

THE TOXICOLOGICAL DATA AND INDUSTRIAL EXPERIENCE
WITH VINYL CHLORIDE

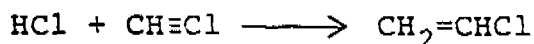
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I. INTRODUCTION - SCOPE OF VINYL CHLORIDE INDUSTRY

Vinyl chloride based plastics are among the oldest of the major plastic materials. The first commercial plants to make PVC resin were constructed in the 1930's. The initial PVC plastics were rather similar to rubber products. Today about two-thirds of PVC products produced are still rubbery in nature, but now PVC is also made into rigid end products such as pipe, siding and phonograph records. A unique property of PVC resin is one which permits it to be combined with many other raw materials to form hundreds of different compounds with wide ranges of properties; from very soft to very hard materials. This property along with its flame resistance and low cost have resulted in PVC being one of the most important plastics in existence today throughout the world.

The quantity of vinyl chloride produced in the world has grown quite rapidly to approximately 20-22 billion pounds in 1973. In the U.S. production increased from approximately 321 million pounds in 1952 to one billion in 1960; two billion in 1965; four billion in 1970; to an estimated 5.3 billion pounds in 1973.

There are two commercial processes for production of monomer. One route involves the addition of hydrogen chloride to acetylene.



However, the principal process, used by Dow and most other producers in the U.S., involves the thermal dehydrohalogenation of ethylene dichloride.



Vinyl chloride is one of the purest organic compounds produced commercially. A typical analysis of vinyl chloride produced by Dow shows less than 20 ppm of total organic impurities. These trace organic impurities are acetylene, 1,3-butadiene, methyl chloride, and vinyl acetylene.

The diversity of plant and process operations for producing vinyl chloride is quite varied. Commercial plants range in capacity from modest size up to six to eight hundred million pounds. Some are new plants, some are 15 to 20 years old. All are continuous processes carried out in open air plants.

Vinyl chloride monomer is converted to PVC resin by using suspension, emulsion, bulk or solution polymerization techniques. As shown in Slide 2, most of the PVC is produced in the U.S. by the suspension method. Historically, PVC production has been a batch operation and manufacturing has been conducted in relatively small reactors to maintain product flexibility, quality and more importantly, large capacity reactors were not available until recently. In the U.S. today and I believe world-wide, there is a definite trend to larger reactors. In 1972 approximately 85% of PVC resin was made in the U.S. in reactors of less than 7500 gallons, but by 1975 it is expected that less than 60% of the PVC will be made in these small reactors. In the U.S., 58% of the PVC plants are older than 10 years and only ten plants are located in warm climates where open structures are used; the remaining 26 plants are located in states having moderate to cold temperatures and, consequently, are enclosed in heated buildings. I have emphasized the use of small reactors and enclosed plants because I believe these two factors, along with the belief that vinyl chloride was relatively non-toxic, have had a considerable significance on the health of the workers.

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As I stated previously, PVC is the most versatile type of synthetic resin produced and, as such, has become an essential product in our society today. It is used in more individual end products than any other type of plastic material and over 25 individual end use product areas can be identified for PVC, each of which accounts for between 1% and 29% of the total PVC resin market⁽¹⁾. As shown in Slide 3, over half of all PVC resin is used in the U.S. to make products that are classified as building and construction materials; including pipes, conduit, flooring, wire and cable, siding, etc. Slide 4 shows usage for home furnishing and household goods which requires 12% of the PVC produced. Consumer goods, shown on Slide 5, also represent about 12% of the resin used in such items as phonograph records, footwear, etc. Packaging materials, illustrated on Slide 6, account for about 8% of the total PVC resin sales. The transportation equipment industry, mainly motor vehicles, in total represents about 6% of the PVC resin market as shown on Slide 7. The remaining 9% of the U.S. domestic PVC resin market, shown on Slide 8, is composed of miscellaneous products with hundreds of individual applications.

Now before I discuss our experience relative to the relationship between engineering, work practices, and monitoring in the reduction of the release of vinyl chloride and concomitantly the reduction in possible employee exposure, Dr. V. K. Rowe, Director of Toxicological Affairs in Health and Environmental Research for Dow Chemical U.S.A. will discuss the toxicological information of vinyl chloride.

(1) United States Polyvinyl Chloride Industry Impact Analysis, Arthur D. Little, Inc., Aug. 1974.

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II) TOXICOLOGICAL INFORMATION

Years ago, as far back as 1930, no one was particularly concerned about vinyl chloride. The acute toxicological work that was done (Patty, Yant and Waite) indicated that it was primarily a central nervous system depressant with little capacity to cause organic injury. Actually, attempts were made to use it as an anesthetic but it didn't work very well.

