as cosmetics and shampoos and a variety of other products, are shipped in PVC.

The plastic packaging business is expected to grow at substantial rates in the future, at least in keeping with the 31% annual growth rate of the past two decades [91]. Much of this will be at the expense of existing glass, paper, and metal markets, but significant new applications are expected also. Just how high a growth rate is maintained, and what position PVC will command, will depend largely on the regulatory position of the FDA. A more specific discussion of the regulatory status of individual components likely to be present in food packaging was presented in Section II.A above.

Concern has arisen for the evolution of toxic gases during the use of PVC products. Stabilizers are used for the express purpose of preventing significant formation of hydrogen chloride during the heat history experienced in fabrication operations, and sufficient stabilization capacity remains for normal service. A symptom termed "meat wrapper asthma" has been described as arising from continuing exposure to vapors of HCl and plasticizers generated by the hot wire melting of PVC film [92, 93].

Ordinarily, the ventilation used in the processing operations for other industrial hygiene reasons is adequate to protect the employees from this hazard, and no occupational problem has developed in fabrication employees similar to that described for meat wrappers. A more realistic, and higher risk hazard does develop occasionally when an inadequately stabilized batch of compound is processed. An explosive release of HCl can occur under these conditions, and there are reports of extruder heads being blown off the equipment with serious results. Simple "press heat stability" tests of each batch of compound can anticipate this condition.

Sangha et al. have shown [94] that in the 150–175°C (300–350°F) temperature range normally used for plasticized PVC processing, the emitted vapors are less toxic than those from Douglas fir at the same temperature. The toxicity increases rapidly at higher temperatures, but of course PVC never is exposed deliberately to such temperatures. Workers at Harvard report that little HCl is found in hot wire cutting of PVC film below 150°C (300°F) but reaches a maximum by 200°C (400°F), and that the acid is associated with particular plasticizer emissions [95].

Studies by NIOSH have led to the conclusion that the solution to the "asthma" problem is to supply adequate point ventilation at the workplace, and/or to use lower temperature cutting devices [96].

C. Potable Water Use

One of the major growth areas of PVC has been in the extrusion and molding of rigid shapes for water use. Irrigation pipe, drains, conduits and

vents, and associated fittings, have made up a substantial portion of this application, but potable water pipe has been the major contributor. It also represents an area of great controversy.

Much of the growth has come at the expense of conventional metal products [97, 98] and has been accelerated by the greater ability of the homeowner to perform repairs and installation with plastics as compared to metals, and to the lower price of plastics. The manufacturers of the metal pipe and the organized labor groups involved have defended their positions vigorously and have invoked various health and safety matters in their efforts to preserve the past ascendency of metal.

Three issues in particular have been involved: the leaching of materials from or through plastic into potable water [99, 100], and the combustibility of plastics [101–103], and the health effects of working with plastic pipe [104, 105]. Each of these is discussed below.

Combustibility is covered in greater detail in the subsequent section. Regarding the possibility of a significant problem of combustion of plastic water supply and drain piping in the average home, it is most unlikely that these items will be involved in early stages of a fire because of their location within walls and because they contain water, often under pressure. Thus, by the time the piping is involve, the home is not habitable and even if toxic products were involved, there would be no measurable contribution to human risk.

A contractor for the EPA has estimated that the average home contains about 500 lb of PVC in its building materials, exclusive of consumer goods and plumbing or siding [106]. This compares to about 200 ft of PVC pipe for a house fully plumbed with plastic and several tons of combustible clothing and furniture. As is discussed in the next section, it is unlikely that the plumbing, specifically, or plastics in general, make any significant contribution to fire toxicity under real-life conditions.

The controversy over leaching has several facets. These include the extraction of substances from the pipe, the passage of external ground contaminants through the pipe into the water, and the addition of solvents from joint cements to the water.

The argument reached a crescendo when a union coalition persuaded the California Housing and Community Development Commission to reject the recommendation of its staff that California adopt the Uniform Plumbing Code, which would extend the use of CPVC and other plastic pipe to uses inside residential structures. These materials had been acceptable for distribution lines, for drain, waste, and vent lines inside homes, and for all uses in commercial buildings for several years. One basis for this decision was a study [107] that reported the presence of several organic solvents and DEHP in water after laboratory tests of simulated use conditions. The DEHP later was found to be the result of laboratory contamination of the samples, and the solvents were those expected as by-products of either chlorination of PVC or CPVC or from raw water chlorination, or were from the cements used to join the pipe sections [108].

The issue of pipe permeation was raised by a later report that found that water inside plastic pipe immersed in a bath of solvents showed traces of those solvents in the water [109]. The solvents chosen were some of those for which plastic pipe service is not recommended. The report had several technical faults, including the lack of suitable controls and of proper quality assurance procedures. For example, the samples of water from metal pipe showed solvent contamination in some cases also.

The Society of the Plastics Industry sponsored an extensive review of the problem at the contractor selected by the state, SRI International (SRI), which released a report [110] in March 1983 that made the following points:

1. Plastic pipe has been used without apparent ill effect for many years.
2. No clear environmental preference between plastic and metal pipe has emerged.
3. No evidence has been presented that either metal or plastic pipe ought to be banned. No immediate and obvious threat to the health of workers in California is apparent.
4. In fire-rated construction, fire stops and other construction details permit the plastic drain, waste, and vent systems to pass the fire rating tests.

The report suggested further studies of worker health effects from solvents, and pointed out that plastic pipe reduced the frequency of traumatic injury to plumbers as compared to the use of metal fittings.

This latter conclusion was supported by an analysis of the OSHA data for lost work days of California plumbers in 1979 [111], which showed a significantly lower incidence of lost-time accidents for causes traceable to plastic pipe use than for accidents caused by metal pipe working.

There had been suggestions that persons working with plastic pipe are exposed to harmful materials during the cutting of the pipe and from the cementing steps. Much plastic pipe is cut with knives or tubing cutters, which generate no particulate matter; when cut with saw, however, plastics yield "sawdust" that is coarser than that from either metal or wood. In one test [79], an 18-tooth handsaw gave no material below 150 μm size when cutting PVC or CPVC pipe, and the exposure of the worker to respirable dust was 0.4 mg/m^3, or approximately background, during the test. Under the same conditions copper and iron pipe gave material down to, but not below, 30 μm, and maple wood produced 0.1% of particles below 30 μm. Thus, while the particles from plastic are coarser than those from metals, neither material generates a significant amount of particles in the respirable range below 10 μm.

Efforts have been underway by NIOSH for several years to obtain plumbers' workplace exposure data for solvents, but a lack of appropriate available work sites has delayed completion of the study. Interim results released in mid-1983 state that no exposure exceeding OSHA permissible limits were found [105]. The SRI report also contains a collection of field measurements, all of which are several orders of magnitude lower than OSHA limits.

The solvents most commonly used in cements for PVC and CPVC pipe are mixtures of cyclohexane, tetrahydrofuran, and methyl ethyl ketone. Less commonly, dimethylformamide, and occasionally toluene, are used. Table 4 summarizes the recommended exposure limits to these materials and offers some toxicity data [12]. Each of these materials is a powerful solvent for natural oils and will cause skin irritation from continued exposure. The cement is a viscous solution of resin, and contact with the skin leaves a deposit of polymer that is difficult to remove without exposure to a great excess of fresh solvent. Thus, care should be taken to prevent skin contact. Each of these materials is flammable and presents toxicity problems

TABLE 4 Toxicity Data for Several Common Pipe Cement Solvents[a]

	CHO Cyclo-hexanone	MEK Methyl ethyl ketone	THF Tetra-hydrofuran	TOL Toluene	DMF Dimethyl-formamide
Oral, rat LD_{50}, g/kg	1.6	3.4	3.0	5.0	2.8
Irritation					
Eye, ppm	75	350	—	300	—
Skin	Mild	Moderate	Moderate	Mild	Mild
OSHA exposure Limit, ppm	50	200	200	200	10
Aquatic toxicity, TL_{96}, ppm	10–100	>1000	—	10–100	—
Biodegradability	Good	Good	Good	Good	Good
Bioassay	—	—	—	Negative	—
ITC test program	Yes	Yes	No	No	No

[a]Data primarily from Ref. 12.

at high concentrations. Particularly in home use, the containers should be kept tightly closed and out of the reach of children. The manufacturer's directions for use should be followed closely.

