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WORKER EXPOSURE TO VINYL CHLORIDE IN VINYL CHLORIDE AND POLYVINYL CHLORIDE PRODUCTION AND FABRICATION

James H. Jones

U.S. Department of Health, Education and Welfare
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations
and Field Studies

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In assessment of worker exposure to vinyl-chloride (75014) (VC) and polyvinyl-chloride (9002862) (PVC) was reported. Toxicological data were presented, including acute and chronic animal and human studies, as well as reported worker exposures. Common methods of VC production, including the acetylene-hydrogen-chloride, oxyhydrochlorination, and ethylene-dichloride pyrolysis processes were described. A description of PVC polymerization processes, including suspension, emulsion, bulk and solution polymerization, were presented. A study to determine worker exposure to VC in monomer, polymerization and fabrication plants was described. Monomer and fabrication plant personnel had generally low levels of VC exposure, as compared to workers in polymerization plants. Workers in polymerization plants had the highest VC exposures. The author concludes that VC concentrations in polymerization plants are hazardous to the workers.

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INTRODUCTION

On January 30, 1973 as part of continuing effort to collect data to be used for establishing criteria for standards, the National Institute for Occupational Safety and Health (NIOSH), published a request in the Federal Register for information concerning potential hazards associated with occupational exposure to 23 chemical substances and physical agents, including vinyl chloride (VC).[104]

On March 16, 1973, the Manufacturing Chemists Association (MCA), announced that a group of U.S. chemical companies was sponsoring a research program to study the potential health effects from exposure to vinyl chloride beginning with a contract with Industrial Bio-Test Laboratories to study the toxicology of vinyl chloride through animal studies.[76] Later, on June 27, 1973, MCA announced that they had sponsored a contract with Tabershaw-Cooper Associates, Inc., to conduct an epidemiological survey to document the health experience of past and present workers exposed to VC.[76] On July 17, 1973, MCA met with NIOSH officials to present the protocols for the two studies to inform NIOSH of industry research efforts with regard to VC.[76,104] At that time MCA also informed NIOSH of preliminary results of a European study showing tumors in animals after exposure to VC. There had been no reports at that time of tumors in humans caused by VC.

On January 22, 1974, NIOSH was alerted by representatives of the B.F. Goodrich Chemical Company that the deaths of three of its Louisville, Kentucky plant employees, caused by angiosarcoma of the liver, may have been related to occupational exposure to VC. As a result of this report

a walk-through survey was conducted at the Louisville plant on January 24, 1974, by NIOSH industrial hygienists. Representatives from the Kentucky Department of Labor, the Occupational Safety and Health Administration (OSHA), and the Epidemic Intelligence Service (EIS) of the Center for Disease Control (CDC) participated in this survey at the request of NIOSH. As a result of the walk-through survey, NIOSH recommended on January 30, 1974, that certain monitoring and control procedures of a precautionary nature be instituted at the Louisville facility.[86] On the following day, NIOSH recommended to the MCA that similar measures be instituted at all facilities engaged in the polymerization of VC and requested that the MCA disseminate this information to its members.[104]

On February 1, 1974, NIOSH and CDC briefed other Federal agencies with health research responsibilities including the National Cancer Institute (NCI), the Food and Drug Administration (FDA), the National Institute of Environmental Health Sciences (NIEHS), and the Environmental Protection Agency (EPA), about NIOSH findings concerning VC. On February 12, 1974, NIOSH met with management and labor representatives from the VC and polyvinyl chloride (PVC) industries. At this meeting held in Cleveland, Ohio, approximately 100 people were briefed by NIOSH and CDC staff about the information obtained up to that time. Following review of the problem, NIOSH presented plans for future activities including: (a) development of recommended standards; (b) medical surveillance and research programs; (c) additional toxicologic investigations; and (d) industry-wide epidemiologic studies.[104]

It was decided by the Division of Field Studies and Clinical Investigations (DFSCI) at the outset of the planning for the industry-wide study, that only PVC polymerization plants would be investigated based upon the belief that the highest exposures to VC would occur here and upon the limited availability of personnel with which to conduct the studies. A listing of all PVC polymerization plants in the U.S., including information on each plant's age, number of people employed, and type of manufacturing processes used, was made to help decide which plants should be visited for initial walk-through surveys. Criteria for plant selection were as follows:

(a) The plant's age must be fifteen years or more.

(b) The plant must have a workforce greater than 100 persons.

(c) The plant should be located in a state of the union, where NIOSH had established follow-up sources for retrospective cohort studies.

In the Spring of 1974, walk-through surveys were conducted at seven polymerization plants by a team consisting of an industrial hygienist, an epidemiologist, and a physician, that collected information concerning suitability of personnel records for follow-up of all persons ever employed, the extent and availability of environmental sampling results for VC, types of materials used and produced, and the physical layout. Based on this preliminary information five plants were originally selected for epidemiological study. Two of these plants were selected for industrial hygiene surveys because they were judged to be fairly typical of the industry and they used three of the four PVC manufacturing processes.

A third plant was chosen for industrial hygiene study because it used the fourth, newer, process for manufacturing PVC.

During this time it was also decided by NIOSH to document VC exposures in the other two main segments of industry where VC occurs, VC monomer manufacturing and PVC fabrication. A contract was awarded to Bendix Launch Support Division to conduct industrial hygiene surveys at three typical VC monomer plants and at PVC fabrication plants using the following processes: compounding, extrusion, molding, calendering, thermoforming, bonding, and the production of foams, fibers and plastisols.

The initial walk-through surveys of the selected polymerization plants by NIOSH industrial hygienists began in February, 1974. The industrial hygiene surveys conducted by the contractor began in June, 1974, and were completed for the monomer and polymerization plants by January, 1975, and for fabrication plants in April, 1975.

While the study was under way several changes in the OSHA standard for VC took place. On April 5, 1974, a temporary emergency standard was promulgated which lowered the standard from a 500 parts per million (ppm) ceiling concentration to a 50 ppm ceiling concentration.[118]

On October 1, 1974, a permanent standard of 1 ppm for a time weighted average, with a 5 ppm ceiling was announced to be effective January 1, 1975, but subsequently was delayed by court action until April 1, 1975.[110]

All of the VC measurements in the NIOSH field study were taken before the permanent standard went into effect with the exception of one fabrication plant which was surveyed in April, 1975.

HISTORY OF POLYVINYL CHLORIDE PRODUCTION

PVC is first mentioned by Baumann in 1872 with a description of a white powder formed by the action of sunlight on VC contained in a sealed tube.[13] Although the formation of VC had been reported earlier by Regnault in 1835,[103] no further interest in VC was expressed by the scientific community until 1912. A surplus of calcium carbide in Germany in the early 1900's led to the development of a process for the synthesis of acetylene. In 1912, a patent was filed for the production of VC from acetylene, and in 1914 another patent was filed for the use of a family of catalysts in the polymerization of VC. Concurrently in Russia attempts were being made to use the polymer as an intermediate in the production of synthetic rubber. Realization of the significance of the German work failed to develop at this time and the patents were allowed to lapse in 1926. Interest was renewed by 1928 and patents involving polymerization of VC were filed by three companies in the U.S., but the main breakthrough came when B.F. Goodrich demonstrated that PVC could be plasticized. The system was improved, with significant quantities of PVC being produced by the late 1930's. During World War II, PVC was used for electrical insulation, waterproofing materials, and military rainwear. Only after the war, with the development of consumer products using PVC, did the industry mushroom. In 1945, the entire world pro-

duction of PVC was 100 million pounds,[17] while in 1974, the U.S. production alone was over 4 billion pounds.[35]

TOXICOLOGICAL STUDIES

Acute Animal Studies

Much of the initial animal experiments were conducted using concentrations of VC greater than 100,000 parts per million (ppm) to study acute effects. Patty, et al.,[94] in 1930 found that 200,000 to 400,000 ppm was fatal to guinea pigs in a "very short time" and that 100,000 ppm for 30 to 60 minutes was "dangerous to life." They found lung edema and liver and kidney hyperemia in the higher exposure group. Peoples and Leake[95] in 1933 reported that 245,000 to 285,000 ppm for 10 minutes was fatal to mice and that 85,000 to 125,000 ppm for 10 minutes was the minimal anesthetic range. They also reported that 170,000 ppm produced narcosis in dogs and rabbits. Schaumann[107] in 1934 reported that 180,000 ppm exposure produced relative heart insufficiency in cats. Oster, et al.,[92] in 1947, while conducting tests to determine the suitability of VC as an anesthetic, discovered serious cardiac arrhythmias in dogs exposed to 100,000 ppm. Narcosis and sensitization of the myocardium in dogs after exposure to VC was reported by Carr et al.[23] in 1949. In 1960, Mastromatteo et al.[80] tested mice, rats and guinea pigs at 100,000, 200,000, 300,000 and 400,000 ppm for 30 minutes and all animals showed deep narcosis with deaths occurring in all but the lowest exposure group. Animals that died showed lung edema, liver and kidney congestion and a clotting defect, but the survivors showed no changes other than pulmonary congestion. Lester et al.[69] tested rats, in 1963, at concentrations of 50,000, 70,000, 100,000 and 150,000 ppm. At the highest level the

rats experienced deep narcosis with lung edema. Moderate intoxication, loss of balance and corneal reflex were the only effects noted at the lower concentrations. Prodan et al.[97] have reported LD 50's for the following species: mice - 120,000 ppm; rats - 150,000 ppm; guinea pigs - 238,000 ppm; and rabbits - 236,000 ppm.

Chronic Animal Studies

The first chronic VC exposure studies were reported in 1961 by Torkelson et al.[120] They exposed rats, guinea pigs, rabbits and dogs to 50, 100, 200 and 500 ppm for 4½ to 6 months and found liver and kidney changes at all levels of 100 ppm and over. Lester et al.[69] also reported on chronic exposure to rats in their 1963 paper. Exposure levels were 20,000, 50,000, 80,000 and 100,000 ppm for 8 hours a day, 15 days to 3 months. Liver changes were noted in all groups, with the highest exposure group also showing lung edema and spleen changes and death of over half of the animals in the group. Prodan et al.[98] in 1975 reported that guinea pigs exposed to 100,000 ppm VC for 3 months showed liver, kidney, spleen and lung changes. Viola,[131] in 1970, exposed rats to 30,000 ppm for 12 months and found liver, kidney, artery, skin, bone, brain and nerve abnormalities. The following year Viola[132] reported on another group of rats exposed to 30,000 ppm for 12 months and found severe hepatitis, kidney tubulonephrosis, interstitial pneumonia, degenerative brain lesions and tumors of the skin, lung and bone. This was the first report of any carcinogenetic effects of vinyl chloride. Caputo et al[22] reported in 1974 that rats exposed to VC concentrations down to 500 ppm had developed tumors of various sites. Maltoni and Lefemine,[73] exposed rats,

mice and hamsters to 50, 250, 500, 2500, 6000, and 10,000 ppm for 12 months and found tumors at various sites at all exposure levels. Keplinger et al[59] in 1975, also reported tumors in mice exposed to 50, 200, and 2500 ppm for 8 months. Basalaev et al[12] have reported cardiovascular disorders, hyperadrenalinemia, changes in the bioelectric activity of the hypothalamus and bone resorption in rats and rabbits exposed to as low as 12 ppm VC. Vazin and Plokhova have conducted several tests with VC. They have reported changes in the electrical activity of the hypothalamus of rabbits exposed to 3770 ppm VC for 5.5 months.[126] Rabbits exposed to 3500 ppm VC for 5 months were found to suffer from cardiovascular disorders.[125] Rabbits exposed to 8-12 ppm VC for 5 months showed cardiovascular disorders resulting from hyperadrenalinemid caused by changes in the cells of the hypothalamus.[122]

Rats exposed to 12-15 ppm VC for 5 months developed cardiovascular disorders[124] and alterations in the function of the central nervous system.[123]

Human Studies

Again, as was the case with animal studies, all early human studies concentrate on acute effects of VC exposure. Patty et al[94] reported that 25,000 ppm for 3 minutes and 6,000 ppm for 30 minutes produced giddiness and disorientation. Two cases of VC intoxication in workers were reported in 1933 by Dublin and Vane.[32] Lester et al[69] reported on exposures from 4,000 ppm to 20,000 ppm for 5 minutes. They estimated that a prolonged exposure to a level of more than 6,000 ppm is necessary to produce minimum symptoms of intoxication. Danzinger,[29] in 1960, reported on 3 VC poisoning

cases, two of which resulted in death.

Other studies reported in the literature have concerned chronic effects of VC exposure in workers. The first of these was by Tribukh[121] in 1949 and found a "more or less marked hepatitis" in workers processing PVC. There is some question whether the health problem was a result of exposure to VC or to the plasticizers being used: chlorinated naphthalene and polychlorinated biphenyl (PCB). The author suggested that the predominant exposure was to PCB. Filatova,[39] in 1957, pointed out a prevalence of "toxic angioneuropathy" in VC polymerization workers normally exposed to 20-313 ppm. The first more detailed descriptive disease was done by Suciu[115] et al. They described gastrointestinal symptoms, central nervous system disturbances, Raynaud-like syndrome, pseudoscleroderma, alteration of thyroid function, hepatomegaly, and splenomegaly. Numerous authors have reported various combinations of these symptoms along with acroosteolysis, other liver damage, cardiovascular disorders and thrombocytopenia.[5,8,24,27,30,31,40,42,44,48,57,62-66,70,77-79,83,96,100,105,106,113,114,118,127,135]

Pulmonary disorders have also been reported by several authors.[66,70,118] PVC dust has also been implicated in causing pulmonary disorders.[18,82,116,128] Creech and Johnson,[26] in 1974, were the first to link angiosarcoma of the liver with exposure to VC. Since then approximately 30 cases have been reported.[7] These reports have triggered a number of retrospective mortality studies.[75,84,88,117,134]

These studies have suggested that there are multiple tumor sites related

to VC exposure. Besides angiosarcoma of the liver, excesses of lung cancer, brain cancer and lymphoma have been found. In addition, Rannug et al[101] have reported that VC shows mutagenic activity when metabolically activated in a microbial system. Chromosome aberrations in workers exposed to VC have been reported by Funas-Craviota et al[41] and Purchase et al.[99] Infante[52] has reported an increased prevalence of congenital malformations in communities surrounding polyvinyl chloride polymerization plants.

REPORTED WORKER EXPOSURE

The first report in the literature of VC exposure levels for workers appears in the Russian literature. Filatova and Gronsberg[39] in 1957 reported on VC levels in a Russian PVC polymerization plant using the emulsion process to produce PVC. They found that levels in the reactor areas varied from 15 to 16,000 ppm, but the most frequently found concentrations varied from 38 to 310 ppm. In the precipitator and centrifuge area levels were 8 to 3050 ppm and in the drying oven area 4 to 15 ppm. An evaluation of different types of driers used in the PVC industry was reported in 1959 by Gavruseyko and Filatova.[43] VC concentrations up to 27 ppm were found in areas near chamber-type driers. They also reported on PVC dust concentrations varying from 100 to 248 mg/m^3 during drying operations and from 725 to 1200 mg/m^3 during unloading. Levels of 257 to 417 mg/m^3 were found while unloading vacuum-rabble driers. PVC dust levels encountered in screening operations varied from 72-170 mg/m^3. In 1965, Filatova et al[40] reported that levels of VC

in a PVC latex polymerization plant as high as 115 ppm were found and 75% of their measurements were above the maximum allowable concentration (MAC) of 12 ppm. PVC dust concentrations varied from 1 to 6.5 mg/m^3 except at the bagging station where levels as high as 78 mg/m^3 were found.

Filatova and Antonyuzhenko[38] have reviewed the changes in worker VC exposure in the Russian PVC industry from 1953 to 1969. From 1953 to 1958 the percentage of samples exceeding the MAC reduced from 80% to 2%. Also the maximum concentration of VC was reduced by a factor of 900. Increasing production rates brought an increase in levels of VC until in 1969, 76% of samples exceeded the MAC. However, maximum VC concentrations were 8-40 times lower than in 1954.

There have also been a few reports from other countries. Suciu et al[115] reported in 1967 that VC levels in a Romanian plant ranged as high as 2/20 ppm. Anghelescu et al[5] in 1969 reported that levels of VC at work stations in a Hungarian plant ranged from 43 to 213 ppm. Gitsios[46] reported that peak levels as high as 10,000 ppm were found in a Greek plant. Drums containing waste polymer were found to have VC levels as high as 600 ppm. Byren and Holmberg[21] reported in 1974 that VC levels in Swedish plants averaged 18-20 ppm in reactor rooms and less than 5 ppm in drying and packing areas.

Cook et al[25] reported that levels of VC present during reactor cleaning were usually 50-100 ppm with peaks of 600 to 1000 ppm close to the

workers hand during scraping. The remainder of the published data on workspace air concentrations of VC are from one plant. Baretta et al[10] reported extensive exposure data in 1969 showing peak levels above 1000 ppm. Levels of exposure for different jobs exceeded 50 ppm from 5 to 65% of the time. Time weighted average (TWA) exposures ranged from about 5 to over 200 ppm. TWA exposures to VC for one job category showed a daily and shift variation of 105 to 240 ppm. Kramer and Mutchler[63] reported on this same plant in 1972. TWA VC exposures from 1950 through 1965 had been determined. TWA's ranged from less than 10 ppm to 300 ppm. The average TWA exposure in 1950 was 155 ppm while the average in 1965 was 30 ppm. Ott et al[93] provide yet another source of information on VC levels at this plant. TWA's during the period 1950-1959 range from 5 to 825 ppm, but only one job class was above 385 ppm. From 1960 to 1966 TWA's ranged from 5 to 240 ppm with only two job categories above 100 ppm. TWA's were reduced further until at the time of the report in 1975 they were approximately 10 ppm.

Description of the processes involved, the jobs associated with each process and the VC exposures found for each are described in the remainder of this report.

DESCRIPTION OF PRODUCTION PROCESS

Vinyl Chloride Process

At the present time, VC is manufactured in the United States in 15 plants using three basic processes:

(1) Acetylene-hydrogen chloride process.

(2) Oxyhydrochlorination process.

(3) Ethylene dichloride pyrolysis process.[35]

The oxyhydrochlorination process is now the most widely used. The acetylene-hydrogen chloride process had been the major commercial process until the 1960's when plants began switching over due to changing economics of feedstocks for their respective processes. These processes are described as follows:

Acetylene-Hydrogen Chloride Process

Dry acetylene and anhydrous hydrogen chloride are reacted in fixed-bed reactors containing mercuric chloride-impregnated carbon catalyst according to the following equation:

$$C_2H_2 + HCl \text{----------} CH_2CHCl$$

The reaction products are compressed, cooled, and passed to a refrigeration unit for separation of VC by condensation. the condensed vinyl chloride is then passed to a two-column purification train where low-boiling products are removed overhead in the first column and recycled to the fixed-bed reactor along with noncondensed vapors from the first column feed drum. A portion of the recycle is passed to a vent reactor where an additional reaction occurs with resulting vent reactor products returned to the distillation train and inerts vented to the atmosphere.

The partially purified vinyl chloride is passed to the second column where the high-boiling compounds are removed and passed to an incinerator

for disposal. The purified VC removed from the second column is first transferred to holding tanks where purity is checked, and then to storage spheres.[1]

A flow schematic of this process is shown in Figure 1.

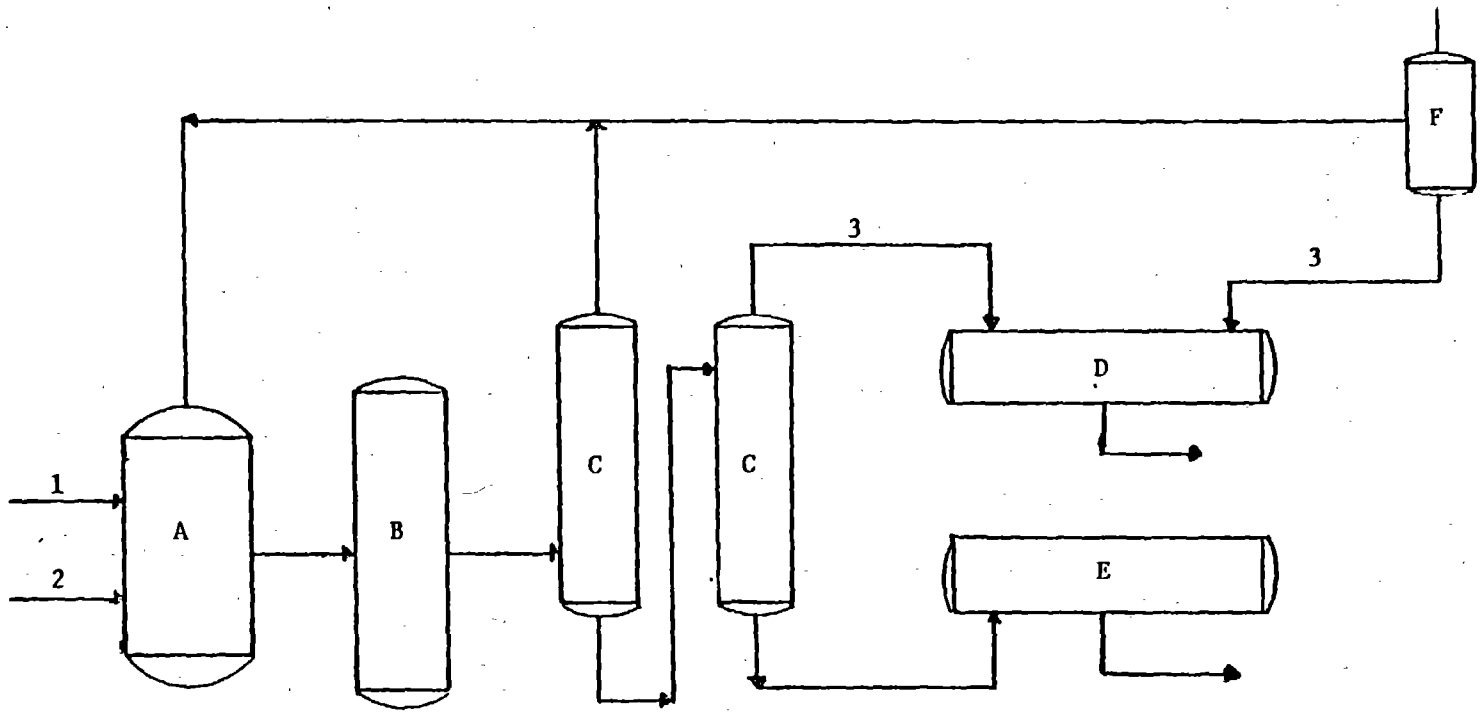
Ethylene Dichloride Pyrolysis Process

The ethylene dichloride pyrolysis process may be expressed as follows:

$$C_2H_4 + Cl_2 \text{----------} ClCH_2CH_2Cl$$

$$ClCH_2CH_2Cl \text{----------} CH_2CHCl + HCl$$

Wet ethylene dichloride produced by the direct chlorination of ethylene is passed through a drying column for removal of water, combined with recycle ethylene dichloride, and sent through a purification train for removal of heavy ends. The purified ethylene dichloride is vaporized and fed into a cracking furnace. The reactants from the cracking furnace are cooled and partially condensed in a quench system. The condensate is fed to a recovery column where ethylene dichloride is removed from the bottom of the column, passed to a column for removal of light ends, and recycled to the purification train. Overhead vapors from the ethylene dichloride recovery column are combined with quench system vapors, compressed, and fed to a hydrogen chloride recovery column where pur hydrogen chloride is removed overhead, transferred to other on-site plants, and used in other processes. The bottoms from the hydrogen chloride



LEGEND: A - Reactor
B - Compressor & Cooler
C - Fractionation Train
D - Vinyl Chloride Storage Tank
E - Heavy Ends Storage Tank
F - Vent Reactor

1 - Hydrogen Chloride
2 - Acetylene
3 - Vinyl Chloride

FIGURE 1. Acetylene-Hydrogen Chloride Process

recovery column is passed to a fractionating column where purified VC is removed overhead and sent to storage spheres.[1]

A flow schematic for this process is shown in Figure 2.

Oxyhydrochlorination Process

The oxyhydrochlorination process may be described as follows:

$$C_2H_4 + Cl_2 \text{----------} ClCH_2CH_2Cl$$

$$ClCH_2CH_2Cl \text{----------} CH_2CHCl + HCl$$

$$C_2H_4 + 2HCl + 1/2\ O_2 \text{----------} ClCH_2CH_2Cl + H_2O$$

Ethylene dichloride produced by reacting chlorine and ethylene is pyrolyzed to form VC and hydrogen chloride. The hydrogen chloride is separated from the reaction products and reacted with ethylene and air (oxygen) to produce ethylene dichloride and water. The ethylene dichloride produced by this reaction is dried and pyrolyzed to form vinyl chloride and hydrogen chloride.