Back in 1949, Russian workers (Tribukh, Tikhomirova, Levin, and Koslov) reported on observations they made on employees working with PVC plastics. Hepatitis, acneform dermatitis and respiratory irritation was observed and the authors were careful to point out that those afflicted had exposure not only to vinyl chloride, but to additives such as phthalate esters, phosphate esters, and chlorinated diphenyls and chlorinated naphthalenes as well.

The chlorinated diphenyls and chlorinated naphthalenes used in those days were notorious for their hepatotoxic effects and for their acnegenic properties. The authors recognized

this but some who have interpreted this paper to indicate hepatotoxicity due to vinyl chloride or polyvinyl chloride have in all probability erred; perhaps they have not read the whole paper. The paper contains no reference to carcinogenicity of any kind.

In 1958 and 59, because we were handling a lot of vinyl chloride, we introduced it into our inhalation program. Back in those days, the typical inhalation experiment involved exposing several species of animals 7 hours/day, 5 days/week for a period of six months. At the end of the exposure period, certain hematological and clinical chemical parameters were studied, the animals were sacrificed and their organs weighed and examined grossly and microscopically. We studied concentrations of 500, 200, 100, and 50 ppm. We found that our Wistar strain rats suffered liver and kidney injury at 500 ppm, slight liver weight increases at 200 and 100 ppm, and nothing at 50 ppm. Although we exposed guinea pigs rabbits, and dogs to concentrations of 200, 100, and 50 ppm we found only liver injury at 200 ppm in the rabbits. No adverse effects were observed in the other two species, either at the 200 ppm level or at the 100 or 50 ppm levels.

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Nevertheless, we had the basic philosophy, that one should strive to keep industrial exposure limits as low as possible practically. In keeping with this philosophy, the Dow guideline of 50 ppm on a time-weighted average basis was established with maximum values not to exceed 100 ppm. As I have said publicly before, we did not always achieve our objective, but that was our goal. The paper describing the work I just outlined was published in 1961 in the American Industrial Hygiene Association Journal.

In 1963, Lester, Greenberg, and Adams took strong exception to our conclusion that 50 ppm should be a maximum time-weighted average exposure for workers. On the basis of 3 months exposure of rats to 20,000 ppm and 19 days to 50,000 ppm they concluded that 500 ppm was acceptable as a Threshold Limit Value despite minor changes which they observed in rat livers and which they considered "were within the normal range and were not pathologic in nature".

Since 1962, numerous European articles on vinyl chloride have appeared, particularly in the Russian literature. For several reasons, these articles are difficult to interpret in terms of chronic toxicity since the reported exposures were to mixtures or were otherwise ill-defined, the exposures are often acute, or the criteria of effect was a minimal change in response or behavior, such as a subtle change in a conditioned response.

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In 1963 and 64, the problem of acroosteolysis came to be known in Europe. To my knowledge, this disease was not recognized in the U.S.A. until later.

In 1967, U.S. industry through the Manufacturing Chemists Association (MCA) undertook an epidemiological study on PVC workers to see whether there was a significant amount of acroosteolysis in the USA. The result was that they did find some acroosteolysis in some kettle cleaners in some of the PVC industries. Dow felt fortunate because no cases were found among Dow workers. Perhaps the explanation for this is that we were using different technology than some of the others. Also, we were confident that Dow workers were not being exposed to the high concentration of vapor experienced by some others and perhaps this was the reason our workers had not suffered the disease. To satisfy any doubts about the health of Dow workers exposed to vinyl chloride, a study was undertaken of all the clinical records available on people who had worked with vinyl chloride monomer and vinyl chloride polymers and copolymers. This study was more or less a monumental study at this time because it used regression analysis, taking into account all the parameters in the medical records. The results of this analysis showed that there were abnormally high values, particularly those measuring liver function (BSP, icturic index and beta-protein), in workers on jobs where their

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exposure was judged to be greater than 300 ppm. Both systolic and diastolic blood pressures also were elevated slightly. No abnormalities were detected in those people whose jobs involved exposure to less than 300 ppm.

This study was reported in the fall of 1968 at the Gordon Research Conference on Toxicology and published in 1972 by C. G. Kramer and J. Mutchler in the American Industrial Hygiene Association Journal.

In 1970, Professor P. L. Viola of the Regina Elewa Institute for Cancer Research in Rome reported on his search for an animal model that might be used to detect materials that might produce the new disease, acroosteolysis. He had exposed a group of rats to 30,000 ppm, for 4 hours/day, 5 days/week for 12 months. He was successful in some respects. He did produce some changes in the phalanges of the rats which he thought were somewhat similar to those observed in the phalanges of the human. Also, he observed tumors of the skin, lung, and bones. The skin tumors were primarily in the area of the submaxillary and parotid glands and were described as epidermoid carcinomas. Later, these tumors were found to have been derived from the Zymbal or ceruminous gland which is particularly prominent in the rat and located in the inner ear canal. The results of this study were reported in Cancer Research in May 1971 by Viola, Bigotti, and Caputo.