The extraction of residual solvent from cemented joints follows a sharply falling exponential curve similar to that for extraction into foods, as discussed in Section B earlier. Only in new homes are significant quantities found in the water, and this is reduced substantially by the flushing of the pipes during the later stages of construction, so that exposure even during the first days of occupancy are far below the recommended acceptable levels for drinking water [110].

The migration of solvents through or from the section of the pipe swollen during the cementing process follows the same exponential decay curve that was described in the preceding section for residual monomer. Some typical results from simulated test systems are shown in Table 5. Reference 80 contains summaries of several other tests for cement solvents, stabilizers, and other organic materials.

In the study summarized in Table 5, lengths of pipe containing joints prepared with common primer and cement were filled with water and held for the indicated time before analysis. The test sections were emptied and refilled with fresh water to obtain the data in the lower section of the table. It can be seen that the concentration reaches a limit quickly and that flushing of the pipe reduces the amount of water substantially. No replicates were used in this study, so the problem of analytical precision at these low levels is apparent, particularly in the refilled tests.

TABLE 5 Pipe Cement Solvents Extracted From PVC Pipe as a Function of Time[a]

Solvent	Concentration (ppm)					
	2 hrs.	8 hrs.	24 hrs.	48 hrs.	120 hrs.	240 hrs.
First filling						
MEK	0.2	0.58	0.7	1.5	2.2	2.3
THF	1.0	2.9	2.7	7.8	5.6	4.2
CHO	0.1	0.2	0.1	1.2	1.9	0.5
DMF	3.1	4.9	16	11	31	7.1
Second filling						
MEK	0.1	—	0.4	0.4	0.5	—
THF	0.5	—	1.9	2.0	2.4	—
CHO	0.7	—	1.9	0.3	0.1	—
DMF	1.9	—	8.3	7.1	5.6	—

[a]Data from Ref. 110.

Suggestions were made by the opponents of plastic pipe that there was reason to expect elevated cancer incidence among persons who consumed water from plastic pipe, or those who installed it. Estimations of cancer risk by the extremely conservative linear-no threshold extrapolation method showed negligible risks for potential animal carcinogens that may be, or have been, present such as chloroform or carbon tetrachloride [110]. The solvents discussed in this section are not suspect carcinogens for either animals or humans; therefore no such risk exists. Actually, DMF and its primary metabolite are undergoing preliminary studies for potential use as a cancer growth controlling substance [112].

A recent report suggested that there should be concern because of the finding of six lymphoma cases in 3 years among active and retired California plumbers when only three were expected [113]. Cancer incidence data by occupation and location are not plentiful, but a 1980 analysis [114] of the San Francisco Area Tumor Registry for 1972–1977 found an unusually low ratio of observed to expected cases of cancer at all sites, and for respiratory cancer. These were found at only 50–60% of the incidence in the nation. There were no lymphoma cases for this group during the study period. Thus, this study does not confirm the excess of lymphomas suggested in the other study.

The use of PVC pipe is expected to continued to expand for both potable water and other uses. There is no evidence that there is any detectable hazard involved in this use, and there are many economic and social benefits from this application.

Federal regulation of potable water pipe has been assigned to the EPA by a memorandum of understanding between it and the FDA (44 FR 42775). No direct rulemaking has been started by the EPA, but many potential contaminants are regulated by the Interim Primary Drinking Water Regulations (40 CFR 141). Local use is controlled by a variety of buliding codes and local regulations, most of which are permissive for the use of plastic plumbing in the absence of specific regulations to the contrary. Included in the codes that allow unlimited application of plastic piping are those of the Southern Building Conference, the Building Officials and Code Administrator International, the National Plumbing Code, and the Department of Housing and Urban Development of the Federal Housing Administration (29 CFR 200.929 et seq.). The aim of the industry has been to get direct approvals in place, rather than simply the absence of disapproval. These efforts undoubtedly will be the center of continuing controversy by their opponents.

Self-policing of potable water pipe is supplied through participation in the voluntary National Sanitation Foundation (NSF) program of inspection and certification. Many plumbing codes require the presence of the NSF seal on plumbing supplies, either directly or indirectly by requiring adherence to the ASTM standards, which in turn specify compliance with NSF standard 14. Under this system the NSF performs on-site inspection of production facilities and makes nonscheduled tests of pipe and resin formulations for physical properties and extractability. Extraction levels for water contaminants must not exceed the maximum contaminant levels (MCL) set by the EPA under the Safe Drinking Water Act. Typical results from the NSF program are shown in Table 6 [85].

Trace amounts of VC have been found in some water distribution systems plumbed with PVC pipe [119, 120]. These samples were from systems prepared several years ago from resins containing 1–2000 ppm of residual VC as compared to the 1–3 ppm now common under the voluntary industry standard of 10 ppm maximum that is enforced by the NSF. Recently the NSF has stated that pipe producers consistently are producing pipe now that contains less than 10 ppm residual vinyl chloride and that water exposed to this pipe does not attain detectable levels of vinyl chloride by a test sensitive to 2 ppb [116].

Further studies on this problem sponsored by the SPI have shown that the suspected permeation of plastic pipe is due more to the pipe gasket materials rather than the pipe itself [117] except under conditions of extreme ground contamination. No solvent contamination was found within ungasketed plastic pipe unless sufficient solvent was present outside the pipe to swell and soften it to the point of being unsuitable for pressure service. Toluene swelled PVC pipe badly in 37 days, and 1,1,1-trichloroethane and hexane showed no permeation in unjointed pipe in 42 days. Toluene penetrated gasket joints of all types of pipe in about 1 week, hexane in about 2 weeks, and trichloroethane in about 3 weeks. Asbestos cement pipe showed permeation by toluene in unjointed pipe in 1 week, and by trichloroethane in 2 weeks. It was not permeated by hexane. Unjointed ductile iron pipe was not permeated by any of the solvents during the 42-day test. Most localities have existing rules prohibiting the installation of water supply pipe in contaminated soil, and adherence to common sense in the design and placement of water mains should avoid any hazard from external contamination.

TABLE 6 Static Extraction of Chloroorganics from New PVC or CPVC Pipe

Substance	Extraction no.[a]	No. of samples	Results, ppb ND[b]	1–3	3–5	5–10
PVC pipe						
Total haloforms[c]	1	7	7	0	0	0
	2	7	4	3	0	0
	3	7	5	2	0	0
1,1,1-trichloroethane	1	6	6	0	0	0
	2	6	5	1	0	0
	3	6	6	0	0	0
Trichloroethylene	1	6	4	2	0	0
	2	6	4	2	0	0
	3	6	3	3	0	0
Tetrachloroethylene	1	6	5	1	0	0
	2	6	6	0	0	0
	3	6	5	1	0	0
CPVC Pipe						
Total haloforms	1	11	3	4	4	0
	2	12	2	7	3	0
	3	12	1	7	2	2
1,1,1-trichloroethane	1	11	8	3	0	0
	2	11	10	1	0	0
	3	11	11	0	0	0
Trichloroethylene	1	11	9	2	0	0
	2	11	11	0	0	0
	3	11	9	2	0	0
Tetrachloroethylene	1	11	4	7	0	0
	2	11	10	0	1	0
	3	11	9	1	1	0

[a]First extraction, 24 h at 37°C, second extraction 24 h at 37°C, third extraction, 72 h at 37°C.
[b]Limit of detection, 0.3 ppb.
[c]Primarily chloroform.
Source: Adapted from Ref. 79.

One case illustrating the wisdom of such rules has been seen at Lekkerkerk, Netherlands [118]. About 270 homes were built on a former dump site that was heavily contaminated with solvents, including toluene, which was shown in the Battelle study discussed above to be a powerful swelling agent for the PVC plumbing that was used in the water distribution system for these homes. Solvent vapors entered the homes from the soil and also penetrated the plumbing, assisted by the high water level in the area. The solution chosen for this case was to replace both the

contaminated soil and the existing piping system. PVC was chosen again as the material for the piping.

In addition to the standards above, the NSF periodically retests the products for compliance as well as each time a resin compounder or processor changes the formulation.