Ethylene and chlorine are reacted in a water-cooled direct chlorination reactor to produce crude ethylene dichloride. The crude ethylene dichloride is sent through a purification train where light ends are removed overhead in the first column and heavy ends from the bottom of the second column. Purified ethylene dichloride removed overhead from the second column is sent through an ethylene dichloride cracking furnace. The reaction products from the cracking furnace are passed to a hydrogen chloride column where crude VC is removed as bottoms and sent to a purification column. Pure

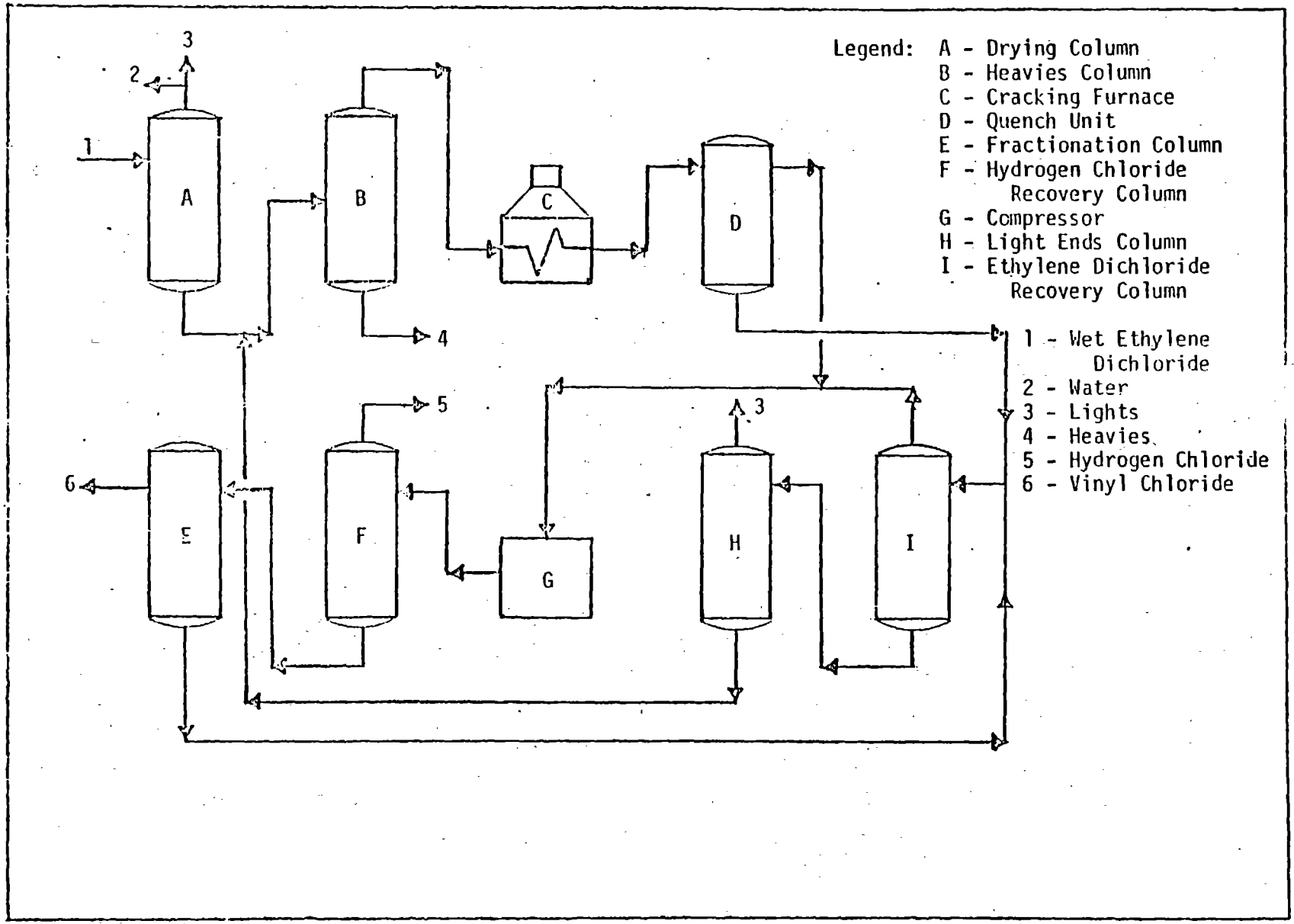


Figure 2 Ethylene Dichloride Pyrolysis Process

VC is recovered from the top of the VC column and transferred to a storage area where it is stored in large spheres. The bottoms from the VC column are recycled to the ethylene dichloride purification train.

Pure hydrogen chloride from the top of the hydrogen chloride column is sent to the oxyhydrochlorination reactor where it is reacted with ethylene and air to produce ethylene dichloride and water. The reaction products are sent through an oxyhydrochlorination primary recovery unit where the water is removed as bottoms and sent to waste. The overheads are passed to a second column where crude ethylene dichloride is removed as bottoms and cycled to the ethylene dichloride purification train. The overheads are passed to a secondary oxyhydrochlorination recovery unit. Vent gas is removed overhead in the first column, and the bottoms are sent to a second column. The overheads from the second column are recycled to the second column of the oxyhydrochlorination primary recovery unit.[1]

A flow schematic for this process is shown in Figure 3.

DESCRIPTION OF POLYVINYL CHLORIDE POLYMERIZATION PROCESSES

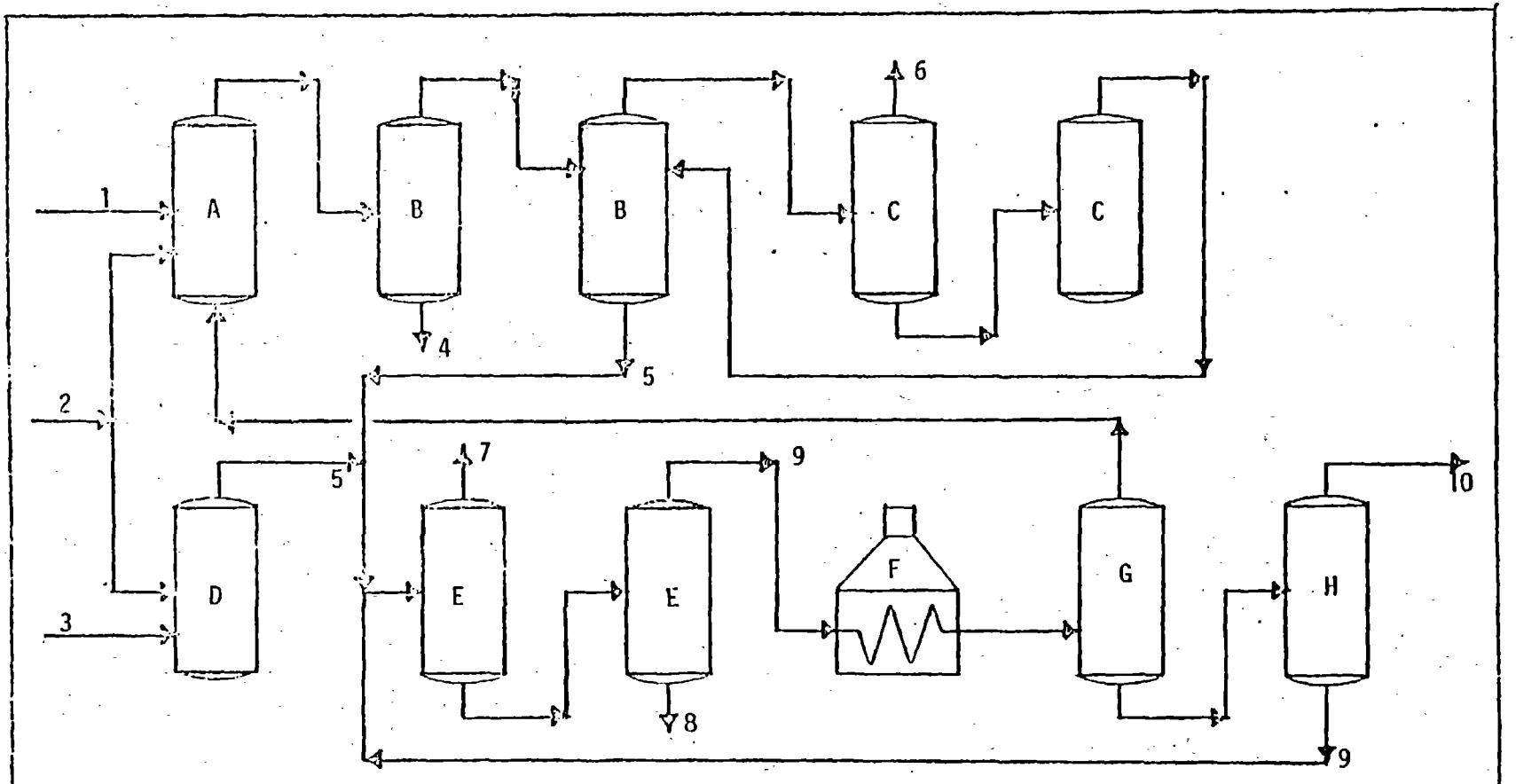
VC is currently being polymerized using four processes:[35]

(1) Suspension polymerization (78 percent of total production)

(2) Emulsion polymerization (13 percent of total production)

(3) Bulk polymerization (6 percent of total production)

(4) Solution polymerization (3 percent of total production)



Legend:

A - OHCL Reactor
B - OHCL Primary Recovery
C - OHCL Secondary Recovery
D - Direct Chlorination Reactor
E - EDC Purification
F - EDC Cracking Furnace
G - HCL Column
H - VCL Column

1 - Air
2 - Ethylene
3 - Chlorine
4 - Waste Water
5 - Crude EDC
6 - Vent Gas
7 - Lights
8 - Heavies
9 - Recycle EDC
10 - Vinyl Chloride

Figure 3 Oxyhydrochlorination Process

These are described as follows:

Suspension Polymerization

The suspension process is a batch aqueous polymerization of VC to produce PVC granules in the approximate size of 100μm. Polymerization is carried out in glasslined or stainless steel reactors, most with 2000 to 6000 gallon capacity, but some considerably larger reactors are found in new plants with capacities up to 15,000 gallons. The reactor is first charged with deionized water, VC, then a dispersing agent, a buffer, and an initiator after which the agitator is started and the contents of the reactor brought up to polymerization temperature (445-60°C.) by steam injected into the jacket of the vessel. After a short induction period, during which the exothermic reaction begins, cooling water is fed to the jacket to maintain a predetermined temperature. When the polymerization is essentially complete, the much reduced reaction rate makes it uneconomical to take the conversion above approximately ninety-five percent of completion. The contents of the reactor are dumped into a "blowdown tank" located directly beneath the reactor (usually each "blowdown tank" serves several reactors) and the excess VC is removed by a recovery system which usually consists of several compressors and a condenser to recover monomeric VC. The PVC slurry is sometimes heated to facilitate recovery of the monomer. The slurry is then blended with that from other reactors to reduce small variations in composition from batch to batch after which it is dewatered in a continuous centrifuge resulting in a polymer cake containing about ten to twenty percent moisture. The polymer particles are then dried in a rotary dryer, screened to remove coarse

particles, and sent to storage silos, packed in multiwalled paper bags, or loaded into bulk railroad cars.[4] A flow schematic of this process is shown in Figure 4.

Emulsion Polymerization

The emulsion process is also a batch aqueous polymerization of VC, but with emulsifiers, now generally used for the manufacture of paste-forming polymers with particle size distribution of approximately 1 μm. This process is similar to the suspension process with the exception that the deionized water, emulsifiers, initiator, and VC are metered into a stirred pre-mix vessel. Here, the ingredients are mixed and then fed through a homogenizer into the reactors. After the reaction is complete, the slurry is dropped to a "blowdown tank" where excess VC is removed and then recovered. The contents of the "blowdown tank" are then dropped to a blend tank where it is blended with slurry from other reactors to reduce variations in composition. The slurry is then concentrated and fed to a spray dryer where it is dried, ground (to remove agglomeration), and bagged. Because of its small particle size, emulsion resin is not stored or shipped in bulk. A flow schematic of this process is shown in Figure 5.

Bulk Polymerization

The bulk process is a batch polymerization of VC, without the use of water or a solvent, to produce PVC. The bulk or mass process has only relatively recently been used commercially in the United States. The

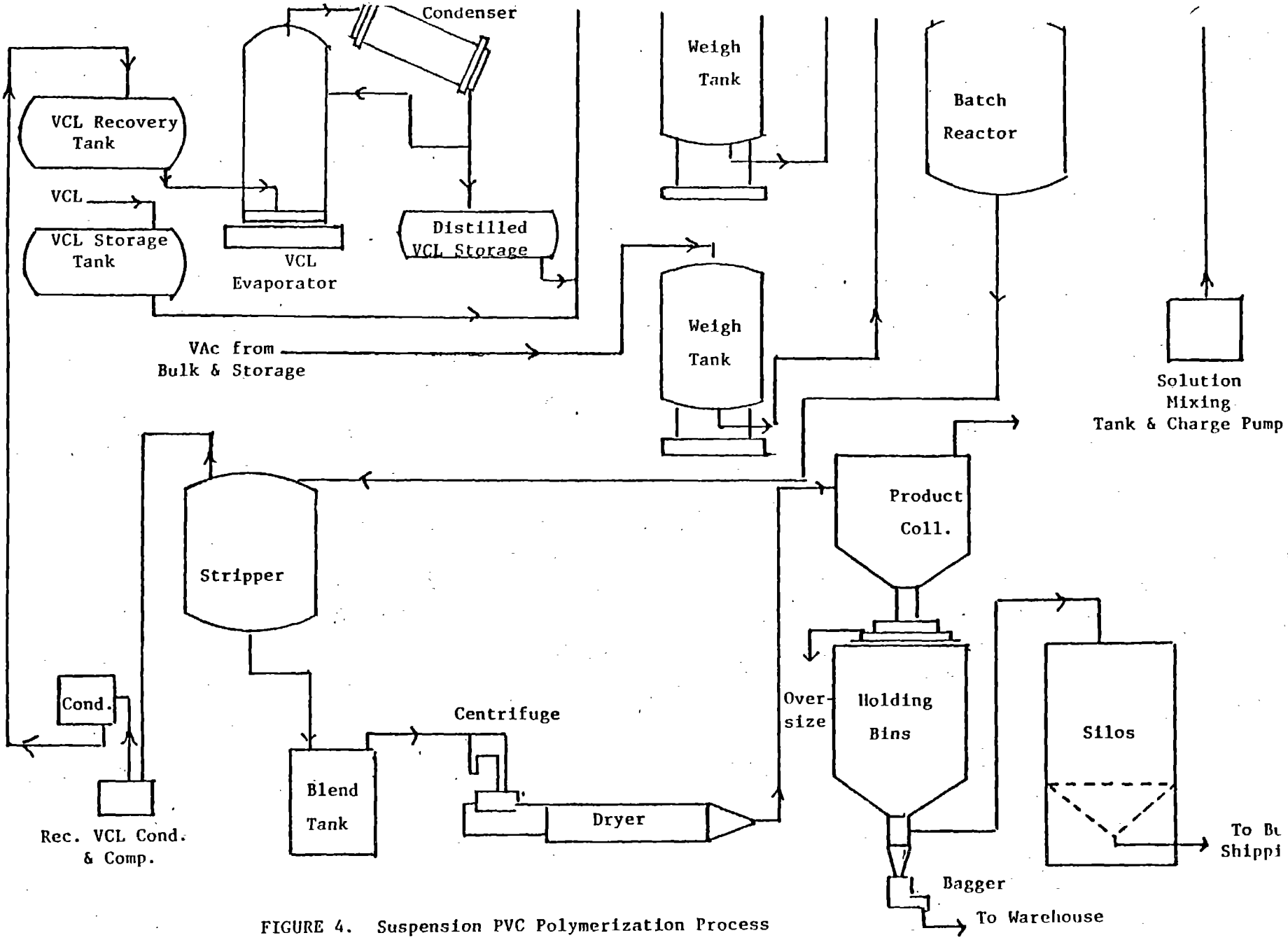


FIGURE 4. Suspension PVC Polymerization Process

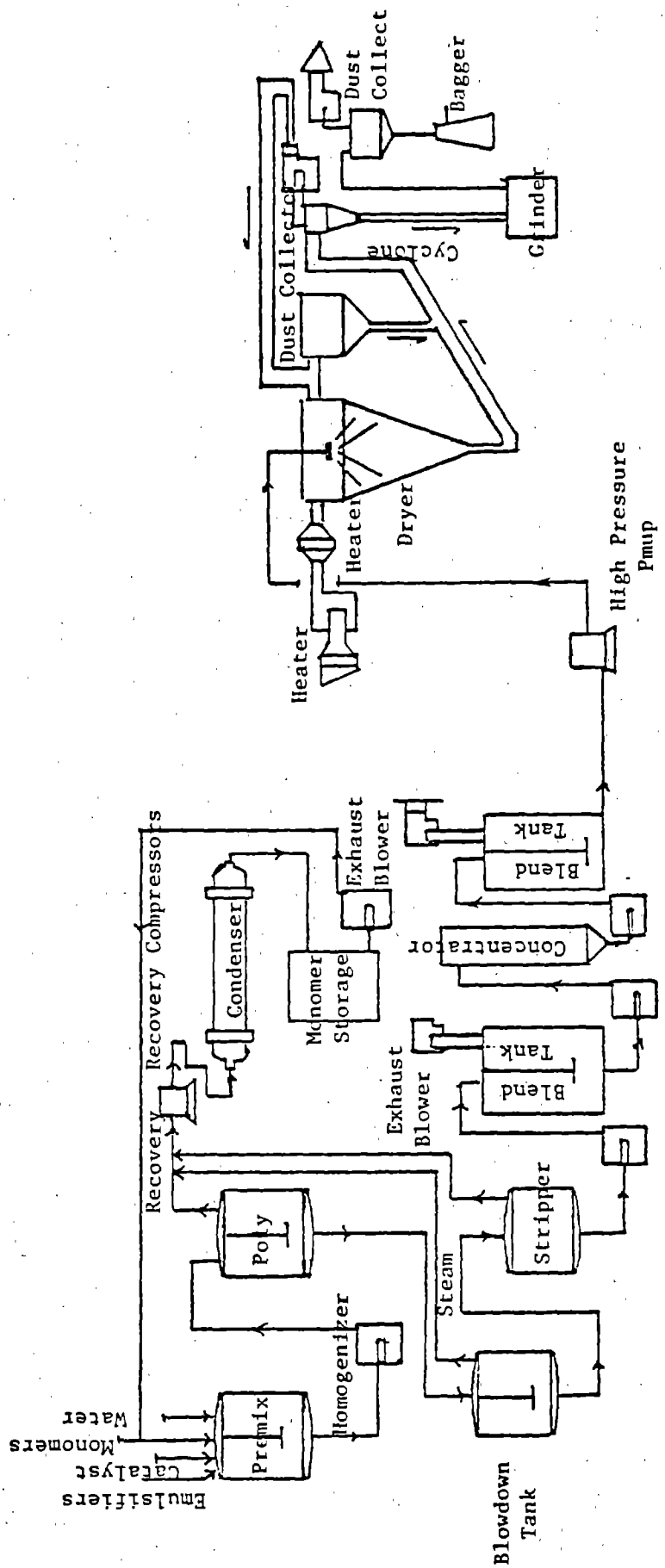


FIGURE 5. Emulsion PVC Polymerization

process was developed by and is licensed from a French company (Pechiney-St. Govain), and the major process equipment is manufactured in France. In this process, VC and initiator are fed to a prepolymerization reactor where the reaction is started and polymer seeds are produced in slurry form in liquid VC. The slurry is then transferred to other reactors where the polymerization is continued to form a free flowing PVC powder. When polymerization has reached the desired completion, unreacted VC is removed from the reactor and recovered. The granular polymer is then conveyed by air to a series of screens and grinders where the product is ground and classified before going to storage or bagging.[3] A flow schematic of this process is shown in Figure 6.

Solution Polymerization

The solution process is the oldest commercial PVC polymerization process in the United States, but it is also the least used. This process is unique in that the polymerization is carried out continuously in an organic solvent in which both the reactants and products are soluble. VC is pumped as a liquid under pressure to a reactor along with the solvent and initiator. After the polymerization has reached the desired completion state, the solution is transferred to a stripping column where excess VC is removed and then recovered. Next, the PVC is precipitated, separated from solution in a centrifuge, washed, dried, screened, and packaged. A flow schematic of this process is shown in Figure 7.

Polyvinyl Chloride Fabrication

Compounding

Compounding is the mixing of polyvinyl chloride resin with other materials,

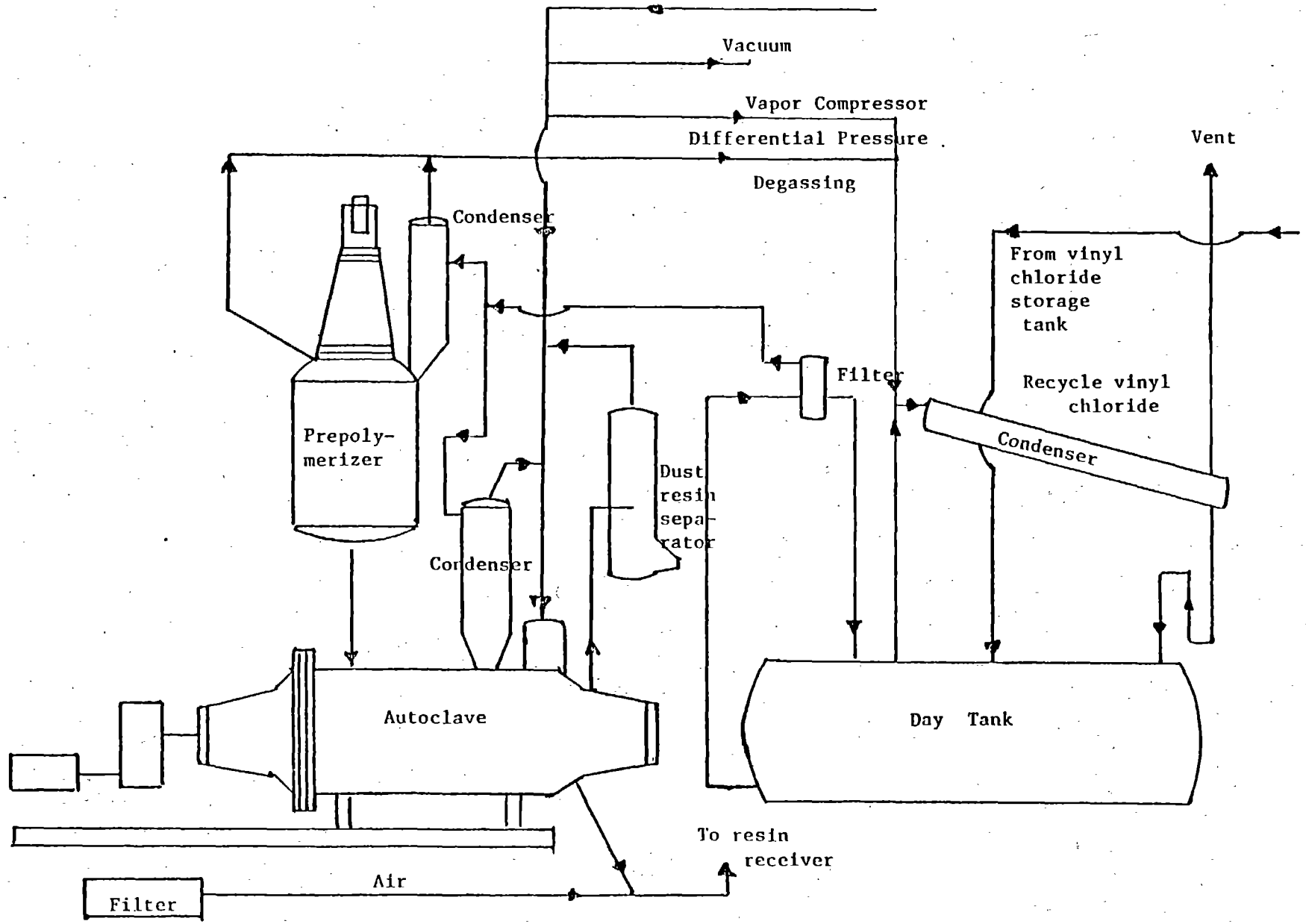


FIGURE 6. Bulk PVC Polymerization

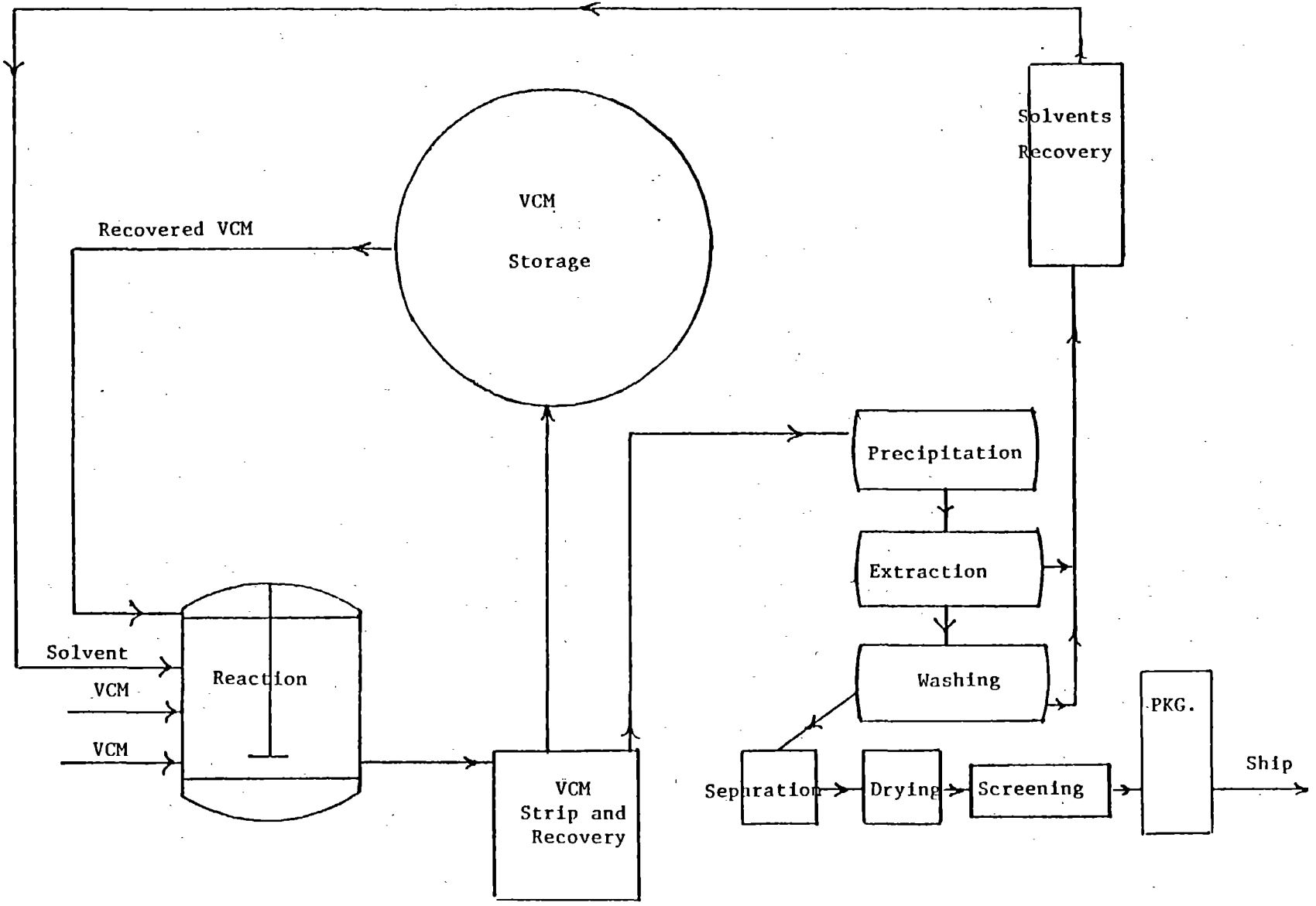


FIGURE 7. Solution PVC Polymerization

i.e., plasticizers, stabilizers, pigments, toners, fillers, lubricants, blowing agents, anti-oxidants, fungicides, sanitizers, and modifiers to give the PVC specific properties so that it can then be used in the manufacture of desired products.