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In the fall of 1971, American industry learned that additional work was being carried out in Italy, at concentrations ranging from 30,000 ppm to 50 ppm but the protocols for this work were not available. This information dealt with the work that Professor Maltoni subsequently brought to light and which will be discussed later.

In 1972, the American industry, through the MCA, mustered support for an epidemiological study involving mortality records of workers in the VC and PVC industries, which hopefully, might compliment whatever was going on in Europe.

In late 1972, protracted efforts resulted in obtaining a protocol from Europe and it was learned that Zymbal gland or ear canal tumors and some tumors of the liver and kidney had been found in rats exposed to 500 and 250 ppm but not at 50 ppm.

In 1973, both the human epidemiological and the animal inhalation studies were initiated under the sponsorship of the MCA.

Also, during this period the MCA was urging the European sponsors of Professor Maltoni's work to disclose whatever information they had, even though it was incomplete. The MCA, during mid 1973, advised the National Institute of Occupational Safety and Health (NIOSH) of its research programs and gave them copies of the protocols for both information and comment.

In December, 1973, angiosarcoma of the liver, a rather unusual type of cancer, was identified as the cause of death of a man who was a worker in the Louisville, Kentucky plant of the B. F. Goodrich Company by Dr. J. L. Creech of St. Anthony Hospital and the Medical Department of B. F. Goodrich Company of Louisville, Kentucky. Dr. Creech remembered having seen a similar type of liver tumor in a worker who had died earlier in the year. Since this was a rather unique experience, he became concerned and began to ask questions about exposure. Consequently, the company, together with Dr. Creech went back into the records and they found another case in which a workman had died with angiosarcoma in 1968. After they had had a chance to verify their records, very early in January of 1974, they announced this finding both to the Government and to the public.

On February 15, 1974, our Occupational Safety and Health Administration of the Department of Labor (OSHA) held a fact-finding hearing in Washington and Professor Maltoni was present and did report on his findings to date. He had found Zymbal gland tumors, nephroblastomas and angiosarcomas of the liver in rats exposed to 250 ppm and at higher concentrations but still had not seen any tumors in animals exposed to 50 ppm. On April 5, OSHA published its Emergency Temporary Standard stipulating a ceiling of 50 ppm.

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On April 15, 10 days later, the MCA disclosed that the studies it was sponsoring at the Industrial Bio-Test Laboratories had revealed that angiosarcomas of the liver had been observed in mice exposed to 2500, 200, and 50 ppm. This was somewhat of a 'bombshell'. It should be noted, however that the animals in Professor Maltoni's studies received only about one half the exposure that the animals in the MCA sponsored study received; 4 hours/day versus 7 hours/day.

On May 10, 1974, OSHA proposed a permanent standard calling for limitation of employee exposure to vinyl chloride to a "no detectable level" as measured by an analytical method sensitive to $1 \text{ ppm} \pm 0.5 \text{ ppm}$. The proposal called for many precautions, procedures and records too numerous to discuss here.

During the weeks of June 24 and July 8, 1974, OSHA held a public hearing in which anyone who wished to be heard was afforded the opportunity to speak for or against the proposed standard. The Dow Chemical Company made a four hour presentation in which it outlined and discussed the data it had.

We will attempt to summarize these data for you together with other pertinent information. Dr. Rausch will discuss later the engineering, monitoring, and personal protective aspects, associated with the manufacturing and handling of VC.

I will outline for you the substance of the toxicological data available and human health data available.

First, I should like to show you a slide which summarizes the most pertinent data so far available from Professor Maltoni. This tabulation is taken from a recent publication to which I have added the last minute data he supplied to OSHA at the June public hearing. The table shows clearly that exposure of Sprague-Dawley rats to VC results in a variety of tumors particularly of the Zymbal gland, kidney, liver but also at other sites. In mice, pulmonary adenomas, mammary carcinomas, and liver angiosarcomas have been observed. Professor Maltoni and Lefemine in their Summary state: "a direct relationship between dose and length of treatment, and neoplastic response has been found".

Professor Maltoni has many experiments in progress such as: to determine the effect in hamsters, mice, and Wistar strain rats; to determine in rats the effects of short-term, intermittent, high-intensity exposure; to determine in rats the effects on progeny of gravid females exposed to 6000 and 10,000 ppm; and to determine the effects upon different species at concentrations below 50 ppm. When the results of these studies are available we will have a much better understanding of the toxicology of vinyl chloride.