In another effort to bring the debate to a conclusion, the Society of the Plastics Industry agreed in early 1984 to fund yet another permeation and extraction study, and allowed the California Department of Housing and Community Development to choose the contractor this time also. In mid-1985 it was announced that the study had been terminated because of "serious errors in testing" — that is, failure to follow the test protocol, especially the quality assurance procedures. The Vinyl Institute of the SPI then decided to go ahead with their own program in an effort to get some credible data on the record. McKesson Environmental Services was engaged to follow the exact protocol selected by California for its unsuccessful attempts to evaluate the leaching of organic materials from CPVC and copper piping systems over a period of 75 days representing construction and early occupancy. The report was released in early 1986 [120b]. The results for CPVC pipe were as follows:

1. Trihalomethanes and three cement constituents are the volatile components found in water in this study.
2. Trihalomethane concentrations found in the discharge from the municipal water tube assemblies during the usage period correlate well with concentrations in the municipal input water, and a contribution from the pipe assemblies cannot be established.
3. Chloroform, found in the preoccupancy period in the protocol water tube assembly discharge, disappeared rapidly and was not found during the usage period.
4. No vinyl chloride or benzene was detected.
5. Other than isolated incidents involving toluene and phthalates at low ppb levels, no other contaminants were found.
6. Concentrations of the three cement constituents (tetrahydrofuran, cyclohexanone, and methyl ethyl ketone) fell rapidly during the preoccupancy period and continued to decline at a slower rate in the usage period.

For metal plumbing, the following summary was provided.

1. Water type has a significant effect on extractability of metals from the tubing assemblies and on the resulting water quality.
2. Higher levels of copper were leached in soft water.
3. Lead was calculated to remain above the 25 ppb level in soft water up to the 105th day.
4. In domestic water (as with any corrosive water), extractable metal levels correlate directly with chlorine concentration.

These results confirmed the data already in the general literature [121] and the rulemaking record in California [110] and found no new or unrecognized hazards from any of the conventional plumbing systems.

Over the years the EPA has received mixed advice from its National Drinking Water Advisory Council on its inquiry about the desirability of banning lead water pipe, and/or lead-containing solders. Congress took

matters into its own hands in June 1986, and the Safe Drinking Water Act reauthorization requires the phasing out of lead-containing solders and potable water pipes. Considerable data has been accumulated on public exposure to heavy metals through these sources [121a], and the EPA continues to consider the steps needed to reduce the health risks involved from these exposures. Much more stringent limits on public water supplies were announced in late 1991.

The EPA has established at 40 CFR 141.50 a recommended maximum concentration limit (RMCL, a nonenforceable goal) of zero for VC (50 FR 46880) and has proposed a maximum concentration limit (MCL, an enforceable limit in public water supplies) of 1 ppb (50 FR 46902).

There appears to be no health, safety, or environmental reason preventing PVC or CPVC pipe from continuing to participate fully in the residential and commercial plumbing market. Brown [121b] reviewed the literature on this problem and concluded: "At present there is no convincing evidence that any of the modern plumbing systems would pose risks to plumbers, the general population, or the nonhuman environment that would be unacceptable. . ." The interrelationship between the self-policing by the industry and the regulatory and building code systems assures that the products will continue to be suitable for their intended uses.

D. Combustion Toxicity

Perhaps no other aspect of consumer applications of plastic products has aroused as much controversy as the question of the safety of the products under fire conditions, and the effects of the combustion products on the health of exposed persons.

Catastrophes such as the fires at the Beverly Hills Supper Club in May 1977, the MGM Grand Hotel on November 21, 1980, the Air Canada airplane in June 1983, and other highly publicized events all brought major attention to the safety questions being discussed.

Almost all compounds of carbon can be oxidized to carbon dioxide when subjected to adequate conditions of temperature and oxygen supply [122]. The major exceptions to this rule are substances in which the carbon already is combined with elements more electronegative than oxygen, such as the halogens. Highly chlorinated and fluorinated compounds are resistant to oxidation, but even the chlorinated substances can be destroyed under proper thermal conditions.

The products of "complete" combustion of chlorocarbons are carbon dioxide, water, and chlorine. Conditions adequate to reach this result seldom are achieved except under careful control, so that the normal products are carbon dioxide and carbon monoxide from the carbon atoms, a mixture of free chlorine and hydrogen chloride from the chlorine components, and water. Even under strenuous incineration conditions, the free chlorine content is minor.

The tendency to form free chlorine is reduced even further when PVC is burned, because of the facile removal of HCl from the polymer chain upon heating [123, 124]. Combustion proceeds at the interface between the air (oxygen) supply and the fuel surface, or interface if a gas [125]. Thus extensive preheating occurs before solid surfaces are hot enough to ignite themselves or to supply a source of combustible gas because of pyrolysis; ordinarily, both solid surfaces and evolved gases are burning at the same time, especially at the flame front, as is apparent by watching the burning of a fresh piece of firewood in a fireplace. Articles of PVC

thus are subject to considerable preheating, and most of the chlorine content is removed as HCl, reducing the opportunity of the chlorine to participate in further reactions. The normal combustion products from PVC are found to be, in decreasing amounts: carbon dioxide, hydrogen chloride, and carbon monoxide, with much smaller amounts of benzene and a variety of C_1–C_7 hydrocarbons. Benzene, and smaller amounts of toluene, are formed by cyclization of fragments of the dehydrochlorinated polymer chain. The shorter alkane and alkene products also are formed by fragmentation and recombinations. The authors cited above show that the fraction of carbon evolving as carbon monoxide is a function of the temperature and the air supply. Reduced oxygen availability increases the carbon monoxide ratio, as expected. Increased temperature also increases that ratio, due to more rapid char formation, with resultant poorer penetration of the oxygen into the burning mass. Increasing temperature and air supply both decrease the amount of the hydrocarbon by-products.

No VC is formed by combustion of PVC; the polymer does not degrade to its monomer in any circumstance. Any residual VC that may be present in the resin is released, of course [126], but currently that is a very small amount, and in plasticized products is almost undetectable (less than a very few ppb).

The physical state of the burning sample affects the composition of the combustion products [127]. Thick cross sections of rigid samples burn less completely than do thin samples: the presence of plasticizers increases the degree of combustion, and fillers and flame retardants decrease the completeness of the reaction with air. Typical weight ratios of CO_2/CO under experimental conditions range from 1.5:1 to 2:1 [124].

Combustion of copolymers of vinyl acetate yields measurable quantities of acetic acid, formed by pyrolysis before combustion, just as HCl is formed. The theoretical quantity of HCl expected from a pure homopolymer is about 58.5% by weight of the sample, which usually is close to the amount obtained [128]. Yields of acetic acid are below the theoretical amount due to the combustibility of that substance [91].

Formulated products produce a much wider range of pyrolysis and/or combustion products because of the presence of plasticizers and stabilizers. These formulations must be evaluated on a case-by-case basis.

The key question relevant to the safety of the public is whether these combustion products are more hazardous than those produced by potential substitutes, particularly the "natural" materials used before the introduction of synthetic materials, such as wood, cotton, and wool. A companion issue is whether the use of synthetic materials has increased the combustibility of interior furnishings, that is, the ease of ignition, and the rate of flame spread once a fire has been initiated. Each of these points is discussed below.

The unfortunate fact is that there are no reliable tests that can measure these important properties under real fire conditions, despite the significant research effort that has been expended during the past two decades [103, 128–134]. One major problem is that results vary with time as the condition of the sample changes during static tests [135]. Laboratory simulation of the amount and toxicity of combustion products can be made under carefully measured conditions, but none of these can depict adequately an area of fire of mixed fuels under real-life conditions.

An advisory committee of NFPA, reviewing the results of a workshop on toxic hazard assessment of combustion products [136], concluded that

lethality was the most appropriate end point for presently available tests and that a tenfold difference in test results is needed to constitute a significant difference in lethality between test substances. The participants were not optimistic that a more accurate test system would be available in the near future [137]. An active test development program is underway at the National Bureau of Standards [138].

The picture is fairly clear in the case of an open fire in a closed area. No person can survive the heat and carbon monoxide under these conditions, and immediate withdrawal is the only solution. Escape is considered a satisfactory conclusion to the problem.

A different situation exists for those who are remote from the fire, such as the occupants of the upper floors of a high-rise building, firefighters downwind of the flames, or even persons asleep in a bedroom with fire smoldering in a living room couch. The relative toxicity of combustion products becomes a serious consideration under these conditions.