Compounding is generally accomplished in blenders, Banburys, two-roll mills, and mixers. Combinations of the above equipment can be employed in a single compounding operation. Blenders are primarily used to make dry compounds. Mixers are normally used to make fluid-type compounds such as plastisols. Compounds containing solids are masticated using Banburys mixers, or two-roll mills. This mixture is then transferred to other operations for final processing.

Extrusion

Extrusion can be used to remove solids from plastic-type compounds, to de-aerate and compact compound, and to generate sufficient pressure to force the material through an extrusion die. The extrusion can be in the form of a rope that is fed to a calender, or a long length of material having a uniform cross section. Examples of extruded items are hoses, pipes, rods, threads, pellets, and shapes of intricate cross section. Extrusions can be rigid or flexible. A specific extrusion application is in the making of fibers.

PVC fibers are thin threads produced from extrusion through a die containing a number of small round or rectangular openings. The thread is passed through a cold water bath, dried, and wound onto spools.

Fibers or webs of fibers can be pressed into or layered onto a sheet of hot polyvinyl chloride in a calender to produce a sheet stock containing fibers or a web of fibers imbedded in the sheet. Polyvinyl chloride sheeting prepared in this manner has superior strength and resists tearing and stretching.

Molding

Molding can be divided into a number of types, i.e., injection molding, blow molding, vacu-forming, and embossing. The equipment used for each type of molding is entirely different in design and operation.

Injection molding is accomplished by forcing a plastic or fluid-like compound into the cavity of a heated mold. The end product assumes the configuration of the mold cavity and can be solid, hollow, rigid, or flexible.

Blow molding begins with the injection of a predetermined amount of plastic compound into the cavity of a mold. Air is then injected into the center of the injection and expands the plastic compound until it reaches the wall of the cavity. Sufficient air pressure is used to make the injected compound assume the configuration of the mold. The mold is heated and sets the design of the molded item. Blow-molded products can be rigid, semi-rigid, or flexible. Examples are plastic containers, wheels for toys, and basketballs.

Vacu-forming is accomplished by laying a sheet of preheated film on top of a mold. The air between the film and the mold is removed by a vacuum pump, and the atmospheric pressure above the sheet forces the hot film against the mold. The cold mold sets the mold design in the film. Vacu-formed items can be semi-rigid or flexible.

Embossing is the imprinting of a design into a sheet of plastic and is normally accomplished by feeding a plastic sheet through a set of rolls. One of the rolls contains the configuration that is to be imprinted into the plastic sheet. The other roll provides the pressure required to form the design in the plastic sheet. An example of embossing is the imprinting of a leather grain into plastic sheet stock.

Calendering

Calendering is generally accomplished using three or four-roll calenders. The calender most often used in the plastics industry is the four-roll "F" form calender which has a stack of three rolls in a vertical plane and two top rolls in a horizontal plane. In using this type of calender, a ribbon, cord, or belt of fluxed plastic is fed evenly across the "V" between the two top rolls of the calender to permit gravity feed of the stock to the calender. An adjustable gap between the calender rolls produces a continuous sheet of plastic having uniform thickness and longitudinal physical properties across the width of the sheet. The calender rolls also impart a smooth finish to both sides of the sheet as it passes through the rolls. A smaller-diameter roll strips the

sheet of plastic from the last calender roll and passes the sheet through a series of tensioning and cooling rolls. The cooled sheet is edge-trimmed and then fed to the windup rolls where the sheet is wound under uniform tension into rolls of desired diameter.

Thermoforming

Thermoforming is the forming of various shapes in thermoplastic sheets through the application of heat and pressure, and employs molds or forming blocks to shape the plastic. Seven basic types of thermo-forming are recognized by the plastics industry. Each type uses various modifications of the molds, forming blocks, clamping devices, frames, and pressures to form the desired end product. The seven types are: straight vacuum forming, drape vacuum forming, male form forced above sheet, vacuum snap-back forming, plug and ring forming, air pressure forming, and matched metal mold forming. Thermoformed products are finding usage in the packaging, automotive, furniture, toy, and garment industries.

Bonding of Polyvinyl Chloride

Bonding is the joining of two or more pieces of polyvinyl chloride through the use of adhesives, or the application of heat with or without pressure. Thermoplastic sheets and films can be jointed by heat sealing. Rigid thermoplastic materials such as laminate sheet, rod, and tubing can be jointed by adhesives or by hot gas welding.

Polyvinyl chloride adhesives contain solvents such as tetrahydrofuran to product tight, quick, and rapid assembly of components. Heat sealing can be accomplished through the use of one or two metal items containing electrical heating elements, oven heat, or high-frequency or electronic heating. Hot gas welding employs a gas or electrically heated gun and polyvinyl chloride welding rod to join the materials. This type of weld is similar in appearance to metal welds.

Plastisol Formulation

Plastisol formulations are fluid or semifluid compositions used to make thin flexible films. Preheated molds are dipped into the mixture, causing a thick layer to coat and partially cure on the mold. The mold is then withdrawn and placed in an oven for final cure of the compound. After oven curing, the plastisol-coated mold is removed from the oven, and the formed item is stripped from the mold using air pressure. The mold is then dipped in or sprayed with a release agent and returned to the preheat oven. The operation can be performed by hand or by automated units.

Plastisol coatings can also be applied to a fabric in a uniform layer and then passed through an oven where the coated stock undergoes partial curing. The coated stock is final-cured in a hot platen press. The platens can be plain or configured, and any design on the platen will be reproduced in reverse on the surface of the finished stock.

Foam

PVC foams are sheets of PVC which contain cells or bubbles of gas within

the material to give the sheet energy absorbing properties. Polyvinyl chloride foam formulations have a fluid or semifluid consistency and contain a blowing agent that produces a cellular structure in the finished item. In the case of sheet material, the formulation is spread onto paper or fabric and then passed through one or two ovens to expand and cure the sheeting. Normally, where paper is used as a backing material, the paper backing is stripped from the foamed sheet after leaving the first tunnel-type oven. The foamed sheet can then be joined to a second sheet to make a sandwich-type sheet stock that is sealed and final-cured in a second tunnel oven. Multi-layer sheet stock can be manufactured by joining a foam-coated fabric to a second vinyl sheet after the foam-coated fabric leaves the first tunnel oven. Sealing of the two layers and final curing of the foam composite takes place in the second tunnel oven.

Heated molds can be dipped into a plastisol formulation containing a blowing agent. A thick coating of the plastisol mixture adheres to and partially cures on the mold. The coated mold is withdrawn from the dip and is placed in an oven for the final cure and blowing operation.

Now, plastisol-type polyvinyl chloride compounds can be added to rubber-type compounds and a blowing agent to produce a compound that is processed on a Banbury and a two-roll mill. The milled stock can be further processed in a tube-type extruder. The extruded stock can be cut into desired shapes and expanded and cured in a series of two ovens, or the tubular stock can be expanded and cured in a tunnel-type oven.

DESCRIPTION OF STUDY

Bendix Launch Support Division conducted the VC monomer plant and PVC fabrication plant part of the study and NIOSH personnel the VC polymerization plants.

Walk-through surveys were first conducted in order to obtain information on processes used, number of workers at the plant, number of workers involved in the PVC operations, plant layout, raw materials used, other products produced at the plant, and any environmental sampling data available. Using this information plants were selected for full industrial hygiene studies, including sampling for VC.

Walk-through surveys were conducted at six monomer plants, six polymerization plants and thirteen fabrication plants.

From the information obtained during these surveys, plants were selected for in-depth surveys. The criteria for selection of plants for in-depth study included consideration of a representative cross section of the various process and production capacities in the PVC industry. The plants selected included three monomer plants, three polymerization plants and seven fabrication plants. Monomer plants selected included one plant using the acetylene-hydrogen chloride process, one plant using the ethylene dichloride pyrolysis process, and one using the oxhydrochlorination process. The polymerization plants included one plant using the solution, emulsion, and a modified emulsion processes, one plant

using the bulk and suspension process, and one using the suspension and emulsion processes. Processes used at the fabrication plants selected are shown in Table 1.

The industrial hygiene surveys primarily consisted of the collection of personal VC samples from which exposures were determined. Also PVC dust measurements were made. Ventilation systems, in selected areas, changes in the process, of work practices to reduce VC exposures, and past and present industrial hygiene practices were described in Appendix A.

Sampling and Analytical Procedures

Sampling for VC was conducted by using a charcoal adsorption method with subsequent desorption in carbon disulfide and analysis by gas chromatography. All samples were collected using Sipin Model SP-1 pumps at a flow rate of approximately 50 milliliters per minute. Commercially available charcoal adsorption tubes were used: Mine Safety Appliance tubes at Plant D, SKC tubes at Plants E and F and tubes supplied by the Anatole J. Sipin Company for the remainder of the plants. The first study conducted (by NIOSH, at Plant D) utilized a sample volume of 1.2 liters. The number of samples collected was such, that a number of samples, for the same man on the same day, were combined to facilitate analysis time (due to heavy lab work loads) thereby reducing the number of analyses. The survey at Plant E utilized

Table 1

FABRICATIONS PLANTS - POLYVINYL CHLORIDE SURVEY LIST

Company	Bonding	Calendering	Compounding	Extruding	Foam Formation	Molding	Plastisols	Thermoforming
1. Plant G	X		X	X		X		
2. Plant H	X		X	X		X		
3. Plant I			X			X	X	
4. Plant J			X	X	X	X		
5. Plant K	X	X	X	X	X		X	X
6. Plant L		X	X					X
7. Plant M	X	X	X	X	X		X	X

the same sample volume, but only a few samples were combined for analysis. At these two plants sampling was conducted according to NIOSH Physical and Chemical Analysis Branch Analytical Method (P&CAM) 127[85] and its May 31, 1974, Supplement for Vinyl Chloride. This method is found in Appendix B.

At Plant F a sample volume of 5 liters was used in accordance with P&CAM 178,[87] shown in Appendix B. All NIOSH samples were analyzed at the NIOSH laboratory in Salt Lake City, Utah. At the plants sampled by the contractor a sample volume of 5 liters was used for Plants A, B, C, G, H, I and J. A 10 liter sample volume was used at Plants K, L and M because of the low VC levels experienced at fabrication Plants G, H, I and J. The contractor utilized P&CAM 127[85] for analysis of the samples which they collected with the exception that Porapak type QS at 100°C, and 0.4 percent Carbowax 1500 on Carbopak A at 50°C were used as the chromatograph column materials.[11]

A small number of PVC personal dust samples were also taken in bagging areas of the polymerization plants and in a few fabrication plants.

Primarily the samples were total dust - gravimetric samples taken for approximately 4 hours at a flow rate of 2 liters per minute. A few samples were collected to allow microscopic examination of airborne dusts. All gravimetric samples were collected on 37 mm diameter MSA PVC membrane filters with a 5 μm pore size. Samples collected for

microscopic examination were collected on 37 mm Millipore AA membrane filters with a pore size of 0.8 μm. Three piece Millipore filter cassettes were used for all samples, with the cap removed for microscopic examination samples. An MSA Model G portable air sampling pump was used to draw air through the filter. Gravimetric sample filters were tared and weighed on the twenty milligram "A" scale of a Cahn Gram Electrobalance.

RESULTS

Monomer Plants

Plant A

A total of 47 VC samples were taken at this plant. A summary of these samples by job may be found in Table 3. VC concentrations ranged from less than 0.01 to 5.89 ppm. None of the TWA concentrations for the various jobs was above 1 ppm with the operator having the highest TWA, 0.86 ppm. The overall plant TWA was 0.55 ppm.

Plant B

A total of 75 VC samples were taken at Plant B and a summary of the results may be found in Table 3. VC concentrations ranged from less than 0.01 to 84.77 ppm. All TWAs except for the loader were below 1 ppm. The TWA for the loader was 21.85 ppm. The overall plant TWA was 3.40 ppm.

Plant C

A total of 109 VC samples were taken at Plant C and a summary of the results may be found in Table 4. VC concentrations ranged from 0.02 to 21.8 ppm. TWA concentrations for all jobs except loader were below 1 ppm. The TWA for loaders was 5.22 ppm and the overall plant TWA was 1.54 ppm.

Summary

A total of 231 samples to determine VC concentration were collected in monomer plants. The VC concentrations found varied from less than 0.01 to 84.77 ppm. TWA concentrations for the different job categories

Table 2

Summary of Vinyl Chloride Sampling Data by Job
in Monomer Plant A

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator	7	0.86	0.43	0.13-2.45
Loader	8	0.71	0.45	0.10-1.89
Maintenance Worker	4	0.17	0.11	0.02-0.32
Lab Technician	8	0.71	0.20	0.04-4.36
Foreman	7	0.10	0.08	0.03-0.21
Total of Personal Samples	34	0.55	0.21	0.02-4.36
Composite of All Area Samples	13	1.51	0.25	<0.01-5.89

* $\bar{x}$ = TWA

Table 3

Summary of Vinyl Chloride Sampling Data by Job
in Monomer Plant B

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator	32	0.34	0.12	0.01-3.46
Loader	9	21.85	13.97	3.00-84.77
Maintenance Worker	4	0.17	0.09	0.01-0.33
Lab Technician	12	0.18	0.08	<0.01-0.88
Total of Personal Samples	57	3.40	0.23	<0.01-84.77
Composite of All Area Samples	18	0.18	0.12	<0.01-1.22

* $\bar{x}$ = TWA

Table 4

Summary of Vinyl Chloride Sampling Data by Job
in Monomer Plant C

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator	56	0.79	0.27	0.09-18.2
Loader	20	5.22	1.16	0.06-21.8
Maintenance Worker	8	0.35	0.33	0.16-0.55
Lab Technician	16	0.14	0.07	0.02.1.01
Total of Personal Samples	100	1.54	0.30	0.02-21.8
Composite of All Area Samples	9	1.97	1.56	0.57-7.06

* $\bar{x}$ = TWA

ranged from 0.10 to 8.04 ppm. Only the TWA for loaders was above 1 ppm. The average of all personal samples taken at VC monomer plants was 1.89 ppm. A summary of these results is found in Table 5.

POLYMERIZATION PLANTS

Plant D

Solvent Process Area - Forty-five samples for VC were taken in this area. They reanged from none detected (ND) to 77.0 ppm. TWAs for the various jobs ranged from 0.6 to 2.9 ppm with only the reactor area operators and dryer area helpers above 1 ppm. The overall area TWA was 2.1 ppm. A summary of these results may be found in Table 6.

Modified Emulsion Process Area - Thirty-five samples for VC were taken in this area with a range of 0.1 to 82.8 ppm. A summary of these results may be found in Table 7. TWAs for the different jobs ranged from 3.5 to 38.7 ppm with an overall area TWA of 9.8 ppm.

Emulsion Process Area - A total of forty-one VC samples were taken in this area with a range of 0.1 to 82.8 ppm. A summary of these results may be found in Table 8. TWAs for the different jobs ranged from 3.5 to 38.7 ppm with an overall area TWA of 9.8 ppm.

Overall Plant - A total of 121 VC samples were taken in the plant with a range of ND to 82.8 ppm. TWAs for the various jobs ranged from 0.5

Table 5

Summary of Vinyl Chloride Sampling Data by Job
in All Monomer Plants Sampled

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator	95	0.64	0.21	0.01-18.2
Loader	37	8.04	1.67	0.06-84.77
Maintenance Worker	16	0.26	0.18	0.01-0.55
Lab Technician	36	0.28	0.09	<0.01-4.36
Foreman	7	0.10	0.08	0.03-0.21
Total of Personal Samples	191	1.89	0.26	<0.01-84.77
Composite of All Area Samples	40	1.09	0.30	<0.01-7.06

* $\bar{x}$ = TWA

Table 6

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant D

Solvent Process Area

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	20	5.6	2.3	ND-77.0	2.9
Operator - DA**	4	2.2	1.5	ND-3.7	0.9
Helper - DA**	1	2.3	2.3	2.3	2.3
Bagger	6	0.7	1.0	ND-1.1	0.7
Maintenance Worker	2	0.6	1.1	ND-1.3	0.6
Total of Personal Samples	33	3.9	1.8	ND-77.0	2.1
Control Room Area Samples	6	0.6	0.5	0.2-2.6	
Other Area Samples	6	3.4	2.4	0.9-7.1	

* Reactor Area

** Dryer Area

Table 7

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant D

Modified Emulsion Process Area

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	24	1.3	1.3	ND-4.2	1.3
Bagger	1	2.3	2.3	2.3	2.3
Foreman	2	0.3	0.2	0.1-0.4	0.3
Maintenance Worker	1	0.2	0.2	0.2	0.2
Total of Personal Samples	28	1.2	1.0	ND-4.2	1.2
Control Room Area Samples	6	1.3	1.4	ND-2.4	
Other Area Samples	1	1.4	1.4	1.4	

* Reactor Area

Table 8

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant D

Emulsion Process Area

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	14	11.0	6.2	0.1-29.8	8.2
Helper - RA*	12	10.2	6.1	0.7-77.0	8.9
Operator - DA**	2	38.7	20.6	5.2-82.8	38.7
Bagger	6	3.5	1.4	0.1-9.6	3.5
Foreman	3	8.6	2.8	0.3-22.0	8.6
Total of Personal Samples	37	11.1	4.8	0.1-82.8	9.8
Control Room Area Samples	4	7.5	5.3	1.2-11.1	

* Reactor Area

** Dryer Area

to 13.5 ppm and the overall plant TWA was 4.8 ppm. A summary of these results is found in Table 9.

A total of 5 dust samples were taken with an overall average concentration of 3.83 mg/m^3. The baggers in the solvent process area had an average exposure of 1.01 mg/m^3 while the one sample taken for the emulsion process baggers showed 15.27 mg/m^3. The results are shown in Table 10.

Plant E

Mass Process Area - Eighty-five samples for VC were collected in this area with a range of ND to 71.4 ppm. TWAs for the three job classifications ranged from ND to 4.6 ppm. The overall area TWA was 3.9 ppm. A summary of these results may be found in Table 11.

Suspension Process Area - Ninety samples for VC were collected in this area with a range of ND to 245.0 ppm. TWA concentrations for the different job classifications ranged from 0.3 to 16.5 ppm. The overall area TWA was 12.2 ppm. A summary of these results are found in Table 12.

Overall Plant - A total of 175 samples for VC were taken at the plant with a range of ND to 245.0 ppm. TWAs for the individual jobs ranged from 0.3 to 10.3 ppm with an overall plant TWA of 8.1 ppm. A summary of these results may be found in Table 13. Eight samples for PVC dust were taken, all personal samples for suspension resin baggers. The results of these samples can be found in Table 14.

Table 9

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant D

Overall Plant

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	58	5.2	2.3	ND-77.0	3.5
Helper - RA*	12	10.2	6.1	0.7-77.0	8.9
Operator - DA**	6	17.6	3.6	ND-82.8	13.5
Helper - DA**	1	2.3	2.3	2.3	2.3
Bagger	13	2.0	1.3	ND-9.6	2.2
Foreman	5	3.5	1.0	0.1-22.0	5.3
Maintenance Worker	3	0.5	0.6	ND-1.3	0.5
Total of Personal Samples	98	6.0	2.3	ND-82.8	4.8
Control Room Area Samples	16	2.6	1.3	ND-11.1	
Other Area Samples	7	3.1	2.2	0.9-7.1	

* Reactor Area

** Dryer Area

Table 10

Polyvinyl Chloride Dust Sampling Results
Plant D

Job	Dust Concentration mg/m^3
Bagger - E.R.	15.27
Bagger - St.R.	1.62
Bagger - St.R.	0.40
Fork Lift Operator	0.82
Area Sample	1.02

E.R = Emulsion Resin
St.R. = Solvent Resin

Table 11

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant E

Mass Process Area

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	36	4.0	2.5	ND-22.6	3.1
Helper - RA*	32	6.7	3.0	ND-71.4	4.6
Bagger	2	ND	ND	ND	ND
Total of Personal Samples	70	5.2	1.4	ND-71.4	3.9
Control Room Area Samples	15	1.4	1.5	ND-3.8	

* Reactor Area

Table 12

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant E

Suspension Process Area

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	54	16.8	7.4	ND-245.0	16.5
Helper - RA*	8	10.4	6.2	ND-23.6	11.8
Bagger	10	0.3	1.0	ND-0.9	0.3
Total of Personal Samples	72	12.2	4.6	ND-245.0	12.2
Control Room Area Samples	18	15.9	4.4	ND-96.5	

* Reactor Area

Table 13

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant E

Overall Plant

Job	n	$\bar{x}$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)	TWA (ppm)
Operator - RA*	90	11.5	4.7	ND-245.0	10.3
Helper - RA	40	7.5	3.5	ND-71.4	7.7
Bagger	12	0.3	1.0	ND-0.9	0.3
Total of Personal Samples	142	8.8	3.5	ND-245.0	8.1
Control Room Area Samples	33	7.9	2.4	ND-96.5	

* Reactor Area

Table 14

Polyvinyl Chloride Dust Sampling Results
Plant E

Job	Shift	Dust Concentration mg/m^3
Bagger - S.R.	1	0.69
"	1	0.72
"	1	2.50
"	1	1.02
"	1	0.70
"	3	0.38
"	3	1.06
"	3	0.57

S.R. = Suspension Resin

Plant F

Emulsion Process Area - A total of 111 VC samples were taken in this area with a range of 0.2 to 103.8 ppm. TWAs ranged from 1.4 to 16.3 ppm. The overall area TWA was 4.7 ppm. A summary of these results is found in Table 15.

Old Suspension Process Area - Seventy-eight VC samples were taken in this area with a range of 1.0 to 160.6 ppm. TWA concentrations for the various jobs ranged from 7.2 to 19.8 ppm. The overall area TWA was 17.6 ppm. A summary of these results is found in Table 16.

New Suspension Process Area - Forty-eight VC samples were taken in this area with a range of 0.1 to 78.6 ppm. TWAs for the two job classifications were 6.4 and 8.0 ppm while the overall area TWA was 7.8 ppm. A summary of these results may be found in Table 17.

Overall Plant - A total of 237 VC samples were taken at the plant with a range of 0.1 to 160.6 ppm. TWAs ranged from 1.7 to 16.8 ppm. The overall plant TWA was 9.4 ppm. A summary of these results may be found in Table 18. Ten PVC dust samples were taken. Emulsion resin baggers showed an average exposure of 8.08 mg/m^3 while the one sample for a suspension resin bagger showed 0.47 mg/m^3. The sample for a dryer operator showed an exposure of 0.73 mg/m^3. The results of the dust sampling can be found in Table 19. Particle sizing on 2 samples showed

Table 15

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant F

Emulsion Process Area

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	29	8.9	6.3	2.3-98.0
Helper - RA***	24	16.3	10.3	3.5-103.8
Operator - DA**	25	3.1	2.4	0.5-9.6
Helper - DA**	9	1.7	1.3	0.6-3.6
Bagger	10	2.2	1.9	0.2-4.1
Maintenance Worker	1	1.4	1.4	1.4
Total of Personal Samples	98	4.7	3.7	0.2-103.8
Control Room Area Samples	7	3.1	2.4	1.0-5.9
Other Area Samples	6	5.6	5.0	1.4-15.9

*** Reactor Area

** Dryer Area

* $\bar{x}$ = TWA

Table 16

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant F

Old Suspension Process Area

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA**	28	19.8	11.4	5.3-160.6
Helper - RA**	37	17.3	11.2	1.3-160.5
Maintenance Worker	4	7.2	6.6	4.2-12.8
Total of Personal Samples	69	17.6	10.9	1.3-160.6
Control Room Area Samples	9	6.1	4.8	1.0-11.5

* $\bar{x}$ - TWA

** Reactor Area

Table 17

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant F

New Suspension Process Area

Job	n	$\bar{x}$* (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	36	8.0	3.8	0.8-78.6
Operator - DA**	6	6.4	4.0	1.1-21.0
Total of Personal Samples	42	7.8	3.8	0.8-78.6
Control Room Area Sample	6	0.5	0.3	0.1-1.6

* $\bar{x}$ = TWA

** Dryer Area

*** Reactor Area

Table 18

Summary of Vinyl Chloride Sampling Data by Job
in Polymerization Plant F

Overall Plant

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	93	10.6	5.6	0.8-160.6
Helper - RA***	61	16.8	10.7	1.3-160.5
Operator - DA**	31	3.7	2.6	0.5-21.0
Helper - DA**	9	1.7	1.3	0.6-3.6
Bagger	10	2.2	1.9	0.2-4.1
Maintenance Worker	5	5.3	4.0	1.4-12.8
Total of Personal Samples	209	9.4	4.7	0.1-160.6
Control Room Area Samples	22	3.1	1.5	0.1-11.5
Other Area Samples	6	5.6	5.0	1.4-15.9

* $\bar{x}$ = TWA

** Dryer Area

*** Reactor Area

Table 19

Polyvinyl Chloride Dust Sampling Data
Plant F

Job	Dust Concentration mg/m^3
Dryer Operator	0.73
Bagger - E.R.	2.00
"	13.34
"	14.10
"	3.00
"	2.39
"	18.62
"	3.92
"	5.22
Bagger - S.R.	0.47

E.R. = Emulsion Resin
S.R. = Suspension Resin

that all particles were below 6.7 μm in diameter and that 90% of the particles had diameters less than 2.4 μm.