Also, in progress are the inhalation studies being conducted under the sponsorship of the MCA. Rats, hamsters, and mice are being exposed 7 hours/day, 5 days/week to concentrations of 50, 200, or 2500 ppm of VCM. After 11 months, mortality was related to dosage but more pronounced in the mice than in the rats and more pronounced in the rats than in the hamsters. In mice and rats, angiosarcomas of the liver have been observed at the low dose level (50 ppm) and at the higher levels but in hamsters they have been observed only in those exposed at the highest concentration (2500 ppm). Tumors of the lungs, skin, and kidneys have also been observed far more frequently in the mice than in the other species.

In view of the information available on VCM and the realization that pregnant women might encounter it, our laboratory undertook a teratology study on rats, rabbits, and mice(CF-1). All test animals were exposed to 500 ppm, 7 hours each day during the period of organogenesis; days 6-15 for the rats and mice and days 6-18 for the rabbits. Although the study is not quite complete, the data so far available indicate that VCM under the conditions of the study is not a teratogen. It is worthy of note that the exposure did cause appreciable maternal toxicity in the mice but not in the rats or rabbits, again emphasizing the greater susceptibility of mice to VCM. Additional teratological studies are planned in which mice will be exposed to a lower concentration and the rats and rabbits to a higher concentration.

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From a toxicological viewpoint, we also need to consider the ingestion of vinyl chloride that may possibly result from migration from packaging films into food or drink. So far the only oral toxicity study completed was conducted by Central Institute for Nutrition and Food Research (C.I.V.O.) It involved administering the vinyl chloride as a soybean oil solution to rats by gavage once a day, 6 days/week for thirteen weeks. The dosage levels were 0, 30, 100, and 300 mg VCM/kg of body weight. No adverse effects were noted in those animals that received 30 mg/kg/day. Some minor deviations from normal were noted in a few of the many parameters studied at the 100 and 300 mg/kg/day levels but these were neither statistically significant nor dose-related. Studies are being made to determine the feasibility of incorporating vinyl chloride into water or food preparatory to conducting a lifetime study on rodents.

When the data from Professor Maltoni's laboratory became available it was plotted and a projection of the dose-response line suggested that a significantly larger number of cases of cancer should have been observed in Professor Maltoni's rats exposed to 50 ppm than were observed.

One explanation of this would be that a metabolic threshold was being exceeded at the higher exposure levels and therefore the incidence of cancer at the higher levels was

insensitive to concentrations within some range. Therefore, we felt it was necessary to investigate this possibility through studies of the metabolic pathway(s) and of the pharmacokinetics of metabolism. Our studies are still in progress. I will try to summarize for you the most pertinent of our findings to date in the hopes that someone may have an idea that will help us.

- 1) For rats exposed to 50 to 105 ppm of VCM, the half life was 86 minutes.
- 2) For rats exposed to 220 to 1167 ppm of VCM the half-life was 261 minutes.
- 3) The metabolism of VCM by rats was markedly inhibited by pretreatment with ethanol alone or with pyrazole, an inhibitor of alcohol dehydrogenase, xanthine oxidase and other enzymes, when exposure was to low concentrations of VCM (50-100 ppm). At higher concentrations (200-1000 ppm) metabolic inhibition was markedly reduced but not eliminated suggesting that other pathways were being used.
- 4) Pretreatment of rats with SKF-525-A, an inhibitor of certain microsomal oxidases resulted in no inhibition of metabolism when concentrations were low (65 ppm) and only slight inhibition (18.8%) when at a higher concentration (1038 ppm)

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- 5) Exposure to VCM lowers the nonprotein sulfhydryl content of the liver but has no effect on protein bound sulfhydryl. When exposures to VCM are repeated, the nonprotein sulfhydryl contents of the liver tends to increase toward normal suggesting some sort of compensating mechanism.

These preliminary data suggest that the material may be metabolized via different pathways depending upon the magnitude of exposure. The possibility that the ultimate carcinogen may be a metabolite formed by a secondary or even a tertiary pathway when the primary pathway is swamped is speculative, but should not be disregarded without testing. Similarly, the possibility that the material per se or a primary metabolite is directly responsible for the carcinogenic action also needs to be determined.

It also seems absolutely necessary to us to determine which animal species is most like man in its metabolism of VCM so that that animal species can be used in future toxicological work with VCM. At present we do not know how much significance to attach to the dose-response data being derived from the various species being tested.

Answers to these questions are urgently needed. We urge that others also put their shoulders to this wheel as rapidly as possible.