Numerous tests have been developed in the attempts to answer this question. They have addressed variously the overt acute toxicity, the rate of incapacitation, the relative rates of survival of the test animals, and the density of the smoke produced. The latter affects to some degree the orientation ability of the victim, and thus the capacity to escape, but it is not a measure of the toxicity of the fumes [139]. These tests have been conducted on scales ranging from a few grams in a test unit, to small colonies of test animals, to attempted simulations of whole-room fires. Several reviewers have concluded recently that none of these tests are adequate for measuring the risks presented by a specific fire condition, nor are they suitable for the ranking of materials on the basis of toxicity or for establishing regulations as to the suitability of various materials [103, 128, 130, 140].

Nevertheless, test results do find their way into regulatory procedures, and they are useful for making relative evaluations of new products and new combinations of materials under fixed conditions. Some of the more prominent of the toxicity tests are summarized briefly in Table 7.

It can be seen that there is considerable variation among these protocols as to whether the system is static or flowing, the sample is burning or smoldering, and the results are reported as a measure of time exposed or size of the sample used. Smoldering conditions are recognized as producing hazardous conditions no matter what the source of combustible material [131, 134, 141]. Kaplan and coauthors [134], Clarke [131], and Hinderer [142] have summarized the advantages and disadvantages of each method recently, and they and the NFPA Standards Council [143] have suggested directions for future research to develop more meaningful results.

In general, these test methods show that PVC is about equal to or somewhat more toxic than the conventional materials such as redwood, oak, cotton, or wool, depending on the test conditions used. In all test methods, all test materials can impart lethality, and the differences usually are seen in time to incapacitation or degree of irritation [128, 134]. The primary cause of death routinely is from carbon monoxide. The rate at which this result occurs is a function of the interaction of the oxygen and carbon monoxide (CO) concentrations, which are controlled by the amount and type of fuels and by the air supply and temperature [141, 144–147].

The acute toxicity of CO is due to its displacement of oxygen in the hemoglobin to form carboxyhemoglobin (CHG), thus starving the organs

TABLE 7 Summary of Several Prominent Combustion Toxicity Test Methods

Source	Principal investigator	Device type	Toxicity tests	Product analyses
U. San Francisco[a] 1979	Hilado	Static system programmed to set temperature, fixed sample	Incapacitation, lethality, 14-day effects	CO, O_2, temperature
West Germany DIN 53 436, 1980	Kimmerle, et al.	Movable furnace, variable temperature, sample size, fixed air flow	30 min. and 14-day lethality	CO_2, CO, O_2, blood COHb, others
Nat. B. Stds. 1982	Group	Flaming or nonflaming, static gas chamber	Lethality and 14-day effects	CO_2, CO, O_2, blood COHb
Fed. Av. Auth. 1977	Crane	Fixed oven and temp., recirculating air	LC_{50} values for incapacitation and death	CO, HCN, O_2, CO_2
Radiant heat (under development)	Packham	Variable radiant flux for 30 min.	Time to incapacitation, 14-day toxicity	CO_2, CO, O_2, pathology
U. Pittsburgh[a] 1973, 1979	Alaric	Programmed furnace, dynamic flow, variable sample	Irritation, respiratory effects, lethality	CO, CO_2, pathology

[a]Mice used, all others used rats.

of oxygen. Minor effects appear at about 15% CHG, severe effects are seen at 30%, and death can occur above 60% replacement. These effects are seen earlier in persons with reduced circulatory ability, and blood concentration is increased more rapidly for persons who are undergoing heavy exertion or are under stress. Persons in a fire environment may also have their breathing rates increased by high levels of carbon dioxide or other acids. Hydrogen cyanide will act in a very similar manner to CO in displacing oxygen [142, 148].

An equilibrium is established between the ambient and blood levels of CO, so long-term exposure does not result in cumulative effects, and there is a short period at the beginning of high exposure before harmful blood levels are established. A recent estimate suggests 2000 ppm-hours of constant exposure as a threshold for fatalities [144] if the exposure time is less than 4 hours. The results generally are reversible unless extremely high exposures have been received [149]. Kaplan and Hartzell [150a] have reviewed the incapacitation effects of CO on rodents and primates and have concluded that rodents are reasonable surrogates for humans. Their analysis suggest that 750–1000 ppm-hours will result in incapacitation in humans undergoing light activity.

Studies have found an unusually high percentage of victims of fires in public places who have had high blood alcohol levels as well as high CHG levels. Impaired orientation and escape ability may be contributing factors in these cases [130, 145].

Recent studies indicate that hydrogen chloride is not as corrosive to primate lungs as once was thought [150b]. Baboons showed no permanent respiratory effects at 3 days from at 15-minute exposure at 5000 ppm, and survived a similar exposure at 10,000 ppm. Furthermore, the acid concentration decays rapidly after the fire, contrary to the action of the other combustion products. For example, in a fire simulation test that produced a peak hydrogen chloride concentration of 3000 ppm (35% of theoretical), there was found less than 300 ppm after 30 minutes, whereas the other combustion products remained relatively steady. The acid appears to dissolve in the water or on the nonburned residues. Migration from the fire scene was minor.

The question of the relative flammability of synthetic and natural materials has a more definitive answer, but it also is divided into several parts: ignitability, ease of burning, and flame spread rates. Quantitative test methods for ignitability have been in place since the 1950s, and many of the more widely used procedures have been codified in the ASTM series. These often combine flame spread and smoke generation data into the same test.

The original procedure was proposed by the National Bureau of Standards in 1956, adopted by the ASTM in 1967, and revised in 1972 and 1978. It is referred to as ANSI/ASTM E162-78, and is also used by Underwriters Laboratories. A porous refractory element at 670°C is placed 4.75 in. from the test sample, which is held at a 30° angle from parallel to the element. After ignition of the sample by a gas burner, the rate of flame spread and the heat rise of the combustion gases are measured. A flammability index F_I is calculated as the product of the flame spread rate and heat output.

The most widely used test was developed by Underwriters Laboratories in 1944 and codified by ASTM first in 1950 as a temporary standard.

Revisions were made by UL in 1970, and by ASTM in 1972. This document is now referred to as ANSI/ASTM E84-79a, Surface Burning Characteristics of Building Materials. The sample is placed at the roof of a 25 ft tunnel and ignited by two gas pilot lights at one end. The rate of flame spread is reported on a scale of 0 (asbestos board) to 100 (red oak flooring).

Several variations of this tunnel test are in use, such as the Union Carbide 4 ft tunnel, the Monsanto 2 ft tunnel, and the Forest Products 8 ft tunnel [ASTM E286-69 (1975)].

A variation on the ASTM test is described under NFPA-253-79 and reports the heat flux on the sample from the radiant panel at the flame-out point (if any). Results are given in Btu per square foot or watts per square centimeter.

Other ASTM tests are designed for specific forms of products rather than for finishes and surfaces in general. These include ASTM D1929-77, Ignition Properties of Plastics, which measures the self-ignition temperature of plastics in a heated chamber and the flash-ignition temperature of the pyrolysis gases; D1230-61 (1972), Flammability of Clothing Textiles, which reports the flame spread time for a standard sample after a 1-second exposure to a gas flame; and D2633-76, Thermoplastic Insulated and Jacketed Wire and Cable, which includes a flame resistance test, among others.

ASTM reports a normal intralaboratory variation of 15–50% on these tests, and interlaboratory variations of up to 100%. Useful discussions of the principles and applications of these tests can be found in references 133, 134, 146, 147, and 151.

Several other groups (e.g., NFPA, NEMA, ANSI, UL) have published or recommended tests for plastic product flammability, and the tests are used for approval or certification of many types of products.

Another useful method for characterizing the relative flammability of materials is the oxygen index. It is reasonable to term a material as nonflammable if it cannot be ignited at oxygen concentrations in the normal range of about 21% and to classify it as self-extinguishing if it can be ignited but does not continue to burn after the heat source is removed, in the same range of oxygen concentration. The ASTM test D2863 is the accepted method for this property. Rigid PVC has an oxygen index (OI) by this test of 37 and up; that is the minimum percentage of oxygen concentration in which a sample ignites and continues to burn. This value decreases as comonomers or plasticizers are included but generally remains above 21 for most formulations containing less than 38% by weight of plasticizer [152, 153]. Index values may be predicted with reasonable accuracy by a relationship developed by Dickens [154]. The OI is increased by the presence of fillers and fire retardants. The self-ignition temperature in 100% oxygen is 756°F for rigid PVC, and the heat of combustion is just under 5 kcal/g or 7720 Btu/lb. The oxygen index decreases as the heat of combustion increases; thus addition of poor fuels such as chlorinated plasticizers or most fillers would be expected to increase the oxygen index, as it does.