Emulsion Process

A total of 152 samples were taken in emulsion process areas with a range of 0.1 to 103.8 ppm. TWAs for the various jobs ranged from 1.4 to 14.3 ppm with an overall TWA of 7.8 ppm. A summary of these results may be found in Table 20.

Suspension Process

A total of 216 samples were taken in suspension process areas with a range of ND to 245.0. TWAs ranged from 0.3 to 16.7 ppm with an overall TWA of 12.6 ppm. A summary of these results may be found in Table 21.

Summary

A total of 517 samples were taken in PVC polymerization plants with VC concentrations ranging from ND to 245.0 ppm. TWA concentrations for the various jobs ranged from 1.8 to 14.3 ppm. Reactor area helpers and operators had the highest TWAs - 14.3 and 9.1 ppm respectively.

The average of all personal samples taken in polymerization plants was 8.4 ppm. A summary of these results may be found in Table 22. A total of 22 dust samples were taken. Emulsion resin baggers showed an average exposure of 8.88 mg/m^3. The remainder of jobs averaged 1.01 mg/m^3 dust or less. The overall average was 4.18 mg/m^3. These results can be found in Table 23.

Table 20

Summary of Vinyl Chloride Sampling Data by Job in Emulsion Process Areas--All Plants Sampled

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	43	9.4	6.3	0.1-98.0
Helper - RA***	36	14.3	8.7	0.7-103.8
Operator - DA**	27	5.5	2.8	0.5-82.8
Helper - DA**	9	1.7	1.3	0.6-3.6
Bagger	16	2.5	1.8	0.1-9.6
Foreman	3	8.6	2.8	0.3-22.0
Maintenance Worker	1	1.4	1.4	1.4
Total of Personal Samples	135	7.8	3.9	0.1-103.8
Control Room Area Samples	11	5.0	3.4	1.0-11.1
Other Area Samples	6	5.6	5.0	1.4-15.9

* $\bar{x}$ = TWA

** Dryer Area

*** Reactor Area

Table 21

Summary of Vinyl Chloride Sampling Data by Job in Suspension Process Areas--All Plants Sampled

Job	n	$\bar{x}$* (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	118	12.5	5.6	ND-245.0
Helper - RA***	45	16.7	10.6	ND-160.5
Operator - DA**	6	6.4	4.0	1.1-21.0
Bagger	10	0.3	1.0	ND-0.9
Maintenance Worker	4	7.2	6.6	4.2-12.8
Total of Personal Samples	183	12.6	6.1	ND-245.0
Control Room Area Samples	33	6.3	1.6	ND-96.5

* $\bar{x}$ - TWA

** Dryer Area

*** Reactor Area

Table 22

Summary of Vinyl Chloride Sampling Data by Job
-- All Polymerization Plants Sampled

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Operator - RA***	241	9.1	4.2	ND-245.0
Helper - RA***	113	14.3	8.2	ND-160.5
Operator - DA**	37	5.4	2.7	ND-82.8
Helper - DA**	10	1.8	1.4	0.6-3.6
Bagger	35	1.9	1.5	ND-9.6
Foreman	5	3.5	1.0	0.1-22.0
Maintenance Worker	8	4.2	2.6	ND-12.8
Total of Personal Samples	449	8.4	3.8	ND-245.0
Control Room Area Samples	55	3.8	1.5	ND-96.5
Other Area Samples	13	4.4	3.3	0.9-15.9

* $\bar{x}$ = TWA

** Dryer Area

*** Reactor Area

Table 23

Summary of Polyvinyl Chloride Dust Sampling Data
Polymerization Plants

Job	n	$\bar{x}$
Bagger - S.R.	9	0.94
Bagger - St.R	2	1.01
Bagger - E.R.	9	8.88
Fork Lift Operator	1	0.82
Dryer Operator	1	0.73
Total of Personal Samples	22	4.18

S.R. = Suspension Resin
St.R. = Solvent Resin
E.R. - Emulsion Resin

FABRICATION PLANTS

Plant G

A total of 68 samples for VC were taken in this plant with a range of ND to 0.02 ppm. TWAs for all job classifications were less than 0.01 ppm. A summary of these results is found in Table 24.

Plant H

A total of 52 samples for VC were taken at Plant H with a range of less than 0.01 to 0.68 ppm. TWAs for all jobs were below 0.10 ppm and the overall plant TWA was 0.03 ppm. A summary of these results may be found in Table 25.

Plant I

Forty-eight samples for VC were taken in this plant with a range of ND to 0.06 ppm. TWAs for the two job categories were ND and 0.01 ppm. A summary of these results can be found in Table 26.

Plant J

Forty-eight samples for VC were taken in this plant with no VC being detected. A summary of these results is shown in Table 27.

Plant K

A total of 24 samples were taken at this plant with a range of ND to 0.13 ppm. TWAs for all jobs were 0.01 ppm or less. A summary of these results is found in Table 28.

Table 24

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant G

Job	n	$\bar{x}$* (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Compounding Personnel	8	<0.01	<0.01	< 0.01-0.02
Extrusion Personnel	24	<0.01	< 0.01	ND-0.02
Lab Personnel	4	<0.01	<0.01	< 0.01
**Miscellaneous Personnel	16	<0.01	<0.01	ND-0.01
Total of Personal Samples	52	<0.01	<0.01	ND-0.02
Composite of All Area Samples	16	<0.01	<0.01	ND-0.02

* $\bar{x}$ = TWA

** Engineers in Process Area Doing Experimental Work.

Table 25

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant H

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Compounding Personnel	8	0.09	0.06	0.01-0.27
Extrusion Personnel	16	0.01	0.01	<0.01-0.02
Lab Personnel	8	0.03	0.02	0.01-0.06
Maintenance Personnel	8	0.01	0.01	<0.01-0.02
Molding Personnel	8	0.01	0.01	<0.01-0.03
Total of Personal Samples	48	0.03	0.02	<0.01-0.27
Composite of All Area Samples	4	0.37	0.31	0.13-0.68

* $\bar{x}$ = TWA

Table 26

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant I

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}$ (ppm)	Range (ppm)
Lab Personnel	4	ND	ND	ND
Plastisol Dipping Personnel	40	0.01	0.01	ND-0.06
Total of Personal Samples	44	<0.01	<0.01	ND-0.06
Composite of All Area Samples	4	ND	ND	ND

* $\bar{x}$ = TWA

Table 27

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant J

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}_g$ (ppm)	Range (ppm)
Calender Personnel	12	ND	ND	ND
Compounding Personnel	12	ND	ND	ND
Extrusion Personnel	8	ND	ND	ND
Molding Personnel	8	ND	ND	ND
Miscellaneous Personnel	4	ND	ND	ND
Total of Personal Samples	44	ND	ND	ND
Composite of All Area Samples	4	ND	ND	ND

* $\bar{x}$ = TWA

Table 28

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant K

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}$ (ppm)	Range (ppm)
Calender Personnel	6	<0.01	<0.01	ND-<0.01
Compounding Personnel	12	0.01	<0.01	ND-0.13
Maintenance Personnel	2	<0.01	<0.01	ND-<0.01
Total of Personal Samples	20	<0.01	<0.01	ND-0.13
Composite of All Area Samples	4	<0.01	<0.01	<0.01

* $\bar{x}$ = TWA

Plant L

Thirty six samples were collected at this plant with concentrations ranging from 0.02 to 2.44 ppm. TWAs for the various jobs ranged from 0.27 to 1.48 ppm with only one job having a TWA higher than 1 ppm. The overall plant TWA was 0.63 ppm. A summary of these results is shown in Table 29. Ten dust samples were also taken at this plant. All were area samples. The average dust concentration was 8.92 mg/m^3. These results are shown in Table 30.

Plant M

A total of 24 samples for VC were collected at Plant M with a range of ND to 0.02 ppm. TWAs for the two job classifications were 0.01 and 0.02 ppm and the overall plant TWA was 0.01 ppm. A summary of these results may be found in Table 31. Seven area dust samples were taken at this plant with an average dust concentration of 7.21 mg/m^3. These results are shown in Table 32.

Summary

A total of 300 samples for VC were taken in PVC fabrication plants with the concentrations ranging from ND to 2.44 ppm. TWA concentrations for the different jobs ranged from less than 0.01 to 0.57 ppm. The average for all personal samples taken in PVC fabrication plants was 0.14 ppm. A summary of these results may be seen in Table 33. A total of 17 area dust samples were taken in fabrication plants with an average of 8.22 mg/m^3.

Table 29

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant L

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}$ (ppm)	Range (ppm)
Calender Personnel	8	1.48	1.33	0.50-2.44
Compounding Personnel	16	0.42	0.37	0.13-0.69
Extrusion Personnel	10	0.27	0.15	0.02-0.76
Lab Personnel	2	0.33	0.12	0.02-0.68
Total of Personal Samples	36	0.63	0.36	0.02-2.44

* $\bar{x}$ - TWA

Table 30

Polyvinyl Chloride Dust Sampling Data
Plant L

Location	Dust Concentration mg/m^3
Near Blender	12.5
"	7.22
"	6.67
"	8.75
"	11.67
Near Mixer	10.0
"	6.06
Near Calender	11.67
"	8.33

Table 31

Summary of Vinyl Chloride Sampling Data by Job
in Fabrication Plant M

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}$ (ppm)	Range (ppm)
Calender Personnel	2	0.02	0.02	0.02
Compounding Personnel	22	0.01	0.01	ND-0.02
Total of Personal Samples	24	0.01	0.01	ND-0.02

* $\bar{x}$ = TWA

Table 32

Polyvinyl Chloride Dust Sampling Data
Plant M

Location	Dust Concentration mg/m^3
Mixing Area	6.67
Blender Area	1.67
Mill Area	6.67
Banbury Mixer Area	13.33
Calender Area	6.67
Plastisol Mixing Room	7.9
Cast Film Line	7.27

Table 33

Summary of Vinyl Chloride Sampling Data by Job
--All Fabrication Plants Sampled

Job	n	$\bar{x}^*$ (ppm)	$\bar{x}$ (ppm)	Range (ppm)
Calender Personnel	28	0.57	0.24	ND-2.44
Compounding Personnel	78	0.11	0.05	ND-0.69
Extrusion Personnel	58	0.09	0.04	ND-0.76
Lab Personnel	18	0.08	0.05	ND-0.68
Maintenance Personnel	10	0.01	<0.01	ND-0.02
Molding Personnel	16	<0.01	<0.01	ND-0.03
Plastisol Dipping Personnel	40	0.01	<0.01	ND-0.06
Miscellaneous Personnel	20	<0.01	<0.01	ND-0.01
Total of Personal Samples	268	0.14	0.03	ND-2.44
Composite of All Area Samples	32	0.04	0.05	ND-0.68

* $\bar{x}$ = TWA

CONCLUSIONS

Monomer Plants

Monomer plants had generally low concentrations of VC exposure for personnel. The only job category with a TWA higher than 1 ppm was that of loader. The work practices for this job were being modified to lower exposures. One plant had already lowered exposures below 1 ppm and plants were using self contained breathing apparatus or supplied air respirators to limit exposure to VC for this job. So the levels found are indicative of the potential exposure but not necessarily the actual exposure of these workers. These levels also suggest that this has been a high exposure job in the past, before respiratory protection was used.

Polymerization Plants

Jobs requiring the most time in the reactor areas had, as would be expected, the highest exposure to VC. Reactor area helpers had the highest TWA and it was these workers who did the job of cleaning reactor vessels when necessary. Again these workers were using supplied-air respirators when inside vessels or performing other jobs, such as changing filters, that could have high exposures to VC, so the exposures may not be actual exposures. VC exposures in the past, though, were higher because vessels were not purged of VC nearly so well before workers entered. Reactor area operators also had high exposures. Baggers and dryer area helpers had the lowest TWAs, but were still not under 1 ppm.

The workers involved with the solvent process had the lowest TWAs, then the mass process workers, the emulsion process workers

and finally the suspension process workers had the highest TWA. One other variable which was impossible to measure was management attitude towards keeping VC exposures low. It was observed within plants that housekeeping and work practice procedures varied from area to area because of the attitude of foremen in the areas. Dust levels were relatively low for all jobs except the emulsion resin baggers. The high dust levels for this job are probably due to the small particle size of emulsion resin. Better dust control measures need to be initiated for this job.

Fabrication Plants

All job categories in the fabrication plants had TWA exposures that were quite low. Only calender personnel had a TWA above the required action level of 0.5 under the new OSHA standard. Working locations in almost every instance of exposure to VC were amenable to the application of standard control measures, such as local exhaust ventilation. Dust levels were uniformly high for the two plants where measurements were taken. However, the dust is probably not all PVC, since fillers and other additives are being used in the operations. Better dust controls should still be implemented in areas where dusty materials are handled.

Overall, polymerization plants had the highest TWA of 8.4 ppm and also the highest individual job TWA of 14.3 ppm. Also workers in polymerization plants had the widest range of VC exposures, with peaks as high as 245 ppm. Monomer plant workers had the next highest overall

TWA of 1.89 ppm, a factor of 4 lower than polymerization plant workers. The TWA for one job category was 8.04 ppm, almost the same as the polymerization plant workers, while the remaining workers were considerably lower. Fabrication plant workers had the lowest overall TWA of 0.14 ppm, a factor of 60 lower than polymerization plant workers and 13-1/2 lower than monomer plant workers. These results substantiate the initial emphasis of studies on polymerization plant workers as having the highest VC exposures.

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Appendix A

DESCRIPTION OF PLANTS

I. Monomer Plants

Plant A

This facility manufactures VC using the Acetylene-Hydrogen Chloride Process portrayed in Figure 1. The plant normally operates at 10 percent of capacity and then only when acetylene, manufactured at the plant, is available for the manufacture of VC. Nearly all of the acetylene manufactured at this site is sold as product to nearby chemical plants. The VC plant was in operation during the survey.

The VC plant had been in operation for 12 years and involves 25 people. A total of 375 people were employed at the facility, which manufactures acetylene, methanol, ammonia, and VC as major products, with vinyl acetylene, diacetylene, methyl acetylene, dimethyl ether, and 2-chloropropene as byproducts. Liquid air and liquid nitrogen were also manufactured at the facility.

A VC surveillance program was established at this company in April, 1974. The manufacturing areas are monitored at various points using a Miran Infrared Scanner with chart readout, and a Century Organic Vapor Analyzer(OVA). Air samples are collected in mylar sampling bags on a regular basis. The air samples are analyzed for VC concentration using gas chromatography,

The results of the company's sampling program showed a TWA concentration

range of 0.01 to 67 parts per million (ppm) of vinyl chloride.

Except for the control laboratory and control room, all operations are performed outdoors. The control laboratory and control room are air conditioned with one air change per minute.

The following changes have been made to their industrial hygiene program.

All employees are required to wear supplied air-respirators when the VC concentration is expected to be over 50 ppm.

Signs are posted whenever area monitoring indicates high VC concentrations are in the air.

Additional purging time is required on all vessels which handle VC prior to being opened.

High priority has been placed on work designed to eliminate VC leaks.

Gas masks and slicker suits are worn in accordance with current OSHA regulations.

Plant B

This facility produces VC using the Ethylene Dichloride Pyrolysis Process. The VC plant had been operating for 16 years and operates on a continuous basis. VC produced at the plant is sold as a product and was also used

on site for the manufacture of polyvinyl chloride resin and 1,1,1-trichloroethane.

A total of 2,500 people were employed at the facility; however, only 100 people were involved in the manufacture of VC. Other products produced at this facility were tetraethyl lead, tetramethyl lead, sodium, sodium hydroxide, methyl chloride, ethyl chloride, ethylene dichloride, trichloroethylene, and perchloroethylene.

The VC plant and storage areas were located outside with the exception of the control room, which was air conditioned, and the quality control laboratory. The laboratory was equipped with a supply air blower and exhaust air system via the hoods. The laboratory air was changed every 1.4 minutes.

A flow diagram of the process that this company used to manufacture VC is portrayed in Figure 2.

A surveillance program for VC was put into effect in April 1974. In this program, a Miran II Infrared Analyzer is used to monitor the plant air for VC on a continuous basis, and the OVA is used for searching out emission sources or wherever "spot" monitoring is desired. The charcoal tube method is used to obtain 15-minute spot samples and 4-hour personnel samples on a regular basis. Gas chromatography is used to determine the concentration of VC picked up in the charcoal tubes. The results

of this company's sampling program show VC concentration range of 0.01 to 62 ppm.

The following work practice changes had been instituted to protect their employees.

During loading, VC tank car spew guages were previously vented to atmosphere. The spew gauge vent system is now closed with a sensing device to detect liquid, indicating the car is loaded.

After loading, VC tank car load and equalizing lines were previously disconnected with residual vent (mostly vapor) allowed to escape to atmosphere. These lines are now purged with nitrogen (to flare) prior to disconnecting.

VC liquid samples were previously taken and disposed of in such a manner that the potential for release of material to the atmosphere was quite high. Closed systems have been provided to permit purging sample bombs and connections, obtaining samples, and disposing residual sample material without exposure of personnel.

The former practice of draining a gage glass to verify the liquid level has been discontinued.

Procedures for preparing equipment for opening have been revised, and extra precautions taken to minimize risk of VC release to atmosphere.

Example: VC liquid product scrubbers were previously prepared for recharging by displacing liquid (with nitrogen) and venting to flare. Purging to remove residual vapors was minimal at best. The revised procedure calls for thorough purging of the scrubber, utilizing heated inert gas and heating panels on the scrubber shell to ensure negligible release of VC to atmosphere when the scrubber is opened.

While respiratory equipment has always been available for use when needed, personal respirators are now issued to all individuals for use whenever the potential for exposure exists.

It is imposible to ascertain the effect of each work practice change separately, but the cumulative effect is favorable as indicated by the result of personnel and area monitoring.

Changes to their industrial hygiene practices are described below.

Prior to the establishment of the 50-ppm interim standard, VC was considered as one of a family of chlorinated hydrocarbons produced in the Hydrocarbon Area. There were no special hygiene practices in effect for VC. Respiratory equipment was available for use in the event of spills or in doing any job where exposure to excessive amounts of VC (other chlorocarbons, hydrogen chloride, chlorine) was likely to occur. The situation today, of course, is quite different. Area air monitoring for VC is essentially continuous, using a Miran II Infrared Analyzer. Portable OVAs are used for searching out emission sources or wherever

"spot" monitoring is desired. Certain areas have been designated as requiring respiratory protection. All personnel have been issued respirators (and trained in their proper use) and have been instructed to wear them when doing any job (e.g., opening or closing valves) where the potential for exposure to VC exists. Supplied air respirator hook-ups are being extended to all areas of the VC plant.

The Medical Department has instituted a program for routine personnel monitoring utilizing carbon tube adsorption units. A medical surveillance program for all personnel who may have been exposed to VC in the past has been instituted and will be continued.

On-the-job eating, drinking and smoking policies have not been revised as these activities were already restricted to designated areas.

Plant C

The Oxyhydrochlorination Process was employed by this facility to manufacture VC from Ethylene and chlorine as illustrated in Figure 3. This company is a large producer of VC, normally operates on a continuous bases, and has been producing VC at this facility for 12 years. A total of 600 people were employed at this facility; however, only 242 employees were exposed to VC. Products produced at this facility were ethylene, chlorine, ethylene dichloride, hydrochloric acid, VC, trans-1,2,-dichloroethylene, benzene, chloral, carbon tetrachloride, chloroform trichloroethylene, ethyl chloride, and chloropropane. No PVC resin was produced at this site.

The manufacture of VC was a closed-system operation, and all of the production equipment was located outdoors except for the instrument houses, control rooms, laboratory and offices.

The offices, laboratory, control rooms and instrument houses were kept under positive pressure. In addition, the equipment in the instrument houses was purged with nitrogen. No VC was piped to the control rooms. All VC in the laboratory was kept and handled in high-volume ventilation hoods.

All production employees had their own respiratory protection devices. Respiratory protection devices were kept in the control rooms for any maintenance personnel working in the area. All personnel had been trained in the use of the equipment and were required to wear respiratory protection equipment when working areas or performing specific operations where the exposure to VC was higher than, or could have been higher than the permissible OSHA limit. Disposable or washable coveralls were provided for hazardous operations, and gloves were required for personnel performing tasks which could expose their hands to the chemicals. Shower facilities were provided, and safety showers were available in the VC manufacturing areas for emergency use. Smoking and eating were confined to the cafeterias and the control rooms. Good housekeeping was maintained throughout the plant. Loading personnel were required to wear air pressure demand respirators when performing any operation where exposure to VC was possible. Supplied-air respirator hook-ups were provided thorughout the plant.

Each instrument house contained an infrared analyzer and gas chromatograph to detect concentrations of VC and ethylene dichloride in the production areas. The instrument readout equipment was located in the control rooms and was checked out during each shift by the operator. In addition, portable Century OVA's were used to check areas where the exposure limits for organic vapors were higher than permissible.

A surveillance program ofr VC was initiated in July, 1973, using the charcoal tube method to determine the concentration of VC that their personnel were exposed to, and the levels existing in the various work areas. In their surveillance, program 50 percent of all personnel exposed to VC were monitored each week for approximately 10 minutes. The charcoal tube samples were analyzed using gas chromatography. In addition, all exposed personnel were given medical examinations meeting the requirements specified in OSHA regulation 29 CFR 1910.93q.

The following average time-weighted average (TWA) exposures to VC had been determined using OSHA personnel monitoring techniques since August 1974.

Operator Job Classification	TWA Average
North and South Furaaces	0.3 ppm
North Purification	0.7 ppm
South Purification	0.6 ppm
North and South Spare	0.7 ppm
East Furnace and Purification	5.2 ppm
East Spare	1.7 ppm
East Synthesis	0.2 ppm
Vinyl Chloride Tank Farm	8.5 ppm
Laboratory	0.6 ppm
Instrument Laboratory	Insufficient Data
Maintenance	Insufficient Data

Samples were taken while performing activities which gave the greatest probability of exposure.

Numerous changes have been made to the facility to reduce or eliminate the possible exposure of personnel to VC or other suspect agents. A number of these changes are described below.

Major equipment changes that have been made to reduce possible exposure to VC monomer are:

A VC vapor collection and recovery system had been installed in the tank farm. Essentially, this consisted of a compressor and condensing system. The recovered VC was transferred to off-specification storage.

A VC emergency collection and flare system had been installed for the process areas. In case of a VC release from a relief valve or vent, the VC was piped to a flare.

The caustic scrubbers had the greatest potential for exposing people to VC. A VC stripper system was installed to remove hydrogen chloride from VC and return the hydrogen chloride to the manufacturing unit without exposing people to organic vapors.

A system had been installed to supply respirators with breathing air from conveniently located stations throughout the plant.

A continuous monitoring system had been installed in the North ethylene

dichloride unit. By means of a chromatograph, the atmosphere at ten different points in the unit was regularly analyzed for a number of chlorinated organics including VC and ethylene dichloride.

Additional valves had been put on VC tank car loading hoses to almost eliminate exposure due to venting the VC from the hoses at the end of the loading cycle.

The caustic scrubber blowdown had been piped to a blowdown knockout tank which eliminated exposure by venting the VC to flare.

The hydrogen chloride columns had been re-trayed to extend periods between opening for cleaning.

Changes in operating and maintenance practices and procedures which had reduced possible exposure to VC were:

Shift monitoring of the plant areas by the operators for hydrocarbons and chlorinated hydrocarbons had been initiated. This is the single most important change as it gave impetus to the leak detection program and brought the operators and maintenance personnel full awareness of the VC levels in the plant.

Organic Vapor Level	Respiratory Protection Required
Above 50 ppm	Supplied-air Respirator
Between 25 and 50 ppm	Cartridge Mask
Below 25 ppm	No Protection

All vessels were being better prepared for entry and consequently they had shown levels no higher than the general atmosphere outside the vessel during personnel entry. It had not been necessary to use respiratory protection for personnel entry.

Respiratory protection procedures had been improved. A self-imposed policy of requiring cartridge masks for potential exposures to vinyl chloride in the range of 25 to 50 ppm had been instituted. Above 50 ppm, a continuous-flow air-line respirator or self-contained breathing apparatus was used.