Questions have been asked about the possibility of absorption of VCM through the skin from exposure of the body to the vapors in air. Our laboratory addressed this problem by exposing the whole bodies of monkeys, excluding the head, to concentrations of approximately 7000 and 800 ppm of radio-labeled VCM in air. Care was taken to prevent any inhalation. The results clearly indicate that a trace of absorption can occur but it is of no practical significance. For example, the amount absorbed as a result of a 2-hour exposure to 7000 ppm was calculated to be equivalent to a man breathing 0.186 ppm of VCM for 8 hours.

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Now I would like to turn to the results of the studies our Medical Department has conducted on persons who have worked with vinyl chloride together with low concentrations of vinylidene chloride in the Midland, Michigan USA location over many years. I have already mentioned the study of Kramer and Mutchler published in 1972 and dealt with data obtained up to 1967. To reiterate, they found evidence to "suggest that repeated exposure to vinyl chloride at time-weighted average levels of 300 ppm or above for a working lifetime together with very low levels of vinylidene chloride may result in slight changes in certain physiological and clinical laboratory parameters. The possibility of some impairments in liver function tests must be considered, even though no overt clinical disease was evident in any of the individuals studied."

As a followup of this surveillance program, the data obtained since 1967 and up to March of 1974 on 335 employees who had worked with vinyl chloride has been analyzed using the same basic criteria but with some additions and deletions in parameters measured.

The study has revealed that those who were exposed to greater than 200 ppm for at least one month sometime during their work experience exhibited a decreased diastolic

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blood pressure, whereas those who had not had any exposure above 200 ppm exhibited nothing of statistical significance.

The Dow Midland Division Medical Department has also examined the long-term mortality experience of 594 employees to vinyl chloride in a controlled industrial environment between the years of 1942 and 1960. Data on those workers exposed to VCM levels greater than 200 ppm time-weighted average suggest an apparent increase in overall malignancy rate. A decreased rate of malignancy was observed among those whose exposure was below 200 ppm time-weighted average when compared to a control population. No angiosarcomas or other hepatomas of the liver were found at any level. A paper describing this work in detail is in press and publication is imminent.

Since the discovery of angiosarcomas of the liver in employees at the B. F. Goodrich PVC plant in Louisville there has been an intensive search for additional cases of this rare disease among workers with a history of working with VCM or PVC. Numerous articles have appeared in the medical literature describing cases and more can be expected, I believe, because we are now seeing the consequences of gross overexposure 15-20-30 years ago. It appears that almost all of these cases, if not all, can be associated with some period in their working life when they were grossly overexposed.

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Although the numbers of persons in the studies of Dow employees is relatively small they nevertheless seem to support a dose-response relationship. We can only conclude that the absence of hepatic tumors and angiosarcomas of the liver among the Dow workers as revealed by our mortality study must be associated with the overall relatively low exposure levels our employees have experienced over the years.

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III. HEALTH STANDARDS

In the beginning of its commercial existence, vinyl chloride was considered to be virtually harmless and the only apparent dangers were explosion (at around 36,000 ppm) and narcosis. Consequently producers paid little attention to workplace exposure levels so long as they were safely below the point of fire and explosion. Although the TWA* for vinyl chloride was 500 ppm, it is generally agreed that in this early period and into the 1950's, exposures of several thousand parts per million were common. Based primarily on the work of Torkelson, Oyen, and Rowe, Dow set its own TWA guidelines for worker exposure at 50 ppm in 1961.

In 1963, the American Conference of Governmental Industrial Hygienists (ACGIH) revised its value from a 500 ppm TLV** to a 500 ppm ceiling. Dow published findings that suggested that repeated exposure of vinyl chloride to workers at TWA levels of 300 ppm or above for a working lifetime may result in slight changes in certain physiological and clinical laboratory parameters. Primarily as a result of this study, the TLV of vinyl chloride was reduced to 200 ppm in 1971. However, the Occupational Safety and Health Administration (OSHA) when formed in 1970 accepted the 1963 ACGIH ceiling value of 500 ppm and this OSHA standard remained in effect until April 5, 1974, when it adopted an emergency temporary standard of 50 ppm maximum exposure following the reported cases of angiosarcoma of the liver observed at a B. F. Goodrich plant. On October 4, 1974, OSHA issued a permanent standard which will require that no employee may be exposed to vinyl chloride at concentrations greater than 1 ppm averaged over any 8-hour period and no employee may be exposed to vinyl chloride at concentrations greater than 5 ppm averaged over any 15-minute period. The

*(TWA) Time Weighted Average

** (TLV) Threshold Limit Value set by the ACGIH

standard also requires monitoring, training, medical surveillance, record keeping, and other requirements. Although the standard becomes effective on January 1, 1975, employees may decline the use of respirators where exposures are not in excess of a 25 ppm ceiling until January 1, 1976. The major thrust of the standard is to reduce employee exposures to below the permissible limits by engineering controls and work practices. Respirators should only be used where permissible levels cannot be achieved by engineering controls and work practices.