There are only a few formal regulations regarding the combustibility of plastic products. The CPSC regulates the flammability of consumer goods and has adopted standards originating in the Department of Commerce for textiles, fabrics, carpets, rugs, and unsupported films at 16 CFR 1610, 1611, and 1630. The test rule at 1611 applies particularly to

to PVC film in consumer articles. A test for fabric pile is under study [155].

The CPSC rule is the only flammability standard in force on a national basis. The Federal Aviation Authority regulates the flammability of passenger aircraft interiors (14 CFR 25) and has proposed a more stringent test for seats (48 FR 46250). Many localities have adopted building codes developed by major organizations such as the Uniform Building Code (UBC) of the International Conference of Building Officials or the BOCA Basic Building Code by the Building Officials and Code Administrators International.

The UBC contained for several years a requirement that the combustion product of plastic building materials be no more toxic than wood; that criterion was withdrawn in the mid-1970s because of the lack of a suitable test [156]. The current code makes no mention of smoke density or toxicity and sets flame spread criteria based on the tunnel test at a maximum of 25 for class I occupancy, 26–75 for class II, and 76–200 for class III (general residency) uses. Many natural products cannot meet these requirements for public buildings, or class I and II occupancy, excluding common materials such as red oak, because it is used to establish the calibration point of 100 in the test. The UBC and BOCA codes set similar standards for public buildings.

Perhaps the most effective force in controlling the flammability of construction materials consists of the insurance ratings imposed by the risk carriers. Their experience with past losses guides their assignment of premium rates and their recommendations for changes to reduce the risks and therefore the premiums. Such "self-policing" by users through feedback from experience has developed a substantial pool of successful application data.

Smoke density also is of interest in evaluating the relative safety of building materials and furnishings. Several tests have been developed for measuring this parameter, each of which is useful under specific conditions. As for the tests discussed earlier, however, the results vary widely with the configuration of the sample and the test method [157].

Test methods for smoke density can be divided into those that determine the amount of smoke generation by gravimetric or by optical methods. The optical methods may be divided further into static or closed chamber methods, and flow methods.

The most widely used gravimetric method is the Arapahoe smoke test [152] in which a glass filter is used atop a 5 × 7 in. combustion chamber in which a propane burner is used to burn a sample. The results are reported as percentage of particulates captured, based on either initial weight or weight loss of the specimen. Under this high temperature, relatively complete combustion situation, wood and other cellulosics give results in the 0.1–0.2% range, based on initial weight, and rigid PVC produces about 1.3%.

The most widely used static test is that developed by the NBS and described in ASTM E662-79. Either flowing or nonflowing conditions may be used, and the optical density found in the enclosed chamber at the end of the test is reported. The ASTM states that the relative precision of the test within a laboratory varies from 10 to 50%, depending on the material, and the interlaboratory precision ranges from 30 to over 100% for most combustible materials. Wood gives higher results under smoldering conditions than when flaming, whereas most plastics give higher density

values under flaming conditions. The density and thickness of the sample have considerable effect on the results with high density and thicker samples giving higher smoke generation [159]. The NFPA 258-1982 test uses the same procedure. ASTM D2843-77 also is very similar.

A widely used flow test method was developed by Ohio State University (OSU) and is under study by ASTM [158]. It also uses either flaming or smoldering conditions and measures the optical density of the exit gases from the combustion chamber under controlled flow rates. Here, too, flaming conditions produce relatively more smoke from plastics than from wood. Smoke production also increases with airflow, and ASTM E-84, with three times the flow rate of the OSU test, yields higher smoke values than the OSU test. The same is true if the NBS test is run under flow conditions.

All the ASTM, NBS, NFPA, and other tests include a disclaimer at the introduction that cautions that the tests "should not be used to describe or appraise the fire hazard or risk of materials, products, or assemblies under actual fire conditions." Efforts to measure these hazards under conditions more relevant to actual use situations have led to large-scale studies of two types: corner tests and room tests.

These tests are useful more to determine the behavior of materials than the toxicity of the combustion products, because the heat exposure is too intense for any significant exposure period in the test area. An attempt has been made to overcome this problem by using remote animal cages, leading the products to the test animals, and by measurement of the principal combustion products. All these studies have led to the conclusion that carbon monoxide generation and oxygen depletion are the primary causes of incapacitation and that heat is the second most important cause of injury [94, 128, 134, 160]. Rooms containing significant quantities of PVC conduit did not generate sufficient HCl to cause significant symptoms until well after the CO concentration was lethal [161]. These tests show considerable variability in results at the critical flashover point. That is the situation at which the heat output is sufficient to cause rapid propagation of the flame front beyond the immediate fire area as the result of generation of enough flammable pyrolysis products at the flame front to exceed the lower flammability limits [162]. The tests also respond differently to smoldering and flaming conditions. As might be expected, the nature of the product, such as the construction of padded upholstery, wallcovering characteristics, size, and thickness, all play an important part in rate of burning and composition of the combustion products [163–165]. It has been estimated that the heat input to a room required to initiate flashover is about 400–500 kW, at which time a localized temperature rise of about 600°C can be seen [164, 166]. Under these conditions it is surface combustibility rather than physical structure that is more important [164], and almost all combustibles will be involved.

Two large studies to measure the combustion products of actual fires [167, 168] found that, in the accessible sampling areas, carbon monoxide exceeded the ACGIH-recommended short-term levels and that oxygen levels were below short-term survival levels greater than 90% of the time. Hydrogen chloride above acutely toxic levels (500 ppm) was found 36–53% of the time. Other toxic gases reported frequently were acrolein and hydrogen cyanide.

One result of the Boston study [165] was a rule requiring all firefighters to wear breathing equipment when involved in structural fires. This

action was reported to have reduced the inhalation injuries to firemen there by 80%.

A recent test of the effectiveness of smoke detectors and sprinklers in typical hotel settings showed little change in either the smoke density or room temperature from the presence of typical plastic-upholstered furniture from the room contents [169]. The Coast Guard has confirmed that furniture in general is a major contributor to full-scale room fires [170]. As expected, detectors and sprinklers were very effective in these settings. Ionization detectors operated faster than photoelectric types except in smoldering situations. Sprinklers appeared to increase the smoke density in the period after activation.

The director of the NFPA Fire Analysis Division has hailed the widespread adoption of house detectors as "one of the most remarkable fire protection success stories of modern times." Their use is thought to reduce the risk of death by fire by one-half.

The development of flame retardants has been a natural response to some of the flammability problems. These can be divided broadly into two groups: additives that decrease the inherent combustibility of the mixture, such as inorganic fillers, or less flammable (often halogenated) plasticizers; and reactive substances that interfere in the flame chemistry, often by generating free radicals. These too tend to be halogenated, often containing bromine products [172].

However, the suitability of such additives must be judged on a case-by-case basis. In some types of application, the use of flame retardants can increase the toxicity of the combustion gases and the density of the smoke, by holding the material in the smoldering condition longer. On the other hand, the flammability and rate and degree of combustion are reduced, thus lowering the heat output as well as the danger of ignition. Thus, in deciding whether retardants should be used, and if so, what type, the application always should be considered. No general answer is obvious [173], as the problem with "Tris" in children's sleepwear some years ago illustrated. The National Toxicology Program has a significant research effort directed toward the toxicities of fire retardants as well as many of the more widely used plasticizers [174].

Detailed presentation of the results obtained from these many tests is beyond the scope of this discussion. The reader is referred to the monograph [152] or brief review paper [175] by Hilado for summaries and leading references to many combustibility tests, and to Kaplan and coworkers [134] for extensive analysis of toxicity tests. The 1981–1982 edition of *Modern Plastics Encyclopedia* is a good reference for flammability data on specific plastic compositions.

Research continues on methods for more meaningful test methods. Some of the most active institutions include the National Bureau of Standards, the Southwest Research Institute and the University of Utah. The Society of the Plastics Industry and its members are sponsoring or cosponsoring several studies at these and other institutions, and is engaged in a series of demonstrations with fire schools and fire departments illustrating the combustion properties of building and furnishings materials.