The following general guidelines were being used to determine where, when, and what type of respiratory protection was required:

Any job which released VC to the atmoshpere, and all work done on the domes of the tank cars would require air-line respirators.

Any task to be performed downwind or inside the sphere of contaminated air of a known VC leak would require an air-line respirator.

Cartridge masks would be worn for only those equipment jobs where the VC was less than 2 percent by volume of the stream or equipment contents,

and where the wind movement was such that an employee could stay upwind and outside of the sphere of contamination by the released gas.

Casual observers or supervisors in the vicinity of any of the above operations would be required to wear the same respiratory protection as the person assigned to the job.

Air-line respirator usage in the VC tank farm had been made more convenient by providing a connection at each of the loading stations. Short hoses were easily moved from station to station.

The operators in the areas handling VC used the OVA once each shift to monitor designated locations within their areas. Leaks were noted and corrected by the operator where possible. Otherwise the foreman was notified so maintenance personnel could immediately repair the leak.

The Safety Department was using the OVA to thoroughly monitor the production areas at least once a week. Readings were tabulated for each area, and if leaks were noted, they were referred to the area foreman for correction.

Most equipment containing VC was being depressured to the flare stack, to other equipment, or to remote vents to prevent employee exposure.

The purge lines from the process analyzer instruments had been hooked to a common header which was exhausted in a remote area that prevented personnel exposure. VC in the instrument houses had thus been elim-

inated. The operator area OVA readings taken each shift quickly detect leaks that have developed. The process analyzer group then used the OVA to pinpoint the leak for correction.

The laboratory "wet testing" hood had been updated to give higher volume ventilation and conform to the requirements for handling hazardous materials. Tests have shown no vapors were escaping from the hood.

Collected VC samples were no longer permitted to be stored in the process area control rooms. Outside storage was required.

Employees performing tasks where it was possible to contact liquid VC were being required to wear gloves impervious to VC.

In shutting down hydrogen chloride and VC columns, quench towers, etc., extra steps were taken to strip out the VC.

When the topping column was down, the overhead of the lights columns was collected by keeping the condensers very cold. In the past, this vapor had been vented to the atmosphere.

Exposure reduction projects that were in process were:

VC process equipment drainage system

VC tank car gauging system

VC process enclosed sample system

VC flare instrumentation

Re-traying of East hydrogen chloride column

Permanent air monitoring systems in all three cracking units

Corrosion-resistant VC stripper condenser

A method had been devised and tried which would eliminate employee potential exposure on much of the VC sampling. Hardware had been ordered to convert many sample points to closed sampling.

A closed system for liquid blowdown from sodium hydroxide scrubbers was over 50 percent complete.

A system was being worked out which will permit purging tank car loading lines to the flare before they were disconnected.

A continuous analyzer for detecting water in VC would eliminate the need for many samples now taken by operators.

An additional large caustic scrubber to eliminate the need for small scrubbers was planned. This would permit all caustic scrubber operations to be handled in one area, and not only reduce the number of employees potentially exposed, but additionally would make controlling emissions much more feasible.

A program to eliminate pump seal leakage was under way. A full investigation of ethylene dichloride-VC pumps had been completed, and specific programs had been started which promise reduced pump seal failure.

Quotations were being evaluated on providing a corrosion-resistant stripper condenser which would increase uptime and thus reduce exposure due to scrubber operation and stripper repair.

A sampling method was being sought which would eliminate purging VC into the atmosphere during tank car sampling operations. One device had failed to be an improvement, but others would be tried.

Reboiler venting system

Topping column revisions

Larger reboilers

Better level indicators and purges

This list is not all inclusive but is indicative of the planning and efforts going into further improvements.

II. Polymerization Plants

Plant D

This plant is a large chemical manufacturing complex with a long list of chemicals produced. Approximately 1800 persons were employed there with only 150 of them involved in PVC operations. The plant has produced PVC since 1929 and at the time of the survey produced PVC using three processes; a solvent process, an emulsion process, and a modified emulsion process in which VC is copolymerized with acrylonitrile.

All reaction equipment for the emulsion and modified emulsion processes were located outdoors. All equipment for the solvent process and the

drying, bagging, and VC recovery operations of the other processes are indoors.

The three processes are located in separate parts of the plant. The emulsion process control room, VC recovery compressors, and PVC drying and bagging operations are located in one building with the reactors adjacent to the building. The modified emulsion process control room is also loacted in the same building with the recovery compressors, while the reactors are outdoors adjacent to the building. The solution process has one building for the reactors and strippers, one for precipitation and drying of PVC, one for solvent recovery, and one for bagging of PVC.

The plant operates three shifts per day, seven days per week.

This facility has an inplant dispensary with a full time Medical Director and an assistant. Nurses are on duty 24 hours a day. A pre-employment physical examination is required with re-examination every one to two years depending on age and department.

The safety department consists of a director and an assistant. There is also a person assigned to a respiratory protection program. Each production department has its own safety committee, which reviews safety practices, in addition to a central safety committee and a union safety committee.

Industrial hygiene matters are handled by the environmental protection

group. They have 2 industrial hygienists and a technician plus men to take care of solid waste, water, and air pollution. Industrial hygiene surveys for various hazards are conducted on a routine basis.

This plant also has a full time fire department which also handles rescue work. There is also a rescue squad made up of lab personnel trained in first aid.

VC has been sampled at the plant since 1969, although somewhat sporadically until 1974. The initial sampling was done with detector tubes and later with grab samples analyzed by gas chromatography (GC). In 1974 personal sampling using charcoal tubes and GC analysis was begun. Also continuous monitoring for VC in the process areas using GC analysis was started. A continuous monitoring instrument was located in each process area. Each instrument had 20 sampling points which were sampled sequentially. Each sample took two minutes to analyze so each point was sampled once every 40 minutes.

Workers had begun wearing supplied-air respirators while cleaning reactors or other tasks with possible exposure to high levels of VC. Several other changes had been made to reduce exposure to VC, among these were:

Removing lab work from control rooms

Sampling reactors less often

Attempting to eliminate monomer filters

Clean autoclaves less often

Improved VC recovery system

Installed vacuum system on reactors to vent reactors prior to and during entry. This replaced system that vented reactor to atmosphere.

Eliminated several venting points

Plant E

This plant is entirely a PVC production facility with PVC being produced by the mass process and the suspension process. The plant is a relatively new one, having opened in 1970 and the processes are computer controlled.

The work force consisted of 260 persons, 50 of whom were inovlved in the PVC polymerization areas. Process equipment was located indoors. The suspension and mass processes occupy separate buildings with drying and bagging operations in buildings separate from the reactor buildings. The plant operated three shifts per day, seven days per week.

This facility has an in-plant dispensary with a registered nurse on duty Monday through Friday during the day shift. All lead technicians have first aid training. In addition, two physicians each visit once a week. Emergency arrangements have been made with nearby hospitals.

Pre-employment physicals are required. These include a general physical examination, audiometry and semi-annual SMA-12 blood tests.

The Safety Department consists of a safety engineer and an assistant. Hard hat, safety glasses, respirator, and safety shoe programs are in operation. In addition, workers are supplied work clothes which they are required to change each day. Daily showers are mandatory for workers in the polymerization areas. Workers are required to wear supplied-air respirators when entering vessels for cleaning or when performing other jobs, such as cleaning filters that have a high potential for VC exposure.

VC was being sampled by the use of charcoal tubes at this plant. An automatic sequential sampling system had been installed in each polymerization building in early 1974. This system consisted of a Bendix total hydrocarbon analyzer with six sampling points. Analysis time for each sample was two minutes, so each point was sampled every 12 minutes. These sample results were fed to a computer which stored shift peak levels for each point and calculated shift averages. It also actuated a visual alarm in the production areas whenever levels went above a preset limit. This limit at the time of the visit was 25 ppm. In addition, one person per shift spent full time checking for VC leaks using an OVA. Also when a high VC level was shown by the automatic sampling system, he determined the source of the leak, and saw that it was corrected.

Plant F

Plant F is predominately a PVC polymerization facility but also has other operations. PVC is milled and calendered and plasticizers, polyurethanes, and acrylate polymers are also produced. The plant began operations in 1951 with the production of PVC emulsion resins. At present the suspension

and emulsion processes are in use here. The work force consists of approximately 700 persons, with 200 of them working in the PVC polymerization areas. The plant operates three 8-hour shifts per day, seven days per week.

The suspension resin is produced in two buildings, one old and one new, each with a separate dryer building nearby. The emulsion resin is produced in a third building and drying takes place in a separate building. A fourth building also has an emulsion process, but it is used to produce PVC latex. This process was not in operation at the time of the survey and was therefore not sampled.

This facility has an in-plant dispensary with nurses on duty 24 hours per day, 5 days per week. All foremen and guards are trained in first aid. Two physicians each spend two hours per day at the dispensary five days per week. An emergency vehicle is available at all times. Hospitals are ten to fifteen minutes away. The corporate medical department sets guidelines for routine medical tests and physical examinations. Pre-employment physicals, including blood tests, pulmonary function tests, audiometry, and a medical history are required. Retesting of employees is done periodically depending on the work location.

The safety department consists of two safety inspectors. Hard hat, safety glasses and respiratory protection programs are in operation. Workers are required to wear supplied-air respirators when entering vessels for cleaning or when performing other jobs, such as filter cleaning, that have a high potential for VC exposure. Safety is

stressed to the workers through monthly safety meetings, short weekly safety meetings in the operating areas, special safety meetings to discuss new topics, and by posting information on bulletin boards. Equipment inspection is carried out by the plant guards under the supervision of the safety department. These inspections include such things as routine checks of relief valves, rupture discs, and fire extinguishers. All plant personnel receive fire extinguisher and hose training. The plant has a fire truck with foam generation and dry chemical equipment. A yearly safety audit is performed by corporate personnel. Semi-annual safety audits are conducted by plant safety personnel.

Historically, industrial hygiene services were provided by corporate level people. Since 1973, plant safety and environmental control personnel have been performing this function under the guidance of the corporate industrial hygienists. A safety engineer and an environmental control engineer handle this activity. Routine industrial hygiene audits were in the planning stages at the time of our survey. At that time, the priority item was VC sampling to determine regulated areas for the new OSHA standard. Sampling was also being conducted in various parts of the plant for diisocyanate, carbon monoxide, vinylidene chloride, and PVC dust.

Also, two engineers were on full time temporary assignment to implement changes to bring the plant in compliance with the new OSHA standard. One of these changes was the installation of an automatic sequential VC sampling system in each polymerization building. This sampling

system consists of a Bendix total hydrocarbons analyzer in the suspension and emulsion resin buildings and a gas chromatograph in the latex building. Each of these instruments is tied into six sampling points with changes being made to add six additional sampling points to each system. At the time of the visit, analysis time was two minutes for each point, so each point is sampled every twelve minutes. With the additional sampling points, analysis time would be reduced to one minute, so that each point would still be sampled every twelve minutes. These sample results are fed to a minicomputer, which stores peak values for each point and calculates eight hour shift averages for each point along with floor and building averages. These systems also actuate a visual alarm in the production areas whenever levels go over a pre-set limit. At the time of our survey this was twenty-five ppm.

In addition to area sampling, workers on each shift use Century OVA to conduct a routine inspection of valves, pump seals, etc. for early detection of VC leaks. Also, when a high VC level is detected by the automatic sampler, they use the OVA to determine the cause of the reading and see that it is fixed.

Several changes had been instituted to lower VC exposures in the plant.

1. Improved procedures to prevent PVC spillage.
2. Closed containers for waste and recovered PVC.
3. Separate eating facilities provided.
4. Daily change of clothing provided.
5. Recover all vapors before disconnecting tank cars.
6. Improved building ventilation.

7. Improved compressor seals.

8. Improved reactor manhead gaskets.

III. Fabrication Plants

Plant G

This facility processes PVC resins and compounds into numerous extruded, molded, and bonded items and yarn. The company has been fabricating PVC products for 25 years. The present facility was started up in August 1971.

The company normally employs 150 people and operates 24 hours a day on a 5-day-week basis. All manufacturing operations are performed indoors in a modern, well-designed and laid out plant. Approximately 50 people are involved in the manufacture of PVC products. The manufacturing processes employed in the manufacture of PVC products at this plant are: bonding, in the lamination of extruded PVC with plated mylar, or printed PVC film to make automotive or decorating trim; compounding, in the mixing of polyvinyl chloride resin with plasticizers, fillers, lubricants, stabilizers, pigments, and other materials to produce a dry-blend compound; extrusion in the conversion of dry-blend or pelletized compounds into continuous plastic strips of a predetermined cross section; fibers, in the extrusion of pelletized compounds into spools of colored yarns used for the manufacture of woven products; and molding, by the injection of PVC compounds into a heated mold to produce items having a definite size, shape, and color. Compounding at this plant is

accomplished in ribbon-type blenders, and conversion of the dry-blend or pelletized compounds into a plastic mass takes place in the extruders and injection molders. No basic changes have been made to their PVC fabrication operations.

Ventilation in the plant is provided by 16 roof-mounted exhaust fans with a total rating of 50,000 cubic feet per minute at 1/2 inch static pressure which provide an air change once every 30 to 35 minutes. The adjoining offices are air conditioned.

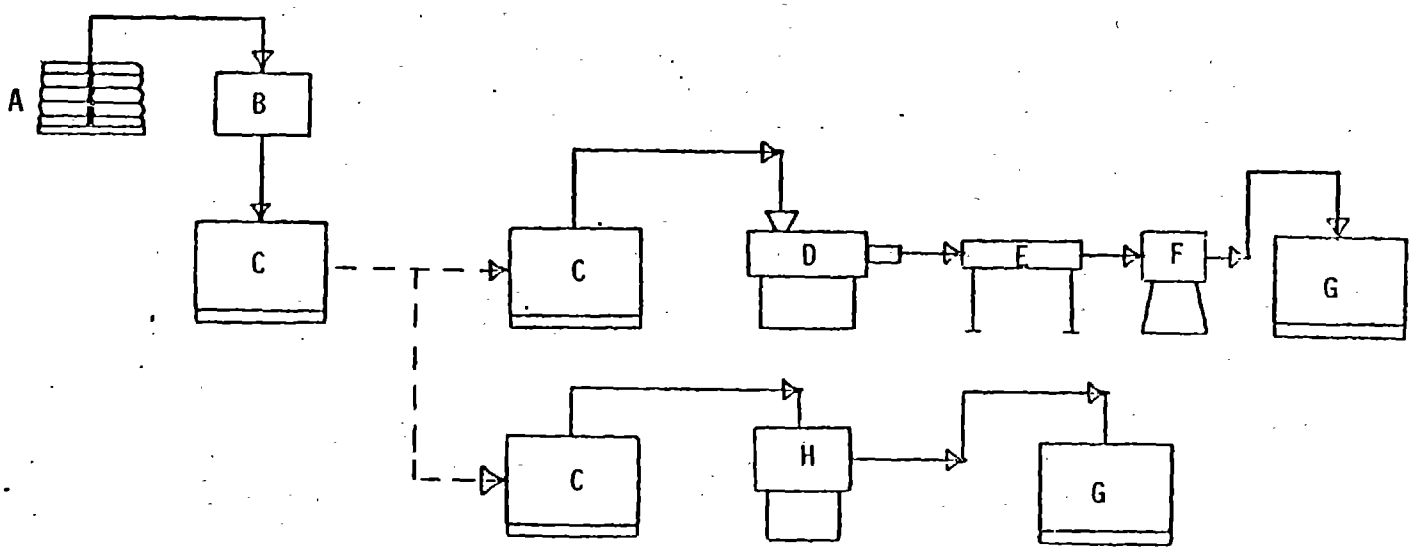
Overall housekeeping is very good and the equipment has been installed in a well-planned, uncrowded manner. An enclosed, air-conditioned cafeteria area has been provided for breaks and lunches. Smoking is restricted to special areas. Special clothing is not required.

The company does not have a VC surveillance program; however, the plant has been surveyed for VC concentrations by an insurance company. The company uses bulletin boards and meetings to keep their employees informed on health and safety programs.

Figure A-1 shows a flow schematic of the processes used by Plant G to manufacture PVC products.

Plant H

This facility processes PVC resins into a wide variety of extruded and injection-molded products. The company has 21 years of experience in the manufacture of PVC products.



Legend:
A - Bagged Materials
B - Blender
C - Storage Container
D - Extruder
E - Cooling Bath
F - Cut-Off Machine
G - Shipping Container
H - Injection Molder

Figure A-1 Flow Schematic, Plants G, H

The company normally employs 260 people and all of the employees are considered by the company to be exposed to VC. The plant operates on a 24-hour-per day, 5-day-per-week schedule, and all manufacturing operations are performed indoors.

The company uses the following processes in the manufacture of PVC products: bonding, by hot-seal welding of flexible extruded profiles such as refrigerator seals; compounding, in the blending of PVC resin with plasticizers, fillers, stabilizers, pigments, and other additives in a semi-automated blender with a 45,000-pound-per-day capacity; extrusion, in the production of a wide range of profiles from powder-type compounds; and molding of dry PVC compounds into items such as automotive seals and cable enclosures by injection molding.

Ventilation throughout the plant is provided by air-circulating fans. Hoods vented to the atmosphere through a duct system have been installed on injection molding presses and the high-intensity compound mixer. Doors and windows are opened as required to assist the plant ventilation system.

The only significant change in the plant is the addition, in July 1974, of the new high-intensity compound mixer. The mixer is vented to the atmosphere through a duct system and should serve to reduce the escape of VC to the plant air.

The company does not have a VC sampling program and does not feel that it has concentrations of VC above the permissible limit in the plant.

The company has an active safety and medical program.

Figure A-1 shows a flow schematic of the processes used by Plant H to manufacture PVC products.

Plant I

This facility processes PVC resins into numerous dip-molded and di-coated products using plastisol-type compounds. The company has been fabricating PVC products by the dip-molding process for 25 years and normally employs 110 people. Due to the design of the plant, all of the employees are considered to be exposed to VC. The plant normally operates on a one-shift-per-day basis, 5 days a week. The company added blow molding units three years ago. Blow-molded products are made from polyethylene compounds.

This company used the following three processes to produce PVC products: (1) compounding, in the mixing of PVC resins with dicapryl phthalate, dioctyl adipate, and tallates as plasticizers; barium, cadmium, and zinc organic solutions as stabilizers; pigments; and fillers; (2) molding, by dipping a heated mold into a plastisol compound and curing the dipped mold in an oven; and (3) plastisols, in the compounding of plastisol mixtures.

The only change that has been made to their PVC manufacturing processes is the addition, 9 years ago, of an automated-conveyorized die-molding line. All of the other die-molding units are hand operated, batch-type

units.

Plant ventilation is provided by roof-mounted fans. All of the ovens and blow-molding units are equipped with hoods which are ducted overhead to the atmosphere for removal of fumes. The adjacent offices are air conditioned.

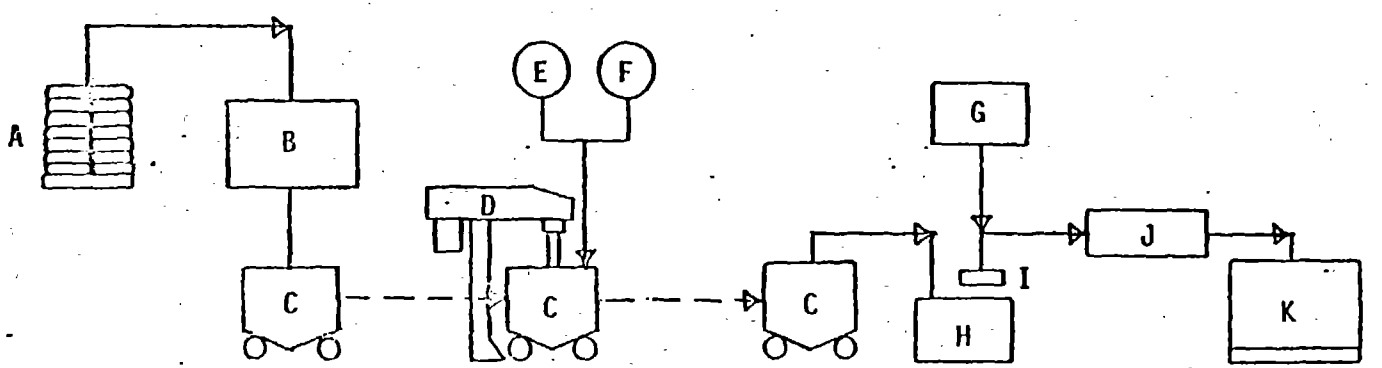
The company has an active safety program and performs area and personnel sampling using the carbon tube sampling method. The carbon tubes are analyzed by one of the PVC resin suppliers. The results of the sampling analysis are posted on employee bulletin boards along with other safety and health bulletins. Sampling results show a range of 0.01 to 18.0 ppm.

An enclosed cafeteria is provided for smoking, drinking, and eating during breaks and the lunch period.

Figure A-2 shows a flow schematic of the processes used by Plant I to manufacture PVC products.

Plant J

This facility manufactures closed-cell expanded products from blends of PVC and rubber compounds. The manufacturing operations are performed in several indoor locations. The company has been making closed-cell expanded PVC/rubber products for 19 years, and no significant changes have been made to the original process.



Legend:
A - Bagged Materials
B - Blender
C - Mixing Tub
D - Mixer
E - Plasticizers
F - Pigments
G - Mold Heating Oven
H - Plastisol Dip Tank
I - Heated Mold
J - Curing Oven
K - Shipping Container

The plant operates on a 24-hour-day, 5-day-per week schedule and performs a batch-type operation. The plant has 1,110 employees; however, only 160 of their employees are exposed to VC in their manufacturing operations. The manufacturing processes performed by this company involving PVC resins and compounds are compounding, extrusion, foams, and molding.

The manufacture of the various closed-cell expanded product line produced by this company begins with the addition, to a Banbury mixer, of predetermined amounts of the materials required to make the desired compound. The Banbury-mixed compound is fed to a two-roll mill where further mixing takes place, and ends up as a sheet of compound on the mill roll. Sections of the sheet are cut off and placed on a portable rack. The milled slabs are fed into a tuber (tube-type extruder) where the extruded compound for the batch-type units is cut into sections. The sections are placed in a multi-leaf platen press where the section is heated under pressure to a definite shape, and partial expansion takes place. The shaped pieces are removed from the presses, loaded onto racks, and moved to a second oven. The loaded racks are placed in the oven where the partially blown sections are further expanded to approximately four times in size. The racks are removed from the oven, and the expanded slabs are unloaded and stacked onto skids for packaging and shipment.

In another building, the milled slabs are fed into a continuous tuber located at the head of a long tunnel-type oven. The tubed stock is

cured and fully expanded into a continuous sheet in the ovens. The expanded sheet is cooled and passed to a cutter where it is cut into sections or wound onto rolls prior to packaging for shipment.

In other operations, the milled sheet can be extruded through heated dies to form continuous profiles of closed-cell expanded extrusions. This type of product would be primarily used for gasket, insulation, or cushioning materials.

The closed-cell expanded products can be coated with a plastisol compound and further cured to provide a clear or colored skin of desired thickness on the coated item.

The company has established a program for personnel sampling using the method called for in the NIOSH publication P & CAM No. 178, Vinyl Chloride in Air and Personal Gas Sampling Pumps. Initial samples collected in May 1974 indicated less than 1 ppm of VC for 10 area samples. The charcoal tube samples were analyzed by an independent laboratory.

Figure A-3 shows a flow schematic of the processes used by Plant J to manufacture PVC products.

Plant K

This facility manufactures plasticized PVC calendered film and sheeting, expanded vinyl sheeting, and printed vinyl film. The company has been

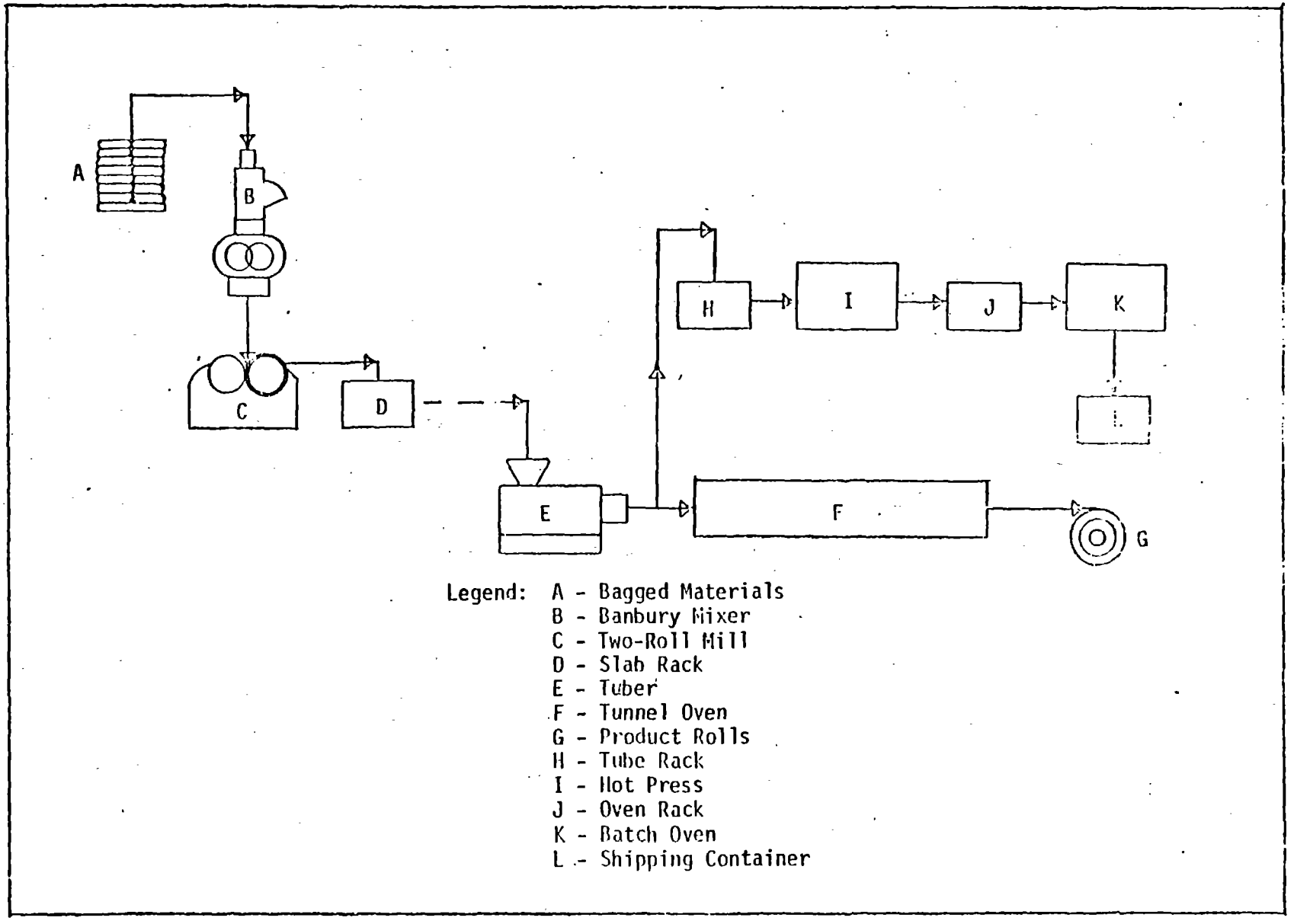


Figure A-3 Flow Schematic, Plant

making calendered products 35 years, and expanded (foam) type products eight years.