Fortunately Dow has been the leader in the chemical industry in reducing its workplace levels of vinyl chloride and I would now like to discuss our experience with you.

IV. ENGINEERING CONTROLS AND MANUFACTURING PRACTICES

Dow Chemical's experience in producing vinyl chloride monomer goes back to 1939 when we began the production of this monomer on a very modest scale in Midland, Michigan. Production throughout the war period remained relatively small. Our oldest currently operating vinyl chloride (VC) plant is located in Freeport, Texas, where commercial scale production was begun in 1948. Over the years, through what we have called incremental expansions, production capabilities have increased in this plant by some 400%. In this slide you will notice that there is little separation of equipment and the close proximity of the control room to the processing area. The control room is located at the middle left of the picture. In this photograph you can get some idea of the size of the plant by noting the size of the cars in the picture. In contrast to this plant, next I would like to show you a photograph of our newest plant located in Oyster Creek, Texas, and which was started in 1969. The most recent plant layout criterion was used at this plant

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and, as you can observe, congestion is minimal. Here the control room is located at an increased distance from the process area. If we were to design another vinyl chloride plant today, even more thought would be given to plant layout and design.

In earlier years, more concern had been for the hazards of fire and explosion of VC. These hazards were the main cause of greater separation of equipment as shown in the slide.

Typical of this concern is illustrated by the flammable gas detector alarms which are strategically placed in the plants to alert personnel in the event of a major leak or spill.

Another thing you may have noted is this trend in recent years towards large single "train" units rather than several smaller "trains." These large single "train" units are advantageous because of improved economics due to such factors as reduction in cost of manufacturing as a result of decreased maintenance costs, improved manpower utilization, and improved raw material yields. There are also advantages in their use from the health standpoint because the use of the fewer pieces of equipment considerably reduces emission losses.

In addition to the trend toward larger single "train" reactors, other engineering controls and techniques have been employed through the years to reduce vinyl chloride emissions. Let us consider for example vinyl chloride recovery. In the thermal dehydrochlorination of ethylene dichloride, the cracking furnaces operate with an outlet pressure range of 20 to 400 psi gauge. The lower pressures are usually used in the older plants and in plants that removed the byproduct hydrogen chloride by absorption. The gases must then be compressed for purification. These types of systems are no longer being built in the more

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industrial-developed countries because of the expense of operation. Reciprocating compressors without packing purges were used initially, but these were changed to compressors with packing purges and are still being used in our oldest plant.

Centrifugal compressors are being utilized in our second generation plants and one of these compressors can replace a number of reciprocating compressors. In addition, potential leaks are reduced manyfold using centrifugal compressors in place of the reciprocating type. Of course, elimination of the compression step is the best solution to this problem and this has been accomplished in our most recent plant.

As I have indicated new plant design and construction has the potential for significantly reducing vinyl chloride exposures in the workplace through such things as plant layout and elimination of equipment. However, from the pictures you have seen that the plants are large and complex with many valves, pumps, and flanges. Consequently, the complete elimination of leaks even in a new plant is not foreseeable. Therefore, I would like to emphasize that to minimize these emissions through engineering controls, workplace practices, and maintenance it is essential to identify these problems through workplace monitoring on a continuous and routine basis. This can be accomplished by analyzing grab samples of air from various locations, by using personnel monitoring techniques based on carbon absorption, and by area monitoring. Using these techniques, problem areas were identified and corrected using various engineering controls and work practice methods. To illustrate what can be done I will now describe several of the problem areas identified and the corrective measures undertaken.

One area of personnel exposure has been in the loading of tank cars. It has been industrial practice for many years to gauge tank car innage on pressure cars using vented slip tubes as shown here. The level of liquid in the tank car is determined by observing for liquid or gas flow from the pipe shown. Even though the 8-hour time weighted average (TWA) is below 50 ppm as determined by personnel monitoring, steps have been taken to completely eliminate this emission by the installation of magnetic gauge devices into the tank cars. Disconnecting loading and vent lines from tank cars was another exposure problem. The exposure potential has been lessened in this case through purging the liquid and vapor lines into the tank car with nitrogen.

Using personnel monitoring as our guide, in-plant sampling problem areas were also brought to our attention. Process and quality control samples are a must in the vast majority of chemical production plants. On-stream analyzers are the preferred method if at all possible. However, in some analysis on-stream analytical technology has not been developed.