The Vinyl Institute (VI), a branch of the SPI, has prepared a series of technical information bulletins presenting detailed information on many of the issues related to the combustion toxicity of common building materials and has developed a computer-based bibliography of references on combustion studies. It has also been very active in testing and in

educational programs with fire fighter associations. Several effective and informative audiovisual aids are available from the headquarters in Wayne, New Jersey. One is a slide/tape program, "Vinyl in Today's Fire Environment," which was produced by the International Society of Fire Service Instructors. A film, also available on video tape, entitled "Vinyl: Trial by Fire," presents actual in-home fire tests that illustrate the resistance of PVC pipe and wiring, window frames, Christmas trees, and tablecloths to ignition or continued burning. A second film, "Fire Safety in America," was cosponsored in 1985 and contains interviews with a number of leading scientists in the field of combustion toxicity.

It is unfortunate that the scientific activities in this area have become entangled with competitive commercial and political actions. A favorable result of this intrusion of emotion into science, however, is to emphasize the additional research that is required, and this may assist in speeding its completion.

The VI recently suggested an education program for further reduction of the concern for, and dangers from, fires. Their recommendation included four major points:

1. Encourage the use of smoke detection systems and sprinklers.
2. Educate the public, especially the children, to the danger from fires, and to their causes.
3. Remain vigilant for unusual hazards.
4. Do not become complacent.

Heating systems remain the primary source of home fires, and their relative contribution has been increasing rapidly since 1980 [176]. Cooking, incendiary acts, electrical systems, and smoking are, in descending order, also major causes. Smoking remains the major cause of fire deaths, with more than 25% of the cases ascribed to that act. It is encouraging that Congress has passed a bill establishing an interagency task force under the CPSC to study a means to obtain a more nearly "fire-safe" cigarette. Heating systems, incendiary acts, children playing, electrical systems, cooking, and open flame are other major identified causes of fire deaths.

It is apparent that the major contribution to continuing the current downward trend in injury and death from fires can be made in the area of reducing their incidence. It is more productive to prevent fires than to try to protect life and property from their combustion products, no matter what the level of toxicity. Proper application of synthetic building materials and furnishings, and especially of PVC, with its inherent noncombustibility, can make a major contribution to that effort. There is no evidence that the increased use of plastics has added to either the incidence of or fatalities from residential fires [143, 177–181]. Nevertheless, because of the economic pressure, and perhaps because of misunderstanding of the relative toxicity of substitutes, pressure continues at the local level to prescribe rules that would ban or restrict the use of plastics in construction [136].

E. Disposal

Either PVC or articles made from it may be disposed of safely by ordinary landfill or by incineration when mixed in its usual proportions with general trash [182]. Some opposition has been raised for each of these methods of

disposal, but no basis has been provided to demonstrate a need for practical concern over these practices.

The EPA has made several estimates in the past that put "plastics" in general at about 2–3% of the total municipal garbage load [183] and show that PVC makes up some 10% of that portion [182]. That estimate appears reasonable when we consider that much PVC is destined for permanent installation, or structural uses from which the discarded materials would not likely be incinerated. Thus, the chlorine content of garbage due to PVC is less than 0.1%, which is in line with estimates of the chlorine content arising from other sources [132]. Higher levels are seen in Europe, where per capita consumption of plastics is several times that in this country.

The nonbiodegradability of PVC products adds to the stability of landfills and does not interfere with restoration efforts, or leach to groundwaters. There are no known reports of harm to the environment or to human health from proper disposal of PVC in landfills. As discussed in Section II.A.2 above, raw stabilizers containing heavy metals are not suitable for land disposal and are controlled by RCRA rules, but in compounded form they are suitable for such disposal.

PVC has been suspected of causing certain environmental problems, but these appear to be attributable to other substances. The case of vinyl chloride contamination of the Dade County, Florida, water supply has been found to be due to biodegradation of higher chlorinated olefins, as was discussed in Chapter III of Volume I of this encyclopedia. Vinyl chloride has been found in the emissions of the West Covina, California, landfill [184], and VC-contaminated PVC was suspected as a cause, despite the absence of any known sources of VC in that area. However, substantial quantities of the other chlorinated olefins were found there also, and it is most probable that they are the sources of the VC in this instance as well as in Florida. Concentrations of VC in the neighborhood since mitigation measures were taken at the dump have not exceeded the California standard of 10 ppb, and the report states that the situation does "not constitute a public health emergency." The gases from several British landfills also contain VC, and in each of these the probable precursor, chlorinated olefins, was present [185]. Earlier studies at other U.S. landfills also found these precursors but did not use an analytical method suitable to detect VC [186]. More recent data show VC present at almost all such facilities in trace amounts [8].

In a third instance the EPA has measured vinyl chloride above a landfill known to have received heavily contaminated PVC sludges before 1974 [187]. None of these cases suggest any concern for low VC resins of the type produced today, nor do they represent any reason to suggest that PVC itself is not suitable for landfill.

Concerns for incineration of plastic-containing refuse arise from the evolution of hydrogen chloride and from the potential for formation of higher chlorinated products, including chlorinated dioxins, during incineration.

The amount of hydrogen chloride actually formed has not been found to be a health hazard. All natural sources of combustible products contain measurable quantities of chlorides and produce hydrogen chloride and small traces of chlorinated organics upon combustion [188, 189]. For example, VC can be found in cigarette smoke [190]. Higher chlorinated materials, including some of the lower chlorinated dioxins, but not significant

amounts of the tetrachloro analogues that are the greatest toxicological concern, have been found from the burning of wood, paper, coal, and municipal garbage [191]. Workers at the National Bureau of Standards point out that the synthesis of dioxins should be "very low" at operating temperatures of 1200 K (1700°F) because of theoretical reasons and conclude that "de novo synthesis from inorganic precursors is unimportant in the gas phase" [191]. They add that destruction paths outnumber formation paths for these complex molecules and suggest the presence of trace amounts of polychlorinated phenols or benzene derivatives in the feed as a more probable source of the dioxin. They also suggest that reactive surfaces such as that offered by fly ash may be involved. This was confirmed by a study [192] at a European high temperature incinerator, where a quadrupling of the normal 1% PVC in the trash showed no increase in either chlorobenzenes of chlorodioxins in the finer fly ash, the location usually reported to have the largest extractable organic combustion products. The work at Tokyo Institute [188] supports the concept that metallic components act both as a sink and a source of chlorine. In any event the quantities of dioxins found are quite low [190–193] and are not expected to add significantly to the natural levels of these substances. In addition, the newer and larger mass burn incinerators are required to have particulate removal equipment that lowers substantially the amount that may be expected to escape. The EPA has made several public statements that municipal refuse incinerators of the type now being installed in many cities will have no deleterious effect on human health.

There are many positive features to incineration of plastics. Their presence helps control the water content of the garbage, and thus the ease of handling and heat yield are improved. They contribute a significant heat output to units having heat recovery, and the heat value of PVC is about twice that of the average garbage. Operators preparing pelletized fuel for shipment to central incineration units rely on the thermoplastic components to help adhere the pellets for easier and cleaner shipment.

Mass burn incinerators are in much more common use in Europe than here, and the level of per capita use of plastics, including PVC, also is several times higher there than here. Several thorough studies of European experience are presented in reference 182, and that technology now is coming into much wider use in this country. In particular, hydrogen chloride emission has not been a problem even in the absence of specific air pollution control equipment for that component.

There appears to be little reason to consider PVC anything other than a desirable component of waste streams. As the pressure toward phasing out of landfills increases, it may be possible to develop economically sound recycle systems for some types of PVC waste but, in any event, incineration offers total destruction with the opportunity for recovery of the energy values present. Thus not only will PVC consume less energy than conventional building and packaging materials during its formation and use [194], it will return much of that energy when its usefulness is done.

The plastics industry recognizes the commercial value of an effective recycling program as well as its contribution to a better public perception of the industry. The Plastics Recycling Foundation was organized in January 1985 with several large resin producers and users joining. Recycling should be encouraged to the maximum practical extent.

It will be necessary to convince the public that the industry is acting responsibly to prevent misuse or abuse of its products if further punitive "bottle bills" and other laws restricting the use of plastic packages are to be avoided. A number of Recycling Forum-type organizations have been formed with the express purpose of restricting the use of plastics.