The PVC plant normally employs 127 people and operates on a continuous basis seven days a week. All production operatons except the offloading of resins from truck-mounted sealed containers to storage bins located on the roof are performed indoors. No basic changes have been made to the manufacturing operations; however, a number of engineering improvements have initiated to improve production and eliminate unsafe working conditions.

The company uses the following processes to produce the PVC products manufactured in this plant: bonding, in the lamination of two sheets of PVC; calendering, in the conversion of a plastic mass of PVC compound into a film or sheet of controlled width and thickness; compounding, in the mixing of PVC resin with plasticizers, fillers, stabilizers, and other materials in ribbon-type blenders, and the conversion of the powdered blend into a plastic mass in Banbury mixers (color pigments and granulated trim are added to the charge in the Banbury mixers); extrusion, in the processing of the Banbury charge through a screen and extruder head to a "rope" that is fed to the calender; fibers, in the combining of a roll of fabric with a sheet of polyvinyl chloride plastisol; foams, in the expansion of a plastisol film in a blowing/curing oven; plastisols, in the compounding of plastisol mixtures; and thermoforming, in the embossing of designs into PVC film and sheeting.

Raw materials used in the production of PVC products are PVC resins, plasticizers, stabilizers (barium, cadmium, and zinc organic salts in solution form), fillers, pigments, and Celogen as a blowing agent.

The plant uses overhead fans ducted to roof-mounted fans and stacks for ventilation. Hoods are located above equipment that gives off fumes, and the hoods are ducted to roof-mounted fans and stacks. The blenders and dryblend transport equipment are vented to the atmosphere through a dust collector.

The company has an active safety and sampling program. Thirty-minute breifings are given to all personnel, explaining the vinyl chloride monomer problem. Annual medical checkups are offered to all employees on a voluntary basis, plus a 6-month blood sampling and analysis program. Air sampling for personnel, and area sampling are employed to detect VC, using the carbon-tube collection method. In addition, Miran II infrared analyzers plus Century OVAs are used to check for VC. The charcoal tubes are sent to their test center or a commercial laboratory for analysis. The analysis on the charcoal tubes can also be performed at this site. The sampling program was initiated in April 1974, and the only change that has been made is an increase in the sampling frequency. The results of their sampling program indicate a VC range of 0.2 to 1.1 ppm for their operating personnel.

Housekeeping throughout the plant is good and their safety department is working to eliminate or reduce employee exposure to VC below the

permissible working levels. Employees performing operations where exposures above the permissible limit are possible must wear protective clothing. Smoking, drinking, and eating are permitted only in enclosed air-conditioned cafeteria areas or offices.

Figure A-4 shows a flow schematic of the processes used by Plant K to manufacture PVC products.

Plant L

This facility processes PVC resins into pelletized PVC compounds, thermoformed products, vinyl film, and vinyl sheeting. The company has been performing calendering operations since 1946, thermoforming since 1958, and compounding since 1959.

The company employs 520 people; however, only 309 of the employees are considered to be exposed to VC. The facility operates on a 24-hour-per-day schedule, 7 days per week depending on the work load. All of the production operations for the processing of PVC into finished products are performed indoors except for the offloading of resins to the roof-located storage hoppers, and the loading of compounded resins into bulk shipping devices.

The manufacturing operations performed in the conversion of PVC resins into salable products are compounding, calendering, and thermoforming. Compounding involves the mixing of PVC resins, plasticizers, stabilizers, fungicides, bacteriastats, lubricants, pigments, and fillers in continuous

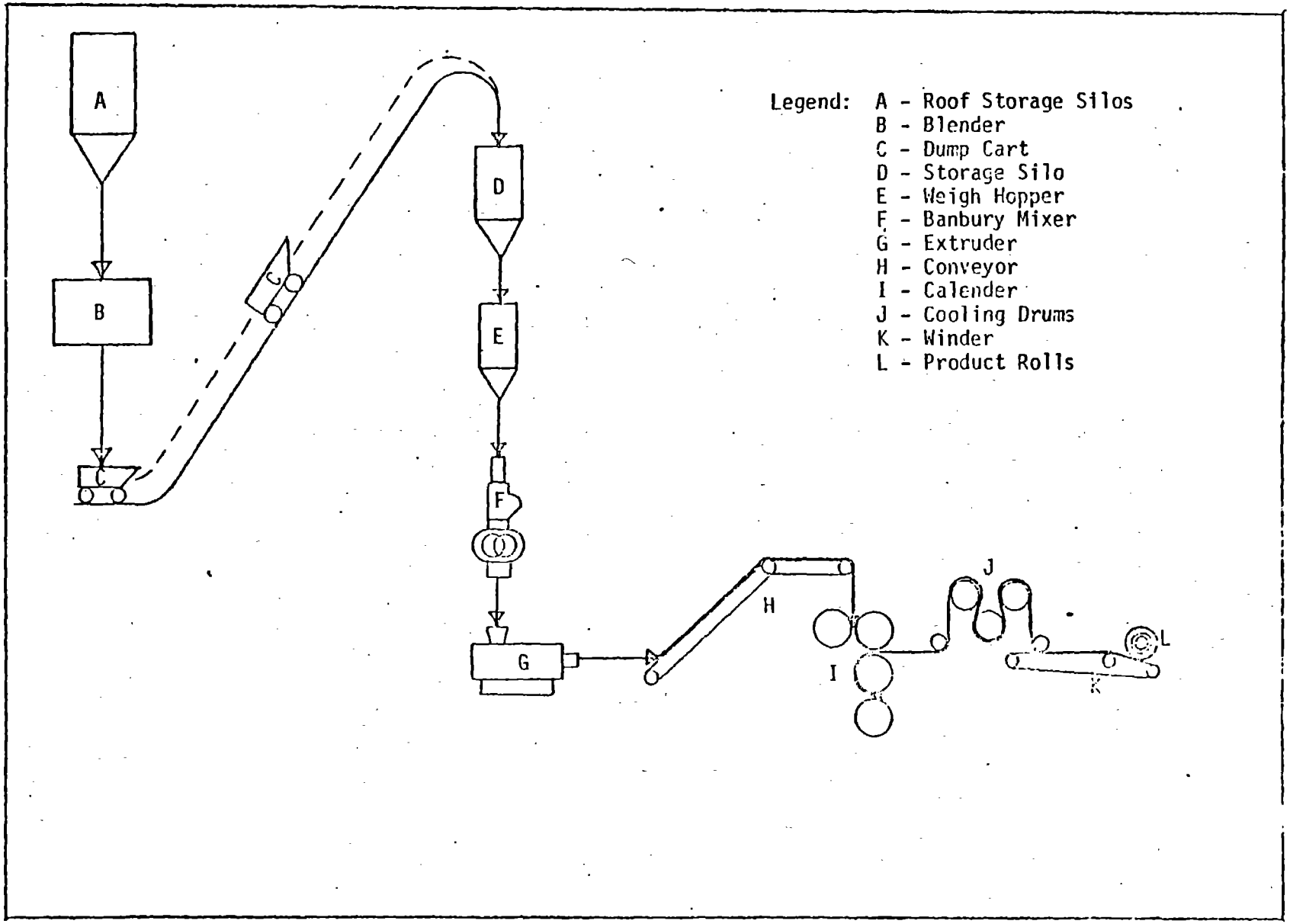


Figure A-4 Flow Schematic, Plant

ribbon-type blenders. After the ingredients are blended, they are further processed into a plastic mass, sheet, or rope in Banbury mixers, two-roll mills, extruders, or a combination of the three units. Calendering converts a rope of plastic PVC compound into a continuous sheet or film of controlled width and thickness in a four-roll inverted "L" form calender. The plastic compound from the Banbury mixer in another product line is passed to an extruder-dicer unit to convert the dry-blend compound into a pelletized compound product. The pelletized compound is bagged and loaded onto skids for shipment as a salable product. Thermoformed products are produced by the vacu-forming process. In this operation, precut sheets of PVC sheet stock are fed to a vacu-forming unit, where the sheet stock takes the form of the hot die, using negative pressure during the forming operation, and positive pressure to strip the formed item from the die. The formed items are stacked and loaded into boxes for shipment. The vacu-formed products are used as custom-formed plastic packaging for the protection and display of items such as candy and fruit.

Roof-type ventilators are used throughout the plant for ventilation. Dust-producing equipment and dust-laden atmospheres are ducted to baghouses and cyclone separators to remove airborne particulate prior to venting to the atmosphere.

The company has an active health, safety, and sampling program to protect its employees and prevent VC excursion to the atmosphere. Safety and health information is transmitted to the employees by way of union-

management meeting, and bulletin boards. Charcoal tubes and Sipin pumps are used to collect area and personnel samples. The air samples are analyzed by gas chromatography in their in-plant laboratory. The company is also very active in the development of more-advanced methods of identifying VC concentrations in the work area through the use of instant readout instrumentation. The only suspected liver toxins that are used in this plant are VC, PVC resins, organic lead stabilizers, and tetrahydrofuran. The tetrahydrofuran is restricted to laboratory analysis usage. The results of their sampling program were not available.

The company is constantly revising its production procedures and equipment to take advantage of methods to increase production, lower operating costs, and increase the overall safety of its employees. The main changes that were made to the compounding operations are the changes in the mixing of compound ingredients in two-roll mills to Banbury mixers and then to ribbon-type blenders.

A cafeteria and designated smoking, drinking, and eating areas have been provided for the employees. Respirators were not worn in the blender areas.

Figure A-5 shows a flow schematic of the processes used by Plant L to manufacture PVC products.

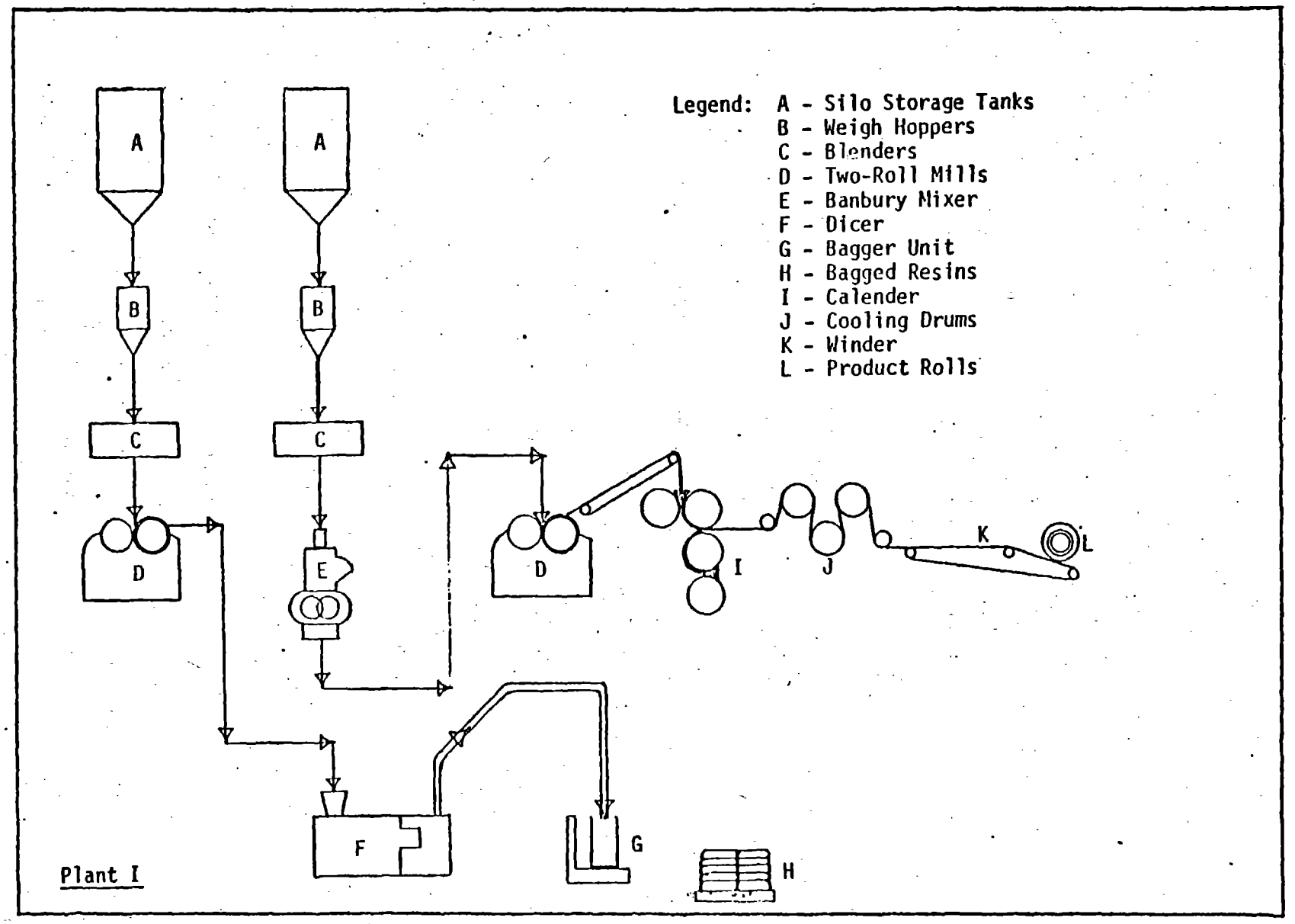


Figure A-5 Flow Schematic, Plant L

Plant M

This facility converts PVC resins and other compounding ingredients into calendered film and vinyl-coated supported and unsupported fabrics that are sold to a number of industries.

The company has been in operation since 1947 for the manufacture of PVC products.

The plant normally operates on a 24-hour-per-day schedule, 5 to 6 days a week. All manufacturing operations are performed indoors except the off-loading of resin from bulk resin trucks to ground level storage silos. Resin from the silos is transferred by an airveyor system to a gravity supply hopper located on the roof of the plant.

The plant employs 325 people; however, only 50 workers are considered to be exposed to VC in their manufacturing operations. The following processes are used by this company to make their PVC product lines: bonding, in the lamination of two sheets of vinyl; calendering, in the high-speed conversion of a rope of PVC compound into continuous film or sheet stock of controlled width and thickness; compounding, in the mixing of PVC resins with plasticizers, stabilizers, fillers, lubricants, and other additives in ribbon-type blenders, and the conversion of the powdered blend into a plastic mass in Banbury mixers (color pigments and granulated trim stock and scrap are added in the Banbury mixers); extrusion, in the processing of the Banbury charge through a screen and

extruder head to form a rope of PVC compound that is fed to a calender; foam: in the expansion of cast plastisol film in a blowing/curing oven; plastisols, in the compounding of plastisol mixtures used in the film casting line; and thermoforming, in the embossing of designs into PVC film and sheeting. The embossing operation is performed on the calendering lines and the cast film line.

The plant uses roof-mounted ventilation fans, exhaust hoods, and ducts to supply fresh air and remove fumes and dust-laden atmospheres. The vented exhausts are passed through an electric precipitator to remove entrained solids prior to venting to the atmosphere. The solids collected in the precipitator are burned as a fuel. Recent changes that have been made to the ventilation system to reduce VC concentrations within the plant are: a 30-horsepower, roof-mounted exhaust fan and duct system has been installed on each of the blenders to prevent the excursion of dry-blend compounds into the plant air; shrouded hoods have been installed on the mills to reduce emissions; and conveyors to the mills have been enclosed. A proposal is in the design stage to enclose the Banbury mixers with a duct system similar to the systems installed on the ribbon blenders.

The company has an active safety program and has recently initiated an area and personnel sampling program using the carbon tube method and personnel sampling pumps. The analysis of the carbon tubes is performed by an independent laboratory. The employees are kept up to date on

safety and health problems by way of bulletin boards and safety meetings. All employees entering work areas where higher-than-permissible levels of VC have been found or are possible must sign a form that lists the specific work area entered, and the time the area was entered and exited. Chemical cartridge type respirators are worn by the employees when working in dusty areas or when higher-than-permissible levels of VC are suspected.

A surveillance program for VC was initiated in November 1974. The results of the survey to date indicate a VC concentration range of 0.1 to 30.81 ppm based on area sampling over a period of four months.

Eating, drinking, and smoking are restricted to specified areas or enclosed office areas.

Figure A-6 shows a flow schematic of the cast film production line for Plant M.

Figure A-7 shows a flow schematic of the calendered film lines for Plant M.

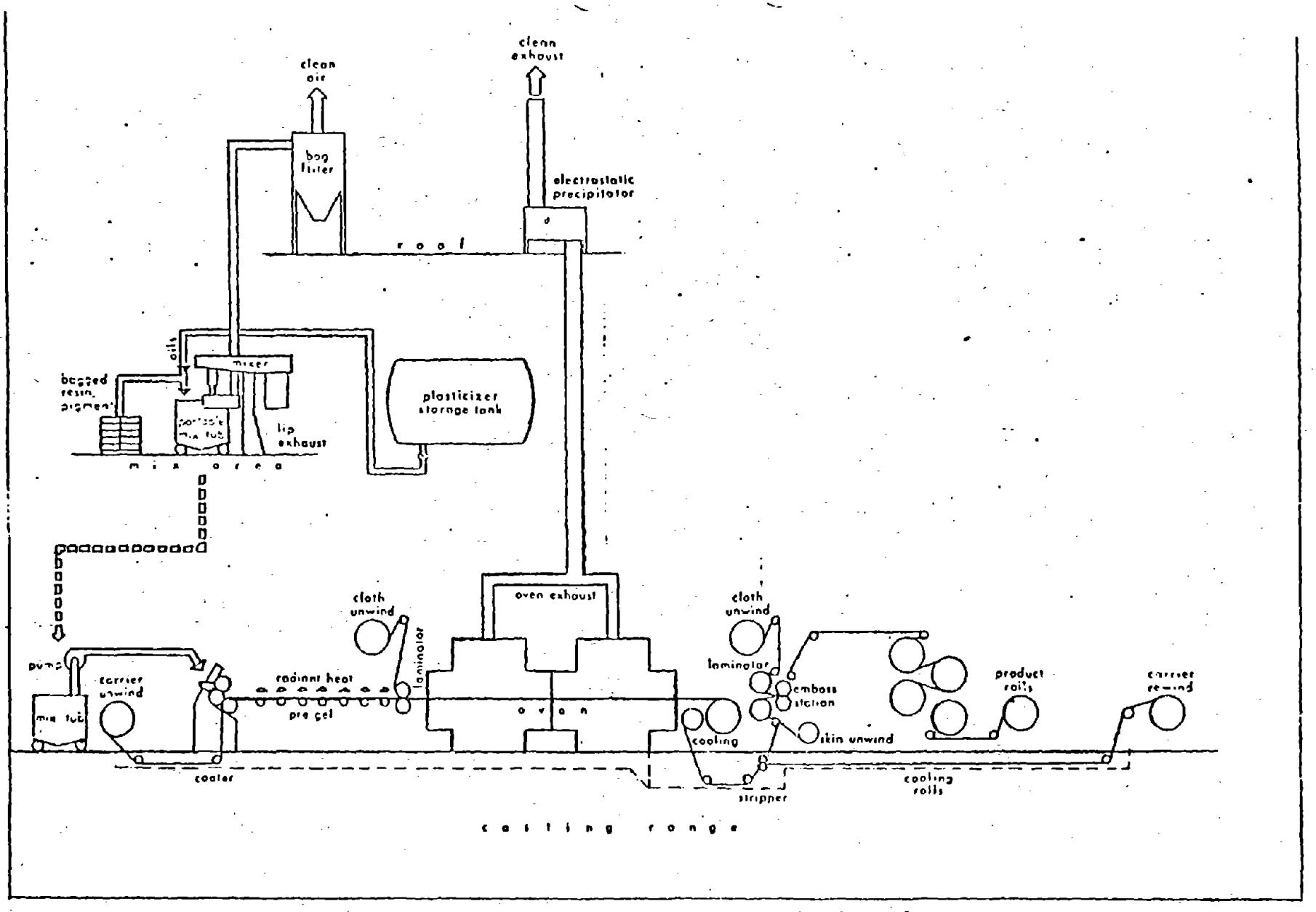


Figure A-6 Flow Schematic, Cast Film Production, Plant

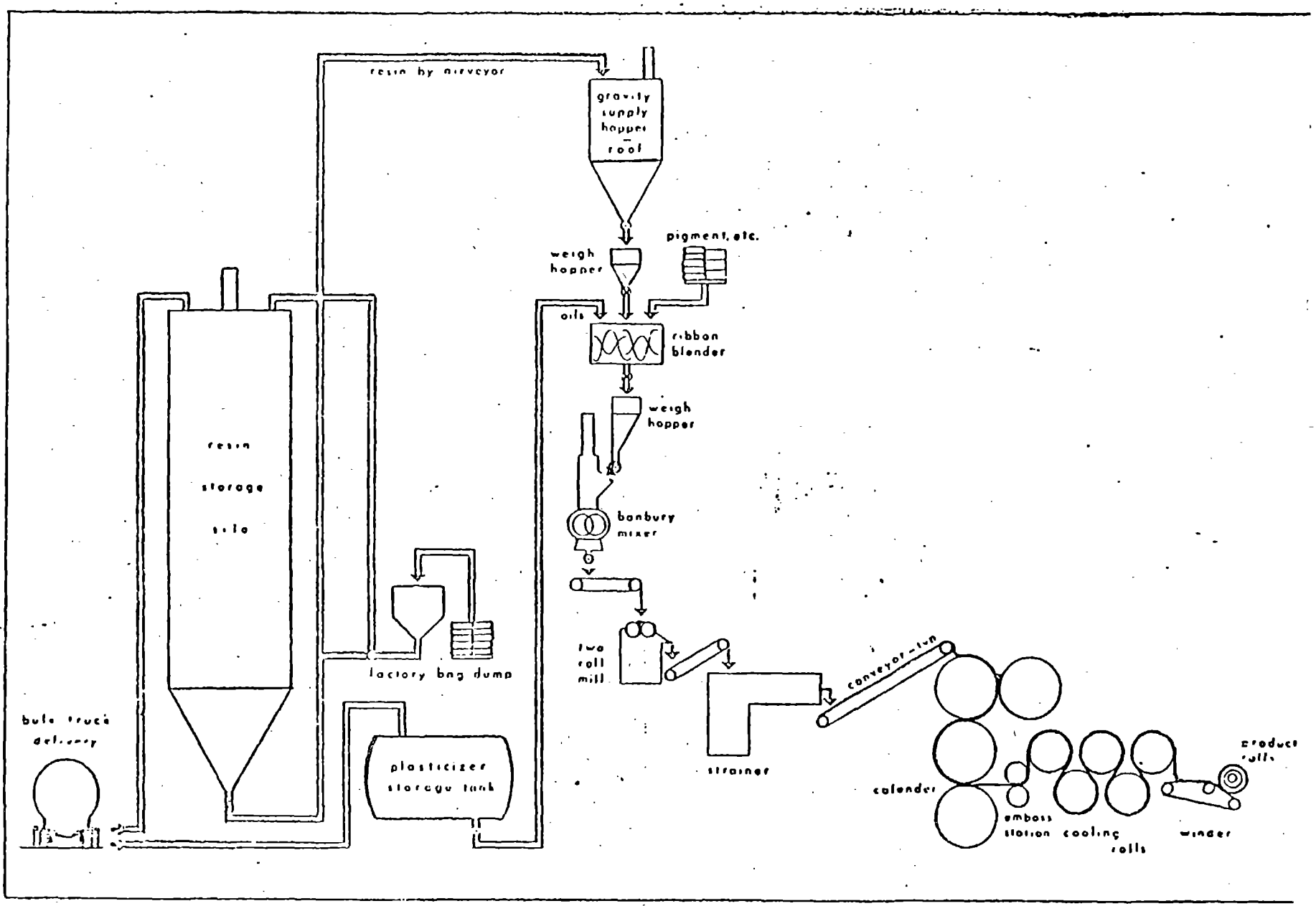


Figure A-7 Flow Schematic, Calendered Film Production, Plant

Appendix B

JOB DICTIONARY

Monomer Plants

Operator - Includes Operator, Furnace Operator, Synthesis Operator, Spare Operator, Cracking Operator job titles. Operators control the equipment vessels required to produce VC. The equipment includes reactors, heat exchangers, pumps, compressors, fractionating towers and attendant instrumentation. They perform these duties in an open plant or an air-conditioned control room building. In most cases approximately 50 percent of their time is spent in the control room. They oversee the equipment and specify when maintenance is required.