The next slide shows how quality control samples used to be obtained, and compares this with the presently used closed-loop sampling system developed to replace potential personnel exposure. Personnel monitoring has verified that this new system eliminates a considerable potential of worker exposure.

Breaking into equipment has also been shown to be a source of vinyl emissions. Consequently, header systems such as this pump drain line, reboiler drain line, and vapor recovery units have been installed to return vinyl chloride containing streams to process when maintenance work must be performed. At present only that equipment requiring frequent maintenance is so headered, such as pumps, reboilers, and filters. In addition, operating procedures have been changed to require purging of liquid through lines using nitrogen prior to maintenance.

As you have seen, engineering controls and workplace practices can reduce the potential exposures of our employees working in monomer production, but again I should like to emphasize that a monitoring system is essential to locate the problem areas.

In the polymerization area, many of the work practice and engineering controls previously discussed can be employed.

Our most recent polymerization plant in Midland, Michigan, was constructed with separation and protection of the major processing phases in mind to minimize potential capital loss. The separation, however, also tends to reduce the potential personnel exposure. Compare this most recent installation with our original plant. You will note the original plant was completely inside the building, while the newest plant utilizes more open construction even though it is built in a cold northern climate.

The new polymerization areas are highly automated using sophisticated computer equipment. The areas were designed and constructed to include: no processing system open to the atmosphere; minimum monomer storage in the polymerization area; minimum number of monomer transfers; no routine opening of monomer lines; larger capacity equipment and a minimum number of vessel openings and entries. In this polymerization plant extensive in-line or on-stream instrumentation is used to minimize the need for taking process samples containing vinyl chloride. As in the monomer area, where samples are required, a closed loop sample system is used.

At the present time even with the best designed system it is occasionally necessary to open lines and equipment which have been in vinyl chloride service. In these cases piping provisions

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have been made to allow draining the monomer, flushing with a non-hazardous material, and purging with an inert gas before opening to the atmosphere. Also in our polymerization plants, just as in our monomer plants, lower explosive limit alarms and area air monitoring probes are strategically located throughout the plant to detect major spills and even minor leaks should they occur.

Through the use of these engineering controls and work practice methods, we have come a long way in reducing VC exposure to employees, and as technology improves we will further reduce these potential sources of exposure. However, from a practical standpoint, the technology does not yet exist to eliminate all sources of emission in these large complex plants. In these and emergency situations, the use of respiratory protection is required and I will now briefly discuss the various types of respirators that can be used.

V. RESPIRATORY EQUIPMENT

As mentioned, respiratory equipment is required for certain routine operations as well as for maintenance and emergency operations. Several types of respiratory equipment have been used in the past. The most convenient and portable pieces of respiratory equipment are the cartridge and canister types as shown in the next slide. This respirator, the nose-mouth cartridge type, is easy to don, but does interfere with certain types of eye protection such as chemical goggles. Its small size and light weight make it ideal to carry at all times for escape should an emergency arise. As shown, the canister for this small respirator gave adequate protection in 1000 ppm vinyl chloride for up to 15 minutes.

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Next, we have the full-face canister type respirator. The improvement that we have here over the nose-mouth type is that the larger canister provides longer protection, up to 22 minutes, and eye protection is an integral part of the mask. However, wearing of a hard hat becomes more difficult with this type of mask.

The full face canister type with a chest mounted canister offers still longer protection, up to 167 minutes for similar conditions.

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Where mobility is not a factor, air supplied respirators are preferred; however, they are required when high concentrations of vinyl chloride may be encountered. A number of different types of air-supplied respirators are available. In this particular type respirator we have the continuous flow air supply as shown in the next slide. In the past we have called it an acid hood and it offers very good head protection against spills. This unit has major disadvantages such as bulkiness, vision restriction, and lack of movement of the head. The continuous flow air supplied half mask shown next offers some good advantages, but again interferes with full eye protection.

The continuous air flow full face mask shown on the next slide is probably the best of the air supplied breathing apparatus. With all these three types, continuous air flow respiratory mask, mobility becomes difficult because of the length of the air hose that must be trailed. However, for specific jobs where mobility is not a problem, such as single tank car loading, this does not pose a great problem.

Where mobility is a necessity, such as in an outdoor vinyl chloride monomer plant, the self-contained breathing apparatus has been used. The major disadvantage of this apparatus shown

on the next slide is that the air supply is limited. In the pressure demand mode, these units are nominally rated for 15 and 30 minutes. Actually, however, we have found that with activity of the wearer, these times are more like 10 and 20 minutes. For specific jobs such as breaking or entering on maintenance jobs, portable breathing air cylinders as shown in the next slide can be used to provide longer respiratory protection. One of these cylinders will provide approximately 2 hours of air when the demand is at 53 liters/minute.