More detailed information on PVC disposability, recycling, and incineration is the subject of Chapter 10, Volume 4 of this encyclopedia.

GLOSSARY

ACGIH	American Conference of Government and Industrial Hygienists, Cincinnati, OH 45211
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers, New York
ASTM	American Society for Testing and Materials, Philadelphia
BOD_5	Five-day biological oxygen demand
CFR	*Code of Federal Regulations*, a compilation of promulgated federal rules. 29 CFR 1910 refers to Chapter 29, Section 1910.
CHG	Carboxyhemoglobin, formed by reaction of carbon monoxide with the blood.
CMA	Chemical Manufacturers Association, Washington, DC
CPSC	Consumer Product Safety Commission, Washington, DC
DEHP	di-2-Ethylhexyl phthalate
EP	Extraction procedure, designated by EPA for use in testing hazardous waste candidates.
EPA	The U.S. Environmental Protection Agency
FDA	The U.S. Food and Drug Administration
FR	*Federal Register*, the official daily publication of the federal government. The number before the letters gives the volume, the following numbers are the page. Volume 56 was published in 1991.
GRAS	Generally Recognized as Safe by the FDA because of broad use before 1958
ITC	Interagency Testing Committee, which recommends substances for consideration by the EPA for toxicity testing
LD_{50}	Lethal dose for 50% of experimental animals within 14 days
NBS	National Bureau of Standards, Washington, DC
NFPA	National Fire Protection Association, Quincy, MA
NSF	National Sanitation Foundation, Ann Arbor, MI
NSPS	New Source Performance Standard by EPA for limiting emissions from new or modified plants
NTIS	National Technical Information Service, Springfield, VA
NTP	National Toxicology Program
OSHA	The U.S. Occupational Safety and Health Administration
PB number	Document identification number used in ordering from NTIS
ppb	Parts per billion. Units are per volume for gases, by weight for solids or liquids
pH	Indication of the presence of absence of acid or caustic in a water stream; pH 7 is neutral
ppm	Parts per million. See ppb for units.
RCRA	Resource Conservation and Recovery Act

SIP	State Implementation Plan, required of states in nonattainment areas for conventional pollutants to demonstrate intention to achieve attainment with national standards
SPI	Society of the Plastics Industries, Inc., Washington, DC.
STEL	Short-term exposure limits recommended by the ACGIH
TLV	Threshold limit value. Registered trademark of the ACGIH for its recommended maximum long-term occupational exposure to workplace contaminants.
TSS	Total suspended solids
TWA	Time-weighted average of exposure to substances in air, usually for 8 hours
UL	Underwriters' Laboratories
VI	Vinyl Institute, Wayne, NJ, a trade association of the VC-PVC producers, and a division of the SPI.

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about the editor . . .

LEONARD I. NASS is President of Technical Information Exchange (TIE), a worldwide network of polymer industry consultants involved in marketing and multidisciplinary engineering and developmental projects. Mr. Nass is a veteran of the chemical and plastics industries with more than 40 years' experience in plastics additives and PVC. He is a Fellow-Emeritus of the Society of Plastics Engineers and has held memberships in the American Chemical Society and the American Society for Testing and Materials. He is the author of numerous patents and publications in areas such as polymer stabilization, catalysis, compounding, processing, testing, and instrumentation. Mr. Nass has been an instructor and guest lecturer for the Society of Plastics Engineers, Plastics Institute of America, and various colleges in the U.S. and Canada, and he has conducted one- to five-day seminars on PVC in Japan, India, Brazil, and Colombia. He received the B.S. degree (1949) in chemistry from Syracuse University, New York, and pursued graduate studies in organic chemistry at Polytechnic Institute of New York, Brooklyn.

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exposure to materials that cause rare forms of cancer attributable to those particular carcinogenic materials--the asbestos that causes mesothelioma, the vinyl chloride that causes liver angiosarcoma--we are left confronting cancer types that seem to have many common possible causes. This raises the issue of small marginal elevations in incidence rates, a very difficult kind of causative problem to sort out.

B. Problems with Risk Assessment

As is widely conceded, the scientific assays currently available for assessing the carcinogenic potential of chemicals, dusts, and radiation (and alcohol consumption, psychological stress, and other lifestyle factors) are frustratingly inadequate. Being for the most part based on rodent assays, supplemented by inferences from inadvertent human exposures and by tests on bacteria and other primitive species, interpretation of these assays requires great inferential leaps: from bacteria and rodents to human beings, from relatively high exposures in the test animals to the relatively low exposures expeienced by workers. These problems have been discussed extensively elsewhere, so I will not review them here [3,4,5].

Concerned over the assessment approaches curently being used (and abused), in 1983 a National Research Council committee recommended to the Congress that a national Board on Risk Assessment Methods be established "to assess critically the evolving scientific basis of risk assessment and to make explicit the underlying assumptions and policy ramifications of the inference options in each component of the risk assessment process" and otherwise to critique agency guidelines and identify research needs [6]. Legislation has been introduced to accomplish this.

The predictive power of these tests will increase only as we accrue experience with more compounds and can discern associations between types of compounds and types of carcinogenic effects, and as we develop biochemical, genetic, and other fundamental knowledge of mechanism of action (see Chapters 3 and 4).

Complementation of laboratory testing comes from epidemiology--surveillance of worker populations over a long term to pick up indications of harm, and retrospective epidemiologic investigation of accidental and troubling exposures. Both are very hard to do. Problems stem from all the confounding factors of smoking, diet, and exposures to solvents, dusts, drugs, and so many other chemicals off the job. Problems arise in the question of "control" populations--who to compare the test group to? And in epidemiologic investigations there may arrive a moment when genuine suspicion exists about the hazard, but no conclusory evidence; this raises very difficult ethical managerial and regulatory decisions about disclosure and interim action.

C. Problems with Risk Evaluation

Nobody wants cancer. Everybody is willing to go to considerable expense to avoid it himself and to prevent it for others. But practical decisions about cancer risk still are difficult, for reasons that have to do with the following several "facts of life."

First, nothing--no material or activity--can be completely free of risk. In reducing one risk we often, in effect, just substitute other risks for it. Second, when we make personal or social decisions it is never only risks that we weigh, but also the benefits from the activities or circumstances that generate those risks, considerations of "fairness," and social power questions about *who decides what for whom*. And third, although human life may be beyond price, ventilation systems and electrostatic precipitators and medical surveillance programs most surely are not.

Thus industrial decisions have to do not with whether, say, leukemia is good or bad (I have never seen it taken as not-bad) but with whether, usually under great uncertainty about the facts, a financially important manufacturing process or product should be foregone, or modified at considerable expense, to reduce marginally an imputed cancer risk.

While there is true difficulty in appraising preventive investments, there are also complaints about regulatory decision frame-

I. INTRODUCTION

Some percentage of cancer in man results from exposure to carcinogenic chemicals, both natural and manmade (see Chapter 1). Some portion of this chemically induced cancer may be prevented by reducing or eliminating exposure. Therefore, given the public concern with cancers, considerable scientific and regulatory attention has centered on efforts to identify actual or potential human carcinogens present in human environments or which may be introduced by certain industrial practices or technological changes.

The purpose of this chapter is to examine the techniques and procedures currently available for identifying those chemical and physical factors in the industrial environment which are carcinogenic or potentially carcinogenic to humans. Further, the methods used to assess or predict the risk associated with low-dose exposure of humans to carcinogenic chemicals is reviewed.

II. METHODS FOR ASSESSING CARCINOGENICITY

The principal techniques available are epidemiology, so-called "short-term" tests, animal bioassays, and structure-activity relationships. Each technique has its strengths and limitations.

A. Epidemiology

Epidemiology plays an important role in identifying carcinogenic chemicals in an industrial environment. It is also useful in identifying exposures which may be associated with an increased incidence of cancer, although the agent or agents responsible for the increased incidences may often not be identified.

In applying epidemiological methods to the detection of cancer in industrial populations, a positive relationship is based on the statistical significance of the data. However, it is important to remember that a positive statistical association does not necessarily mean that a cause-effect relationship has been established. Negative epidemiological studies are also useful in that they help define the upper limit of human cancer risk.