Loader - Includes job titles of loader and tank farm operator. Loaders receive, prepare, load, and sample VC tank cars.

Maintenance Worker - Includes such job titles as mechanic, electrician and insulator. They make necessary repairs to equipment, paint, insulate and change catalyst.

Laboratory Technician - Includes Laboratory Technicians, Laboratory Operator, chromatographer. Laboratory technicians obtain samples of gases and liquids from the process. They perform gas chromatograph and reaction tests on these samples, either in the operating unit or in the laboratory.

Foreman - Includes Foreman and Shift Supervisor. The Foreman is in charge of the operating unit. They make sure that equipment and personnel are performing properly.

Operator-Reactor Area - Includes Autoclave Operator, Dispersator Operator, Varnish Blending Operator, Relief Operator, Transfer Operator, Still Operator, Recovery Operator, Utility Operator, Board Operator, Charge Operator, Lead Technician, Operating Technician, Pearl Technician, Paste Technician, Rover Technician, Blowdown Operator, HRC Operator. Operators control the equipment used to produce PVC. The equipment includes reactors, heat exchangers, pumps, compressors and attendant instrumentation. They perform these duties in the operating area or in an enclosed control room. Forty to ninety percent of their time is spent in the control room.

Helper-Reactor Area - Includes Helper, Serviceman, Utility Man, Utility Fitter, Laborer. Helpers work with equipment used to produce PVC. They assist the operators by performing such jobs as changing filters, cleaning reactors, opening and closing reactors and turning valves. They spend approximately 25 to 40 percent of their time in the control room.

Operator-Dryer Area - Includes Dryer Operator, Flash Dryer Operator, Spray Dryer Operator, Vent Operator, Rodney Hunt Operator, Transfer Operator. Dryer Area Operators control the equipment used to dry PVC resin. The equipment includes rotary dryers, spray dryers, centrifuges, pumps, pneumatic conveyance equipment, cyclone separators and attendant instrumentation.

Helper-Dryer Area - Includes Helper, Truck Driver. The Dryer area helper assists the dryer area operator, turns valves, moves pallets of bagged PVC, marks bags, and takes samples.

Bagger - Includes Bagger, Weighmaster. The bagger operates the bagging machines which put PVC resin into bags.

Foreman - The foreman supervises workers in the reactor area or dryer area.

Maintenance Worker - Includes Operations Mechanic, Insulator, OVA Operator. They make necessary repairs to equipment, insulate, and locate VC leaks in the process and repair them.

Calender Personnel - Includes Assistant Operator, Calender Operator, Chief Operator, Foam Line Chief and Wind-up Man. They operate the calender lines, including the winding of the finished product onto rolls.

Compounding Personnel - Includes Banbury Operator, Blender Operator, Color Weighman, Compounder, Feed Mill Operator, Mill Operator, Mixer Operator, Plastisol Blender, Tower Worker. They operate any equipment in which PVC resin is mixed, or compounded, with additives. This equipment includes blenders, Banbury mixers, mills and mixers. They also weigh and add the additives to the PVC.

Extrusion Personnel - Includes Extruder, Finisher, Foreman, Tuber Feeder, Tuber Operator. They operate extrusion equipment in which compounded PVC is forced through a die and takes on the shape of the die opening. They also cut the extruded PVC to length and inspect the item.

Laboratory Personnel - Includes Laboratory Technicians. They work in the research and development labs, product control labs and analysis labs performing tests on raw materials or products to check quality and develop new additives for use.

Maintenance Personnel - Includes Maintenance Man and Mechanic. They are responsible for the repair of all equipment in the plant, including: production equipment, instrumentation, lighting and other electrical equipment, heating, air conditioning and ventilation systems, trucker and conveyor systems.

Miscellaneous Personnel - Includes Project Engineer, Project Supervisor and Truck Driver. They are personnel not ordinarily in the production areas.

Molding Personnel - Includes Molder and Press Operator. They operate molding equipment such as blow molders, injection molders, vacu-forming units and embossing equipment used to convert compounded PVC into a molded item.

Plastisol Personnel - Includes Dipper, Foreman, Line Girl, Line and Dip Girl and Set-up Man. They operate equipment that utilizes a liquid plastisol or organisol in the production of a product.

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is palced infront of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-mℓ graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.

6.8 Pipets: 0.5 mℓ delivery pipets or 1.0 mℓ type graduated in 0.1 mℓ increments.

6.9 Volumetric flasks: 10 mℓ or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 ℓpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50ℓ air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In prepration for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 mℓ CS_2 should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.

5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µℓ syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µℓ aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete abosrption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 mℓ of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 mℓ CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 mℓ of CS_2. For example, to prepare a 0.3 mg/0.5 mℓ standard, one would inject 6.0 mg into exactly 10 mℓ of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5mℓ versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 mℓ CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \quad \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total mg (Section 10.4) x 1000 (ug/mg)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µℓ of compounds per liter of air

$$ppm = \mu\ell \text{ of compound}/V_s$$

$$ppm = \frac{\mu\ell \text{ of compound}}{V_s} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," *Amer. Ind. Hyg. Assoc. J.*, 31:225 (1970).

11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.

11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ) Minimum[a]	Maximum[b]	GC Column Temperature(°C)	Molecular Weight
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80% DESORPTION EFFICIENCY BUT HAVE NOT BEEN THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile
Allyl glycidyl ether
n-Amyl acetate
2-Butoxyethanol
n-Butyl acetate
n-Butyl alcohol
n-Butylglycidyl ether
Chlorobenzene
Cyclohexane
Cyclohexanone
o-Dichlorobenzene
p-Dichlorobenzene
Diethyl ether
N,N-Dimethyl aniline
Epichlorohydrin
2-Ethoxylethyl acetate
Ethyl acetate
Ethylbenzene
Ethyl butyl ketone
Fufural
Heptane
Hexane
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isoctane
Isophorone
Isopropyl acetate
Isopropyl glycidyl ether
2,6-Lutidine
Methyl acetate
Methyl acrylate
Methyl n-butyl ketone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
α-Methyl styrene
p-Methyl styrene
n-Octane
3-Octanone
Pentane
2-Pentanone
α-pinene
n-Propyl acetate
1,1,2,2-Tetrachloroethane
Tetrahydrofuran
Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10ℓ

VINYL CHLORIDE SUPPLEMENT TO P&CAM #127
31 May 1974

This document is designed to aid the analyst in adapting the procedures of P&CAM #127, "Organic Solvents in Air" to the determination of vinyl chloride in workplace air. Since in-house research on vinyl chloride analysis is still in progress, the following information is as yet incomplete.

Sampling

In-house experiments on the capacity of the 150-mg two-section activated charcoal sampling tube suggest the following: (1) if a concentration of vinyl chloride in air of around 2 ppm (v/v) is anticipated, no more than 3.5 ℓ of the atmosphere should be sampled; (2) if a concentration of around 50 ppm (v/v) is anticipated, sample no more than 1.2 ℓ. Sampling flow rates of 200 ml/min or less are recommended.

Sample Storage

Samples of vinyl chloride on charcoal appear to be stable for at least 3 weeks if stored at -20°C or at least 2 days if stored at 25°C. During storage at room temperature, the vinyl chloride slowly equilibrates throughout the tube, giving the appearance of migrating to the backup section. At -20°C this equilibration is very slow.

Analytical Procedure

Vinyl chloride is desorbed from the charcoal with 0.5 ml or 1.0 ml of CS_2. Vials having a volume of 2 ml are used (thus keeping the headspace

above the solution small) and are capped with septa after addition of the CS_2 to the charcoal. The columns used in the analysis of vinyl chloride by GC include:

Column	Temperature (°C)	Reference
20-ft 10% SE-30 on 80-100 mesh Chromosorb W AW DMCS	60	in-house
20-ft 10% FFAP on 80-100 mesh Chromosorb W AW DMCS	65 (initial)	in-house
5-ft 5% SP-1000 on 80-100 mesh Chromosorb W AW DMCS	65 (initial)	in-house
6-ft 20% Carbowax 600 on C-22 Firebrick	?	1
6-ft Porapak Q, 80-100 mesh	30-50 (initial)	2
6-ft Carbowax 20M alkaline on 60-80 mesh Chromosorb W AW	?	3
100-ft Squalane coated capillary	30	4
100-ft 25% GE-96 silicone/75% oxybis-(2-ethyl benzonte) coated capillary	25	4
200-ft hexadecane coated capillary	25	4
10-ft 7% OV-101 on 60-80 mesh Chromosorb G AW	50	5

Using the 20-ft GC column of 10% SE-30 on Chromosorb W at 60°C, our standard curve extends as low as 0.2 ng/injection. Impurities in the CS_2 interfered with the analyses for low levels of vinyl chloride using the FFAP or SP-1000 columns.

Standards are prepared in either of two ways. (A) Pure vinyl chloride is slowly bubbled into a tared amount of toluene (~ 5 ml) contained in a 10-ml volumetric flask. About 100-400 mg of vinyl chloride are collected in 3 min. The solution is reweighed and diluted to the mark with CS_2. Standards are prepared from this stock solution using CS_2 for the dilution. (B) A series of standard solutions are prepared by injecting known volumes of pure vinyl chloride (gas) into CS_2 in 5- or 10-ml volumetric flasks and diluting to the marks. The relative accuracies of these and other methods has not been determined.

The desorption efficiency is determined using a synthetic atmosphere of vinyl chloride in clean air contained in a Tedlar (in house) or a Seran (reference 5) bag. Known volumes of this atmosphere are sampled using the charcoal tubes and the vinyl chloride desorbed and determined by GC analysis. Concentrations thus obtained are compared with those from GC analyses of 1-ml aliquots of the synthetic atmosphere to give the desorption efficiency (DE):

$$DE = \frac{\text{weight vinyl chloride on charcoal/volume atmosphere sampled}}{\text{concentration of vinyl chloride in atmosphere}}$$

In house values of the desorption efficiency for about 300 μg of vinyl chloride on the charcoal tubes have been around 0.8. Since the desorption efficiency may differ with loading on the charcoal, desorption procedure, and charcoal batch, each laboratory should determine its own values, preferably for the loading expected if an atmosphere containing vinyl chloride at the OSHA standard were sampled.

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VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Vinyl Chloride (Chloroethene, Chloroethylene)	Method No.:	P&CAM #178
Matrix:	Air	Range:	0.2-1500 ng per injection
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		
Date Issued:	9/3/74	Precision:	Unknown
Date Revised:		Classification:	D (Operational)

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the vinyl chloride present.

   1.2 The charcoal in the tube is transferred to a small vial containing carbon disulfide where the vinyl chloride is desorbed.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 The minimum detectable amount of vinyl chloride was found to be 0.2 nanograms per injection at a 1 x 1 attenuation on a gas chromatograph.

   2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5.0 liters. This value is the volume which the front section of the charcoal tube will hold at 200 ppm before a significant amount of vinyl chloride is found on the backup section. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethan foam. [See Section 6.2.]) If a particular atmosphere

is suspected of containing a high concentration of contaminants and/or a high humidity is suspected, the sampling volume should be reduced by 50%.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the capacity of the charcoal for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 It must be emphasized that any compound which has the same retention time as vinyl chloride at the operation conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk material be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

The precision and accuracy of the total sampling and analytical method have not been determined.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more components suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time ~33% of this compound will be found in the backup section. This may lead to some confusion as to whether breakthrough has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at −20°.

5.3 The precision of the overall method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal sampling pump for personal and area samples whose flow can be determined accurately at 50 milliliters per minute.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethan foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing to remove material possibly absorbed on charcoal. The primary absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethan foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% SE-30 stationary phase on 80/100 mesh, Chromosorb W, acid washed, silanized with dimethyldichlorosilane solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Two-ml vials which can be sealed with caps containing teflon-lined silicone rubber septa.

6.7 Microliter syringes: 10 µℓ, and convenient sizes for making standards.

6.8 Gas-tight syringes: 1 mℓ, with open/close valve.

6.9 Pipets: 0.5-mℓ delivery pipets or 1.0-mℓ type graduated in 0.1-mℓ increments.

6.10 Volumetric flasks: 10-mℓ or convenient sizes for making standard solutions. It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

7.1 Spectroquality carbon disulfide.

7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.

7.3 Toluene, chromatographic quality.

7.4 Bureau of Mines Grade A helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and is positioned nearest the sampling pump.

8.3.3 The charcoal tube is placed in a vertical position during sampling, open end pointing upward, to prevent "channelling" of the charcoal.

8.3.4 Air being sampled is not to be passed through any hose or tubing before entering the charcoal tube.

8.3.5 Bulk air samples are taken along with personal samples, i.e. sample 10-20 liters of the air in the environment using a separate charcoal tube.

8.3.6 The flow, time, and/or volume must be measured as accurately as possible. The sample is taken at a flow rate of 50 ml/min. The maximum volume to be sampled should not exceed 5.0 liters (See Section 2.2).

8.3.7 The temperature and pressure of the atmosphere being sampled is measured and recorded.

8.3.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

8.3.9 One tube is handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.3.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. If the samples will spend a day or more in transit, cooling (e.g., with dry ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.3.11 Samples received at the laboratory are logged in and immediately stored in a freezer (~-20°C) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). It should be pointed out that during long periods of storage (more than 2 weeks), the vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This does not constitute breakthrough.

8.4 Analysis of Samples

8.4.1 Preparation and Desorption of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small vial containing 1 ml of carbon disulfide. (Note the addition to the CS_2 is important.) The vial is topped with a

septum cap (See Section 6.6). The separating section of foam is removed and discarded; the second section is transferred to another small vial containing 1 ml of CS_2. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. In any case samples should be analyzed within 60 minutes after addition of CS_2.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 cc/min. (80 psig) helium carrier gas flow
2. 65 cc/min. (20 psig) hydrogen gas flow to detector
3. 500 cc/min. (50 psig) air flow to detector
4. 230°C injector temperature
5. 230°C manifold temperature (detector)
6. 60°C isothermal column temperature (oven).

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn to the 7.4 µl mark (2 µl solvent + 0.4 µl air + 5 µl sample = 7.4 µl). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the

desorption process. Desorption efficiency should be determined on the same batch of charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube) particularly at lower values, i.e., 2.5 µg.

8.5.2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A known volume of vinyl chloride gas is injected into a bag containing a known volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated at room temperature and pressure. A known volume is then sampled through a charcoal tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples (See Section 8.4). Samples taken with a gas tight syringe from the bag are also injected into the GC. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the difference between the average weight of the samples and the weight of the blank divided by the average weight of the vinyl chloride standard gas mixture in the bag or

$$\text{Desorption efficiency} = \frac{\text{Weight on sample - Weight on blank}}{\text{Weight in standard gas mixture}}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. Specifically, the Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. The regulations currently serve as an emergency standard and may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 125, Thursday, June 27, 1974.) Note that the above is an emergency standard (temporary) and will be replaced by a permanent standard in October of 1974.

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/1.0 mℓ versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS_2. The plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (~2%) is present and was found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS_2 and the washings added to the volumetric. The volumetric is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in µg, corresponding to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on µg/1.0 mℓ CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct } \mu g = \mu g_s - \mu g_b$$

where:

μg_s = µg found in front section of sample tube
μg_b = µg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total µg per sample.

10.5 The volume of air sampled is converted to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric pressure in mm Hg
T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg/m^3, which is numerically equal to µg/liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total } \mu g \text{ (Section 10.4)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µℓ of vinyl chloride/liter of air

$$ppm = \mu\ell \text{ of vinyl chloride}/V_s$$

$$ppm = \frac{\mu g \text{ of vinyl chloride}}{V_s} \times \frac{24.45}{62.5}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg
62.5 = molecular weight of vinyl chloride

11. References

11.1 Hill, R.H., C.S. McCammon, A.T. Saalwaechter, A.W. Teass, and W.J. Woodfin, "Determination of Vinyl Chloride in Air," in preparation.

11.2 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Am. Ind. Hyg. Assn. J. 31, 225 (1970).

APPENDIX D

Table D-1

Plant A

Vinyl Chloride Sample Data

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator	12/3/74	1	1	3.34	0.21
			1	4.24	2.45
			1	3.53	0.13
	12/2/74	2	1	4.01	0.74
			1	3.80	0.22
			1	3.84	1.57
			1	2.68	0.17
Loader	12/3/74	1	1	4.34	0.10
			1	4.70	0.74
			1	4.13	1.62
			1	4.22	1.89
	12/2/74	2	1	3.78	0.17
			1	4.04	0.32
			1	4.30	0.35
			1	2.91	0.41
Maintenance Worker	12/3/74	1	1	3.36	0.25
			1	3.22	0.09
			1	3.36	0.02
			1	3.33	0.32
Foreman	12/2/74	2	1	5.14	0.04
			1	4.76	0.08
			1	4.60	0.20
			1	4.67	0.13
	12/3/74	1	1	4.62	0.03
			1	3.92	0.04
			1	3.85	0.21
Lab Tech	12/3/74	1	1	4.32	0.37
			1	4.30	0.07
			1	4.49	0.04
			1	4.52	0.15
			1	5.05	4.36
			1	5.14	0.27
			1	5.28	0.05
			1	5.56	0.32
AREA SAMPLES					
General Area	12/2/74	2	1	3.77	0.56
			1	3.63	2.19
			1	3.49	4.03
			1	3.44	1.10
			1	9.18	1.03

Plant A - (continued)

Vinyl Chloride Sample Data

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
General Area	12/3/74	1	1	3.18	1.28
			1	5.04	5.89
			1	4.45	2.03
			1	3.92	1.33
Loading Area	12/2/74	2	1	9.66	<0.01
			1	7.74	<0.01
			1	6.65	0.01
			1	7.30	0.01

Table D-2

Plant B

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator	12/10/74	2	1	4.02	3.46
			1	3.83	0.46
			1	3.96	0.81
			1	4.30	0.18
			1	3.56	0.07
			1	3.65	0.07
			1	3.25	0.10
			1	3.54	0.04
			1	4.08	0.06
			1	3.28	0.14
			1	2.59	0.11
			1	3.19	0.13
			1	4.27	0.01
			1	4.54	0.06
			1	4.57	0.04
			1	4.40	0.05
	12/12/74	3	1	4.32	3.00
			1	4.52	0.29
			1	4.42	0.73
			1	4.46	0.13
			1	4.08	0.10
			1	4.02	0.08
			1	3.93	0.11
			1	3.81	0.13
			1	3.83	0.20
			1	3.70	0.06
			1	3.85	0.02
			1	4.01	0.09
			1	4.41	0.10
			1	3.37	0.06
			1	3.69	0.06
			1	3.52	0.07
Loader	12/11/74	1	1	2.61	10.80
			1	2.92	28.52
			1	2.66	13.12
			1	4.57	19.32
			1	4.22	14.63
	12/12/74	3	1	4.54	84.77
			1	4.62	3.00
			1	4.88	7.13
			1	4.48	11.59
Maintenance Worker	12/10/74	1	1	3.85	0.33
			1	3.48	0.26
			1	4.25	0.01
			1	3.54	0.08

Plant B - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Lab Tech	12/11/74	1	1	3.67	0.11
			1	4.26	0.55
			1	4.16	0.88
			1	4.93	0.06
			1	4.71	0.06
			1	4.20	0.02
			1	3.98	0.12
			1	3.98	0.06
	12/12/74	3	1	4.26	0.16
			1	3.87	<0.01
			1	3.75	0.09
			1	3.54	0.03
AREA SAMPLES					
Compressor Area	12/10/74	1	1	3.17	0.12
			1	3.12	0.12
			1	3.30	0.14
			1	3.22	0.25
	12/12/74	3	1	3.50	0.17
			1	3.23	0.15
			1	3.34	0.12
			1	3.21	0.09
Loading Area	12/11/74	1	1	2.36	1.22
			1	2.66	0.09
			1	2.48	0.20
			1	3.88	0.36
			1	4.20	0.31
Stock Room	12/11/74	1	1	4.71	0.06
			1	4.86	<0.01
			1	4.80	0.05
			1	4.97	0.38
Cracker Area	12/11/74	1	1	14.22	0.09

Table D-3

Plant C

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator	12/16/74	2	1	4.93	6.24
			1	4.94	0.22
			1	4.85	0.21
			1	4.62	1.95
			1	4.67	3.35
			1	4.57	0.20
			1	4.36	0.25
			1	4.73	0.10
			1	4.69	0.46
			1	4.56	0.19
			1	4.34	0.66
			1	4.36	0.09
			1	5.04	0.11
			1	3.91	0.21
			1	4.82	0.21
			1	5.33	0.75
			1	4.55	0.40
			1	4.50	0.20
			1	4.84	0.17
			1	4.62	0.13
			1	5.00	0.11
			1	5.31	0.21
			1	5.24	0.21
			1	5.49	0.33
			1	4.87	0.28
			1	4.91	0.22
			1	4.72	0.20
			1	4.82	0.11
	12/17/74	1	1	4.97	18.2
			1	5.18	0.61
			1	5.14	0.37
			1	4.70	0.88
			1	4.68	0.49
			1	4.43	0.57
			1	4.48	0.34
			1	4.17	0.27
			1	4.53	0.62
			1	4.17	0.38
			1	3.98	0.27
			1	3.49	0.22
			1	4.68	0.51
			1	4.61	0.15
			1	4.72	0.11

Plant C - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator	12/17/74	1	1	4.70	0.24
			1	4.76	0.13
			1	4.79	0.09
			1	4.68	0.12
			1	4.83	0.22
			1	4.63	0.12
			1	4.40	0.08
			1	4.78	0.15
			1	4.95	0.20
			1	5.03	0.10
			1	4.80	0.10
			1	4.85	0.13
			1	4.55	0.19
Loader	12/18/74	1	1	4.05	1.50
			1	4.12	0.98
			1	4.08	0.34
			1	3.98	0.99
			1	3.94	0.67
			1	3.90	2.31
			1	4.14	0.35
			1	3.76	0.38
	12/19/74	2	1	4.51	17.6
			1	4.51	0.06
			1	5.15	21.8
			1	3.29	0.23
			1	3.85	6.19
			1	3.95	0.34
			1	5.06	20.1
			1	1.82	1.13
			1	3.97	1.74
			1	3.90	0.09
			1	5.64	14.6
			1	2.75	0.37
Maintenance Worker	12/17/74	1	1	5.22	0.55
			1	5.19	0.52
			1	5.24	0.28
			1	5.08	0.25
			1	4.18	0.41
			1	4.30	0.32
			1	4.24	0.16
			1	4.17	0.32
Lab Tech	12/18/74	1	1	5.07	0.03
			1	4.98	1.01
			1	3.71	0.06
			1	4.71	0.04

Plant C - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Lab Tech	12/18/74	1	1	5.13	0.02
			1	5.23	0.27
			1	5.32	0.07
			1	5.29	0.04
Lab Tech	12/19/74	2	1	4.88	0.19
			1	4.62	0.10
			1	4.76	0.08
			1	4.89	0.06
			1	5.28	0.09
			1	4.07	0.11
			1	5.04	0.09
			1	5.03	0.07
AREA SAMPLES					
Scrubbers	12/18/74	1	1	3.27	7.06
			1	3.26	1.60
			1	3.32	1.61
			1	3.45	2.73
General Plant	12/18/74	1	1	17.39	0.57
VC Reflux Pumps	12/19/74	2	1	4.82	0.59
			1	3.53	1.15
			1	3.63	5.19
			1	3.68	3.17

Table D-4

Plant D

Solvent Process Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	6/15/74	1	2	3.43	ND
			1	1.52	77.0
			3	3.26	1.6
			1	0.94	5.4
			1	2.02	ND
			1	1.54	2.9
			1	1.63	5.4
			3	6.71	5.4
			1	1.75	ND
			2	2.65	ND
	6/19/74	1	4	7.28	2.6
			6	5.14	0.7
			7	10.56	0.9
			5	15.92	9.4
			4	6.72	11.1
		2	4	7.07	1.2
			4	4.94	0.2
			4	4.70	0.7
			4	7.44	7.8
			4	9.12	8.8
Operator-Drying Area	6/15/74	1	3	3.16	2.4
			1	1.24	ND
	6/19/74	1	7	7.21	3.7
		2	4	4.43	0.4
Helper	6/15/74	1	3	6.59	2.3
Bagger	6/19/74	1	5	13.15	0.6
			5	7.63	1.1
			5	3.94	ND
			5	8.30	0.9
		2	4	4.24	1.0
			4	2.19	ND
Maintenance Worker	6/15/74	1	1	2.16	1.3
			1	2.72	ND
AREA SAMPLES					
Control Room	6/15/74	1	3	3.95	2.6
			2	4.77	1.5
	6/19/74	1	5	11.13	0.3
			6	12.43	0.4
		2	4	7.97	0.3
			4	4.22	0.2
Reactor Bldg.	6/19/74	1	3	6.55	1.9
		2	3	8.64	1.3
Solvent Recovery Bldg.	6/19/74	1	3	7.93	7.1
		2	2	5.35	6.5
Packaging Bldg.	6/19/74	1	5	5.18	2.3
		2	4	4.56	0.9