Those industrial situations where chemicals have been shown by epidemiological studies to be causally related to the occurrence of cancer in humans have been the result of high exposure of relatively small population groups. Therefore, as noted by Tomatis [1], the identification of human carcinogens has occurred under conditions of exposure similar to those used in experimental carcinogenesis. That is, conditions where a limited number of experimental animals are exposed to high levels of the chemical or mixture of chemicals in order to increase the sensitivity of the animal surrogates.

The first uses of epidemiology to identify an occupational cancer hazard were the observations of Pott in 1775 [2]. Pott correctly concluded that scrotal cancer in chimney sweeps was caused by exposure to soot. An example of the recent use of epidemiological evidence to establish cancer causality with chemical exposure is the increase in the incidence of angiosarcoma of the liver of vinyl chloride-exposed workers [3]. The International Agency for Research on Cancer (IARC) has identified 16 chemicals and industrial processes, in addition to soot and vinyl chloride, for which there is sufficient epidemiological evidence to indicate a causal relationship between exposure and an increased cancer incidence in humans [4]. The IARC identified 18 additional chemicals for which the epidemiologic evidence was more limited but which suggested these chemicals were *probably* carcinogenic for humans [4].

Thus, epidemiology is indeed an important technique in the identification of human carcinogens. However, there are major limitations to it. Epidemiology obviously cannot be used to assess the potential carcinogenicity of chemicals to which human exposure is anticipated. Because most human exposures are to such low levels as to preclude the direct measurement of risk, negative results do not necessarily demonstrate the absence of hazard because of the insensitivity of epidemiological methods in detecting increases in cancer incidences. Although an increase in the incidence of a rare human cancer may be detected using epidemiology, an increase in common cancers such as cancer of the lung, breast, or colon will not likely be detected except in the case of

the inspections. If it is assumed that a direct ratio exists between inspections and number of workers, then approximately one-sixth of this total number of workers (or about 175,000) were reached by health inspections. These numbers should be contrasted with the approximately 5 million establishments assigned to OSHA under the Act and the approximately 75 million workers entitled to OSHA protection.

In summary, based on Table 5 data, in an average year OSHA will conduct approximately 64,000 inspections. Of these, about half will be construction and 350,000 workers will receive the benefit of health inspections. These figures, though of recent vintage, reflect a problem OSHA has faced for years; namely, that only a small proportion of workplaces can be inspected in any given year. One can only conclude that the OSHA inspection process cannot have a direct, major impact on reduction of exposure to carcinogens or, for that matter, to any potentially toxic agent in U.S. workplaces.

The establishment of standards does create the requirement for employer compliance with standard ingredients, particularly permissible exposure limits. Most employers do not wish to be in technical violation of the law. Therefore, it is reasonable to assume that at least in the areas that OSHA has promulgated standards, major reductions in exposures have occurred. Although OSHA has only promulgated standards for a few carcinogens, we can examine the impact in selected areas. Table 6 indicates the reduction of exposures to asbestos, as judged by U.S. asbestos standards from 1938 to the present. Once again, if it is assumed that a linear relationship exists between the dose and response to carcinogens, and that exposures to asbestos have, indeed, been reduced from 12 fibers per cc in 1970 to 2 fibers per cc or less in 1983, then OSHA has reduced the future harvest of occupational cancer due to asbestos by five-sixths, or approximately 84%.

In the case of vinyl chloride, 70 U.S. plants employed 940 workers. Forty plants with about 5600 workers produced polyvinyl chloride in 1973 [17]. At that time, exposures apparently varied from 50 to 500 ppm. After promulgation of an OSHA permanent standard for a PEL of 1 ppm in 1974, all of the above

Table 6 U.S. Asbestos Standards

				Million particles/ cm^3	Fibers/ cc	STEL, fibers/ cc
1938	Ref. [19]	Recommended	TLV	5	30[a]	
1946	ACGIH	Adopted		5	30[a]	
1970		Adopted		2	12[a]	
1971		Proposed		–	5	
1971	OSHA	Emergency	TWA	–	2	10
1975		Proposed		–	0.5	5
1976		Adopted		–	2	10
1976	NIOSH	Recommended		–	0.1	0.5
1983	OSHA	ETS			0.5	
1984	OSHA	Proposed		–	0.4 or 0.2	

[a]Approximate fiber equivalent.

employers can be considered to have experienced an exposure reduction of *at least* 98%.

Similar approaches to other carcinogens regulated by OSHA will show the same extraordinary impacts of the standard on the health of workers exposed, when exposure concentration is used as a surrogate measure of subsequent health impact. Using this methodology, it is difficult to predict the future incidence of cancer in exposed populations because of the weaknesses in previous exposure monitoring. It is necessary to assume some average exposure value in the past and, on the basis of dose-response curves, to predict future incidence of cancer. Notwithstanding these limitations, we conclude that in the areas in which permanent health standards have been promulgated, OSHA has had a major impact.

Early in this chapter, the total number of proven or suspect human carcinogens in the workplace was noted. Obviously, the substance-by-substance approach to regulation by OSHA, while effective, has left the majority of such chemicals unregulated. Awareness of the need for more rapid regulation of carcinogens led to development of the OSHA Generic Standard for Carcinogens [7].

Among the objectives of the program are: to protect against dangerous substances, to establish a statistical methodology for assessing accidents and the etiology of disease, to improve working situations to increase safety with due regard to health requirements in the organization of the work, to improve knowledge in order to identify and assess risks and to improve prevention and control methods thereby, and to improve human attitudes in order to promote and develop safety and health consciousness. Under this program of action several specific directives have been adopted or proposed: the directive on the protection of the health of workers exposed to vinyl chloride monomer which comprises technical preventive measures, establishment of (technical long-term) limit values for atmospheric concentration of vinyl chloride monomer in the working area of three parts per million, provisions for measuring and monitoring atmospheric concentrations, personal protection measures, guidelines for medical surveillance of workers, and the like; the directive on the protection of workers from harmful exposures to metallic lead and its ionic compounds at work, which includes a time weighted average (TWA) concentration of lead of 150 $\mu g/m^3$ in air, biological parameters for blood, hemoglobin and creatinine, and other values relevant to protective measures; and the directive on the protection of workers from risks related to exposures to agents at work, such as asbestos. Further, a framework directive on the protection of workers from harmful exposures to chemical, physical, and biological agents at work was proposed [8]. The Council agreed that 14 actions could be undertaken up to the end of 1982. Two of these make specific reference to occupational carcinogens. They embody the following actions: to develop a preventive and protective action for substances recognized as being carcinogenic by fixing exposure limits, sampling requirements and measuring methods, by establishing satisfactory conditions of hygiene in the workplace, and by specifying prohibitions where necessary; and to establish information notices on the risks relating to, and handbooks on, the handling of a certain number of dangerous substances such as carcinogenic substances.

In an overall approach to worker protection the most important legal instrument is Directive 80/1107/EEC, adopted by the Council in November 1980, on the protection of workers from the risks related to exposure to chemical, physical, and biological agents at work [8]. The measures established in this directive cover all agents including occupational carcinogens, and thus its application will affect the majority of workers in the community. It will result in member States following a similar legislative path in the future, including short-term and longer-term measures. The short-term measures require that workers and/or their representatives at the place of work receive appropriate information about asbestos, arsenic, cadmium, lead, and mercury; and that there is appropriate health supervision of workers during the period of exposure to asbestos and lead.

The longer-term measures are to be taken by member states to ensure that worker exposure is avoided or kept as low as is reasonably practicable. These measures are to be taken when member states adopt provisions to protect workers against an agent; however, the extent to which each measure applies has to be determined by the member State in question. Fourteen measures can be taken for all agents, plus 5 additional measures for 11 specifically named agents, 7 of which are carcinogens (among them asbestos, benzene, cadmium and compounds, and nickel and compounds). The Council will lay down for these agents, in individual directives, limit values and other specific requirements as applicable.

A second program of action [9] was issued at the end of 1982. In this program the protection of workers against dangerous agents is the first action, indicating the need to develop preventive and protective actions for agents recognized as being carcinogenic. The principles for dealing with carcinogens and other dangerous agents and processes which may produce serious health effects need to be defined and applied, such as fixing exposure limits, defining measuring methods, and determining satisfactory conditions of hygiene at work, and, when necessary, to prohibit use. It is also stated in the second program that an inventory of cancer registers