Plant D - (continued)

Modified Emulsion Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	6/13/74	1	1	1.65	4.0
			2	1.97	2.4
			2	3.51	<0.1
			2	2.75	0.1
			1	1.52	2.6
	6/14/74		5	6.71	1.2
			1	0.91	4.2
			1	1.51	ND
			1	2.40	2.6
			1	1.79	3.0
			1	1.52	ND
			1	1.58	ND
			1	0.87	ND
			1	1.03	2.7
			1	1.50	2.1
	6/17/74	1	4	3.71	1.6
			2	1.02	3.5
			3	5.24	ND
			2	3.12	0.3
			5	6.55	ND
			4	8.44	1.2
	6/18/74	1	3	3.32	3.9
			3	6.25	0.4
			4	3.96	2.3
Bagger	6/18/74	1	4	3.38	2.3
Foreman	6/13/74	1	2	5.58	0.1
	6/14/74	1	3	8.67	0.4
Maintenance Worker	6/13/74	1	2	1.80	0.2
AREA SAMPLES					
Control Room	6/13/74	1	3	3.14	ND
	6/14/74	1	5	4.75	2.0
			5	3.60	2.4
	6/17/74		6	7.67	1.9
			6	9.33	0.8
	6/18/74		5	9.23	1.1
General Area	6/18/74		3	2.00	1.4

Plant D - (continued)

Emulsion Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	6/11/74	1	1	1.99	5.3
			2	3.61	9.3
			2	3.34	12.9
			2	1.91	29.4
	6/12/74	1	4	1.89	6.2
			4	2.61	15.1
			3	3.09	7.6
			4	6.98	1.5
	6/13/74	1	5	3.33	22.9
			1	1.97	10.2
			1	0.90	4.4
			2	4.83	0.1
	6/18/74	1	2	2.45	9.4
			3	3.92	29.8
Helper-Reactor Area	6/11/74	1	3	8.79	19.2
			3	5.19	3.6
			3	6.41	3.6
			2	6.43	6.6
	6/12/74	1	2	2.54	11.0
			2	4.10	11.4
			4	4.60	13.4
	6/13/74	1	3	11.14	0.9
			1	2.39	77.0
			4	5.47	0.7
	6/18/74	1	1	1.39	17.0
			1	3.96	6.1
Operator-Dryer Area	6/12/74	1	4	5.06	82.8
	6/13/74	1	4	6.65	5.2
Bagger	6/11/74	1	7	7.71	9.6
	6/12/74	1	4	6.80	1.3
			4	4.34	1.4
Bagger	6/13/74	1	4	4.98	0.1
			4	5.15	2.6
	6/18/74	1	2	2.41	2.9
	6/11/74	1	2	3.57	3.6
	6/12/74	1	1	2.87	22.0
	6/13/74	1	2	2.46	0.3
AREA SAMPLES					
Control Room	6/11/74	1	5	5.41	11.1
	6/12/74	1	4	8.96	5.6
	6/13/74	1	6	9.20	11.7
	6/18/74	1	4	6.70	1.2

Table D-5

Plant E

Mass Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	8/5/74	2	1	1.13	2.2
			1	1.05	ND
			2	2.47	6.3
			2	0.87	9.3
	8/6/74	2	1	1.41	7.3
			1	0.85	4.0
			1	1.57	19.9
			1	1.05	ND
			1	1.05	ND
			1	1.23	ND
			1	1.31	2.8
			1	0.75	7.6
			1	0.83	7.0
			1	1.05	3.0
	8/7/74	1	1	1.22	4.2
			1	1.55	2.1
			1	0.98	ND
			1	0.93	ND
			1	0.99	2.9
			1	1.45	2.8
			1	0.97	3.4
	8/8/74	1	1	1.17	2.5
			1	0.87	22.6
			1	0.61	4.9
			1	0.94	ND
			1	1.63	14.8
			1	0.98	ND
			1	0.77	13.7
			1	2.04	ND
			1	2.02	1.5
	8/9/74	3	1	1.56	ND
			1	1.36	ND
			1	1.15	ND
			1	1.40	ND
			1	0.88	ND
			1	1.10	1.6
Helper-Reactor Area	8/5/74	2	1	0.92	2.9
			2	1.48	2.7
			1	1.08	20.7
			1	2.71	2.0
			2	0.43	13.4
	8/6/74	2	1	1.15	1.8
			1	1.14	1.5

Plant E - (continued)

Mass Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Helper-Reactor Area	8/6/74	2	1	1.65	2.0
			1	1.09	4.7
			1	2.14	0.9
			1	0.19	ND
			1	0.93	2.3
	8/7/74	1	2	2.61	2.2
			2	2.99	5.1
			1	1.59	1.8
			1	0.58	4.4
			1	0.55	5.3
			1	1.06	11.1
	8/8/74	1	1	1.10	14.3
			1	1.03	ND
			1	2.34	11.7
			1	1.73	71.4
			1	0.87	10.9
			1	1.21	1.4
			1	0.19	ND
	8/9/74	3	1	1.27	ND
Helper-Reactor Area	8/9/74	3	1	1.44	ND
			1	1.19	5.9
			1	1.48	ND
			1	1.12	ND
			1	1.21	ND
			1	2.59	3.1
Bagger	8/8/74	1	2	2.15	ND
			2	1.31	ND
AREA SAMPLES					
Control Room	8/5/74	2	2	3.00	3.8
			2	3.28	3.6
	8/6/74	2	1	1.42	ND
			1	2.27	0.9
			1	1.42	ND
			1	1.45	2.0
			1	1.22	1.7
	8/7/74	1	2	3.16	1.8
			2	3.61	1.8
	8/8/74	1	1	1.53	ND
			1	1.60	ND
	8/9/74	3	1	1.44	ND
			1	0.95	ND
			1	1.27	ND
			1	1.85	ND

Plant E - (continued)

Suspension Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	8/5/74	2	1	0.63	8.0
			2	2.14	4.7
			1	1.81	2.3
			1	1.09	8.7
			1	0.60	3.1
			2	1.47	23.8
			2	1.71	11.5
			1	0.93	6.0
			1	0.53	10.7
	8/6/74	2	1	0.89	25.8
			1	1.55	11.5
			1	1.20	30.6
			1	1.36	18.6
			1	1.55	36.8
			1	0.91	37.9
			1	1.37	51.4
			1	0.44	80.0
			1	1.50	8.1
			1	1.06	14.5
			1	0.22	22.9
	8/7/74	1	1	0.71	245.0
			1	0.80	8.0
			2	1.70	6.6
			1	0.91	ND
			1	1.06	3.1
			2	1.95	1.0
			1	1.07	1.6
			2	2.17	3.8
			1	1.20	4.7
			4	1.20	1.9
	8/8/74	1	1	0.64	4.7
			1	1.36	8.4
			1	2.00	8.3
			1	1.99	3.4
			1	0.51	7.6
			1	0.51	22.4
			1	1.63	2.2
			1	2.39	8.9
			1	1.93	ND
	8/9/74	3	1	0.98	1.7
			1	0.98	ND
			1	0.70	54.5
			1	0.52	ND
			1	0.82	ND
			1	0.79	6.2

Plant E - (continued)

Suspension Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	8/9/74	3	1	0.52	191.0
			1	0.42	ND
			1	0.99	1.8
			1	0.37	28.1
			1	0.51	158.8
			1	1.03	27.6
			1	2.46	2.5
			1	0.79	46.7
			1	1.22	5.0
Helper-Reactor Area	8/5/74	2	2	1.60	7.2
			2	3.02	3.2
	8/6/74	2	1	0.64	ND
			1	2.34	23.6
			1	1.52	16.0
	8/8/74	1	1	1.59	6.9
			1	1.16	16.9
			1	0.77	ND
Bagger	8/7/74	1	2	2.77	ND
			1	1.22	ND
			2	3.12	ND
			1	1.33	ND
			2	0.83	ND
			1	0.11	ND
	8/8/74	1	2	2.56	0.6
			2	2.61	0.7
			2	4.35	0.9
			2	2.78	ND
AREA SAMPLES					
Office	8/5/74	2	2	3.13	8.3
			1	0.61	8.2
	8/6/74	2	1	1.50	43.09
			1	0.59	23.8
			1	0.65	8.7
			1	2.25	96.5
			1	0.56	50.6
	8/7/74	1	2	2.27	ND
			2	2.99	2.2
			1	0.80	4.1
	8/8/74	1	1	1.04	2.6
			1	2.50	4.1
			1	1.05	1.8
			1	1.07	6.4
	8/9/74	3	1	0.41	ND
			1	1.04	ND
			1	0.56	ND
			1	0.71	ND

Table D-6

Plant F

Emulsion Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	12/4/74	1	1	4.31	5.1
			1	5.10	6.1
			1	5.54	6.7
			1	4.74	33.8
			1	0.02	98.0
			1	1.91	8.4
	12/5/74	1	1	4.30	6.5
			1	5.39	3.9
			1	5.76	6.3
			1	5.14	4.7
			1	3.28	13.5
			1	2.24	2.3
			1	5.78	3.8
			1	4.62	6.8
			1	7.22	13.4
			1	5.67	12.1
			1	6.30	31.5
	12/6/74	1	1	4.87	5.1
			1	9.11	6.2
			1	5.80	5.6
			1	5.64	6.8
			1	7.30	5.5
			1	5.28	7.4
			1	4.94	6.8
			1	9.24	12.8
			1	6.20	4.4
			1	4.24	5.2
			1	7.63	6.3
			1	5.45	6.4
Helper-Reaction Area	12/4/74	1	1	4.32	6.9
			1	4.23	3.5
Helper-Reactor Area	12/4/74	1	1	9.09	5.6
			1	8.63	6.5
			1	4.99	7.3
			1	5.19	5.0
	12/5/74	1	1	4.82	19.4
			1	5.97	6.1
			1	4.75	10.1
			1	4.76	68.0
			1	2.85	10.3
			1	6.10	11.3
			1	4.74	103.8
			1	2.77	16.4
			1	5.94	36.1

Plant F - (continued)

Emulsion Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Helper-Reactor Area	12/6/74	1	1	5.27	16.2
			1	7.06	8.7
			1	6.01	7.4
			1	3.05	12.5
			1	5.11	10.2
			1	0.64	9.2
			1	4.10	21.1
			1	8.97	8.8
			1	5.99	5.0
Maintenance Worker	12/6/74	1	1	7.10	1.4
Operator-Dryer Area	12/9/74	1	1	12.11	3.6
			1	7.43	5.5
			1	9.78	4.2
			1	5.84	3.9
			1	11.00	4.3
			1	5.24	5.4
	12/10/74	1	1	0.97	1.6
			1	12.19	1.2
Operator-Dryer Area	12/10/74	1	1	6.47	1.3
			1	12.10	1.2
			1	6.50	1.4
			1	9.48	1.9
			1	5.74	1.5
	12/11/74	1	1	4.21	9.6
			1	4.92	1.4
			1	5.27	0.5
			1	2.85	9.5
			1	4.46	3.8
			1	4.71	2.6
			1	3.95	4.9
			1	5.83	2.3
			1	5.49	2.9
			1	3.99	4.5
			1	6.12	1.9
			1	4.62	4.8
Helper-Dryer Area	12/9/74	1	1	9.05	2.4
			1	5.53	3.3
			1	11.96	2.3
			1	6.59	3.6
	12/10/74	1	1	8.38	0.6
			1	4.07	0.8
	12/11/74	1	1	6.63	1.0
			1	8.72	0.7
			1	7.06	0.7

Plant F - (continued)

Emulsion Resin Area

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Bagger	12/9/74	1	1	10.71	2.0
			1	6.82	3.2
			1	10.94	2.5
			1	6.75	3.4
			1	10.84	3.5
			1	5.60	4.1
			1	17.20	1.0
			1	10.31	0.2
			1	11.13	2.1
			1	7.09	2.6
AREA SAMPLES					
Control Room-Reactor Area	12/4/74	1	1	5.02	2.5
			1	4.70	1.4
	12/5/74	1	1	3.92	3.7
			1	5.50	1.9
			1	5.43	1.0
	12/6/74	1	1	8.54	5.9
			1	6.16	3.6
Operators Desk-Reactor Area	12/4/74	1	1	6.18	7.4
			1	4.86	8.5
	12/5/74	1	1	3.92	15.9
			1	5.83	7.9
	12/6/74	1	1	12.18	2.2
			1	9.07	1.4

Plant F - (continued)

Suspension Resin Area - Old

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	12/4/74	1	1	3.13	18.3
			1	2.47	16.5
			1	1.76	12.2
			1	2.94	9.9
			1	1.79	9.6
			1	2.26	11.6
			1	4.01	12.8
			1	3.23	5.7
			1	2.25	20.0
			1	3.04	5.5
			1	3.28	160.6
			1	2.15	114.3
	12/5/74	1	1	4.69	15.0
			1	2.76	6.1
			1	5.68	9.0
			1	5.14	13.8
			1	3.13	19.7
			1	2.88	5.9
			1	3.61	5.3
			1	4.81	8.1
			1	4.42	11.4
	12/6/74	1	1	0.68	31.1
			1	0.43	33.7
			1	3.01	13.3
			1	0.53	9.6
			1	2.49	11.8
			1	2.16	5.6
			1	4.36	6.2
Helper-Reactor Area	12/4/74	1	1	2.86	8.8
			1	3.02	33.4
			1	2.19	16.3
			1	2.87	7.6
			1	2.70	30.3
			1	1.69	11.4
	12/5/74	1	1	2.90	12.8
			1	2.33	6.2
			1	4.20	6.4
			1	0.76	11.9
			1	3.55	13.1
			1	3.05	1.8
			1	5.73	18.3
			1	4.44	21.2
			1	3.33	13.8
			1	4.77	28.3

Plant F - (continued)

Suspension Resin Area - Old

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Helper-Reactor Area	12/5/74	1	1	4.43	8.1
			1	3.30	15.7
			1	5.37	27.0
			1	5.18	9.8
			1	4.11	11.2
			1	2.82	5.8
			1	4.46	5.8
			1	3.25	5.9
			1	2.67	1.3
			1	3.85	12.1
			1	3.45	17.3
			1	5.85	18.3
	12/6/74	1	1	1.37	160.5
			1	2.66	13.6
			1	3.77	57.8
			1	1.55	10.9
			1	4.85	7.7
			1	3.42	51.3
Helper-Reactor Area	12/6/74	1	1	1.11	4.9
			1	5.37	10.3
			1	4.30	9.5
			1	1.94	8.7
Maintenance Worker	12/5/74	1	1	3.43	12.8
			1	2.98	4.2
			1	3.88	6.5
			1	4.31	5.5
AREA SAMPLES					
Control Room	12/4/74	1	1	3.26	8.3
			1	3.47	9.9
			1	2.55	11.5
	12/5/74	1	1	2.85	1.8
			1	5.66	4.2
			1	4.26	9.4
	12/6/74	1	1	4.10	5.1
			1	3.08	1.0
			1	4.54	4.8

Plant F - (continued)

Suspension Resin Area - New

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Operator-Reactor Area	12/9/74	1	1	5.56	9.8
			1	6.41	2.7
			1	5.14	2.8
			1	6.02	4.1
			1	7.02	5.4
			1	5.80	5.7
			1	4.66	2.6
			1	5.69	4.5
			1	4.67	5.9
			1	3.99	6.9
			1	6.83	4.3
			1	3.74	6.8
			1	4.27	7.8
			1	5.99	19.8
			1	4.29	78.6
			1	5.46	4.4
			1	7.17	55.1
			1	4.82	3.6
	12/10/74	1	1	3.80	0.8
			1	8.15	1.1
			1	5.37	0.8
			1	6.35	0.8
			1	7.32	1.1
			1	4.77	1.2
			1	4.45	2.1
			1	5.55	1.3
			1	4.58	7.2
			1	5.14	0.8
			1	6.63	1.3
			1	5.14	6.4
			1	3.91	4.1
			1	7.90	2.3
			1	4.33	13.3
			1	4.21	14.4
			1	6.38	2.8
			1	4.42	2.8
Operator-Dryer Area	12/9/74	1	1	3.93	8.2
			1	5.81	3.4
			1	5.42	6.1
	12/10/74	1	1	4.84	1.1
			1	7.65	1.2
			1	5.31	21.0

Plant F - (continued)

Suspension Resin Area - New

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
AREA SAMPLES					
Control Room-Reactor Area	12/9/74	1	1	3.19	1.1
			1	5.17	1.4
			1	4.09	1.6
	12/10/74	1	1	6.82	0.1
			1	11.22	0.1
			1	7.27	0.1

Table D-7

Plant G

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	2/4/75	1	1	4.60	<0.01
			1	4.64	0.01
			1	6.21	<0.01
			1	3.15	0.02
	2/3/75	1	1	5.02	<0.01
			1	2.50	<0.01
			1	3.71	<0.01
			1	3.69	<0.01
Extrusion Personnel	2/3/75	1	1	5.42	<0.01
			1	2.67	ND
			1	4.00	ND
			1	4.06	<0.01
			1	5.92	<0.01
			1	2.91	<0.01
			1	4.41	<0.01
			1	4.45	<0.01
	2/4/75	1	1	4.75	0.01
			1	4.79	<0.01
			1	6.16	<0.01
			1	3.33	<0.01
			1	3.99	<0.01
			1	4.02	<0.01
			1	5.76	<0.01
			1	3.44	<0.01
	2/6/75	1	1	4.44	<0.01
			1	5.76	<0.01
			1	4.30	<0.01
			1	2.85	<0.01
	2/5/75	1	1	4.79	0.01
			1	4.69	0.02
			1	5.65	0.01
Extrusion Personnel	2/5/75	1	1	3.78	0.01
Lab Personnel	2/6/75	1	1	4.73	<0.01
			1	6.15	<0.01
			1	3.87	<0.01
			1	3.83	<0.01
Miscellaneous Personnel	2/4/75	1	1	5.10	<0.01
			1	3.58	<0.01
			1	4.83	<0.01
			1	4.60	0.01
	2/5/75	1	1	4.71	ND
			1	4.45	0.01
			1	6.22	0.01
			1	2.74	0.01
			1	4.49	0.01

Plant G - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Miscellaneous Personnel	2/5/75	1	1	4.51	0.01
		1	1	5.71	<0.01
			1	3.29	0.01
	2/6/75	1	1	4.26	<0.01
			1	5.52	<0.01
			1	4.60	<0.01
			1	3.15	<0.01
AREA SAMPLES					
Extruder Area	2/5/75	1	1	4.88	0.02
			1	4.71	0.01
			1	6.08	0.01
			1	3.83	0.01
	2/6/75	1	1	4.60	0.01
			1	6.25	0.01
			1	4.67	0.01
			1	3.16	<0.01
Blending Room	12/3/75	1	1	5.01	<0.01
			1	2.56	0.01
			1	3.76	ND
			1	3.91	ND
	12/4/75	1	1	3.94	<0.01
			1	4.22	ND
			1	5.69	<0.01
			1	3.17	<0.01

Table D-8

Plant H

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	2/10/75	1		4.12	0.03
				4.11	0.06
				4.52	0.02
				4.25	0.01
	2/11/75	1		4.47	0.15
				4.45	0.11
				4.55	0.27
				4.59	0.11
Extrusion Personnel	2/10/75	1		4.44	0.02
				4.74	0.01
				4.66	0.01
				4.48	0.02
				4.57	0.02
				4.66	0.01
				4.62	0.01
				4.63	0.01
	2/11/75	1		4.36	0.01
				3.82	0.01
				4.55	<0.01
				4.44	<0.01
				4.54	0.01
				4.62	<0.01
				4.14	<0.01
				4.66	<0.01
Molding Personnel	2/10/75	1		4.58	0.03
				4.45	0.02
				4.35	0.02
				4.55	0.01
	2/11/75	1		3.85	0.01
				4.49	<0.01
				4.53	<0.01
				4.33	<0.01
Lab Personnel	2/10/75	1		4.49	0.05
				4.71	0.06
				5.52	0.01
				4.41	0.02
	2/11/75	1		4.80	0.04
				4.90	0.01
				4.80	0.02
				4.90	0.01
Maintenance Personnel	2/10/75	1		4.35	0.02
				4.74	0.01
				4.41	0.01
				4.35	0.01
	2/11/75	1		4.70	0.02
				4.72	<0.01

Plant H - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Maintenance Personnel	2/11/75	1		4.64	<0.01
				4.69	<0.01
AREA SAMPLES					
Mixing Area	2/10/75	1		4.39	0.24
				4.39	0.43
				4.40	0.13
				4.37	0.68

Table D-9

Plant I

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Plastisol Dipping Personnel	2/12/75	1		5.17	0.06
				5.44	<0.01
				5.13	<0.01
				5.99	ND
				4.82	0.06
				4.30	0.01
				5.10	<0.01
				4.89	ND
				4.73	0.04
				4.74	0.01
				5.11	ND
				5.24	ND
				4.84	0.03
				4.47	0.01
				5.33	<0.01
				5.22	ND
				5.58	0.02
				5.16	0.02
				6.02	<0.01
				6.06	<0.01
				5.17	0.02
				4.86	0.01
				5.49	<0.01
				5.23	ND
	2/13/75	1		4.74	<0.01
				4.29	ND
				4.64	<0.01
				5.29	ND
				5.36	<0.01
				4.77	ND
				5.19	ND
				6.38	ND
				5.29	ND
				4.96	ND
				5.19	ND
				5.90	ND
				4.92	ND
				4.43	ND
				4.59	ND
				5.52	ND
Lab Personnel	2/13/75	1		4.83	ND
				4.77	ND
				5.18	ND
				5.08	ND

Plant I - (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
AREA SAMPLES					
Mixing Area	2/13/75	1		5.80	ND
				4.88	ND
				4.93	ND
				5.51	ND

Table D-10

Plant J

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	2/17/75	1		4.80	ND
				4.99	ND
				5.03	ND
				5.49	ND
	2/18/75	1		4.62	ND
				4.64	ND
				5.39	ND
				4.21	ND
				4.78	ND
				4.69	ND
				5.39	ND
				4.46	ND
Calender Personnel	2/17/75	1		5.12	ND
				4.67	ND
				5.28	ND
				5.64	ND
	2/18/75	1		5.01	ND
				4.97	ND
				5.51	ND
				4.45	ND
	2/19/75	1		5.30	ND
				5.03	ND
				5.31	ND
				6.35	ND
Extrusion Personnel	2/19/75	1		4.93	ND
				4.45	ND
				4.84	ND
				5.88	ND
				4.48	ND
				3.94	ND
				4.24	ND
				5.25	ND
Molding Personnel	2/17/75	1		4.04	ND
				4.06	ND
				4.47	ND
				5.40	ND
				5.29	ND
				4.91	ND
				7.03	ND
				5.37	ND
Miscellaneous Personnel	2/19/75	1		4.84	ND
				4.13	ND
				4.30	ND
				5.23	ND

Plant J (continued)

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
AREA SAMPLES					
Mixing Area	2/19/75	1		4.20	ND
				4.06	ND
				2.58	ND
				6.18	ND

Table D-11

Plant K

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	3/11/75	1		10.73	ND
				10.15	ND
				9.49	ND
				9.50	ND
	3/12/75	1		9.74	0.13
				9.51	<0.01
				10.71	<0.01
				10.38	<0.01
		2		9.09	<0.01
				8.51	<0.01
				9.03	<0.01
				8.64	<0.01
Calender Personnel	3/12/75	1		10.32	<0.01
				10.29	<0.01
		2		8.71	<0.01
				9.05	<0.01
	3/13/75	1		9.58	<0.01
				9.63	ND
Maintenance Personnel	3/13/75	1		8.89	<0.01
				8.73	ND
AREA SAMPLES					
Blender Area	3/14/75	1		10.63	< 0.01
				11.46	< 0.01
				8.77	< 0.01
				10.09	< 0.01

Table D-12

Plant L

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	3/17/75	1		8.39	0.69
				5.32	0.54
				10.53	0.68
				7.11	0.46
				10.91	0.53
				7.37	0.58
				10.52	0.60
				5.85	0.37
				9.59	0.32
				5.10	0.48
				4.88	0.26
				8.41	0.24
	3/18/75	1		9.88	0.39
				12.90	0.31
	3/19/75	1		10.62	0.13
				10.86	0.14
Calender Personnel	3/18/75	1		8.80	1.68
				11.16	1.92
				10.49	1.15
				10.42	2.44
				9.17	1.05
				11.48	1.36
				7.98	0.50
				9.63	1.56
Pelletizer Personnel	3/18/75	1		11.27	0.26
				11.39	0.13
	3/19/75	1		8.27	0.38
				9.64	0.02
				4.58	0.76
				15.77	0.02
				10.23	0.57
Pelletizer Personnel	3/19/75	1		10.18	0.13
				9.31	0.48
				3.61	0.03
				8.27	0.38
				9.64	0.02
Lab Personnel	3/19/75			10.62	0.68
				11.78	0.02

Table D-13

Plant M

Job Classification	Date	Shift	No. Tubes Combined	Sample Volume (liters)	Sample Concentration ppm
Compounding Personnel	4/9/75	1		9.27	<0.01
				9.20	0.01
				9.20	<0.01
				11.34	<0.01
				7.37	<0.01
				8.14	<0.01
				9.84	<0.01
				8.83	<0.01
				9.43	<0.01
				10.03	<0.01
	4/10/75			10.21	<0.01
				8.38	<0.01
				10.10	0.01
				8.83	<0.01
				8.48	<0.01
				8.82	ND
				8.81	<0.01
				8.35	<0.01
				10.09	0.02
				9.82	0.02
				11.70	0.02
				11.42	0.02
Calender Personnel	4/9/75	1		8.22	0.02
				8.79	0.02