VI. MONITORING

Continuous area monitoring and personnel monitoring are essential tools for controlling the environment in vinyl chloride monomer and polymer plants.

Four analytical techniques are available for the continuous area monitoring of air for the presence of vinyl chloride. These are combustion conductivity, gas chromatography, infrared spectrometry, and flame ionization spectrometry. Gas chromatography is very specific and requires above 10 minutes per sample. Flame ionization detectors have no specificity, responding to all carbon-hydrogen bonds but are portable and the measurements are instantaneous. The combustion conductivity method responds to any material which burns to produce ions. It responds rapidly. Infrared analyzers are very specific, respond quickly and are portable. All of these techniques have adequate sensitivity detecting concentrations of 1 ppm.

Continuous area monitoring systems with probes judiciously located throughout the plant can give three types of information. It can provide information as to the vinyl chloride concentration at specific locations and at specific points in time. After some finite interval, sufficient data will be generated to permit a concentration profile to be calculated for each specific location. If the monitoring system is adequate in scope, a plant-wide average concentration profile can be calculated.

Secondly, a continuous area monitoring system can provide a history of employee exposure. If an employee spent his work day only in the areas monitored and divided his time equally among these locations, the plant-wide average concentration would be equivalent to the employee's exposure.

A third and perhaps the most valuable of the continuous monitoring systems is that it provides the capability of early detection of leaks of vinyl chloride into the atmosphere. The flammability of vinyl chloride is recognized throughout the industry and plant facilities are usually well monitored with flammable gas detectors. However, these detectors would normally alarm only when vinyl chloride levels reached approximately 4000 ppm. However, if the continuous monitoring system is broad enough in scope and the sampling locations are judiciously selected and warning alarms are used, the probability of leak detection before employee exposure occurs is high.

The use of personnel monitors is the second element of a comprehensive vinyl chloride surveillance program. Personnel monitoring is achieved through the use of absorption tubes filled with activated carbon. If the sampling device and analytical workup are properly designed, samples collected on the employee's person will document his time weighted average exposure for the duration of the sampling period.

One obvious shortcoming of this approach is that the level of an employee's exposure is known only after the fact. Secondly, this technique, as stated earlier, produces a time weighted average exposure value and, therefore, gives no indication of the maximum or minimum concentrations in the employee's work area. Finally personnel monitoring systems available today do not provide on-the-spot data and, therefore, offer no warning when an employee is in an area where concentrations are

above permissible levels. However, in addition to providing documentation of the average exposure throughout the work day, personnel monitors do provide a tool for evaluation of work practices and engineering controls. When time weighted average exposure values approach the levels allowed by standards, the industrial hygienist will perform an in-depth study to determine whether or not specific job steps might account for the bulk of the employees time weighted average exposure. After identifying sources of exposure, either something that is employee controllable or something that is inherent in plant design, changes can be instituted. Follow-up personnel monitoring will provide data for evaluation of the effectiveness of the change.

VII. CONCLUSIONS

In conclusion, we believe the operation of a safe plant involving the handling of toxic, hazardous materials revolves around:

1. Establishment of safe, practical allowable environmental levels.
2. Implementing appropriate engineering and operating procedures to achieve or better these levels.
3. Providing analytical monitoring capability to insure the environment is maintained below the established levels and to detect excursions above such levels.
4. Initiating appropriate corrective action when breakdowns occur and environmental levels are exceeded.
5. Developing and supporting an appropriate medical surveillance program.

Dow has a safety philosophy that the safety of our employees, our customers and our neighbors is of prime and utmost importance. This safety philosophy permeates our operations.

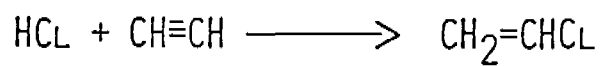
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Careful application of these principles has led essentially to the attainment of TWA values with few exceptions of less than 5 ppm with occasional brief malfunctions and other temporary situations resulting in short-term concentrations in excess of 10 ppm. Based on the data we have, we believe our plants producing vinyl chloride and its copolymers are being operated in an appropriate manner.

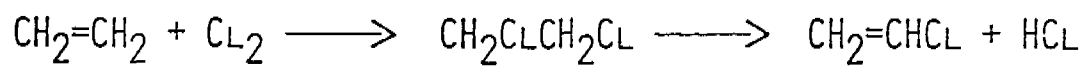
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MANY ROUTES TO VINYL CHLORIDE

ACETYLENE



ETHYLENE



PVC RESIN TYPE

<u>TYPE</u>	<u>AMOUNT (#)</u>	<u>%</u>
SUSPENSION	3.5 M	78
EMULSION	.6 M	13
BULK	.3 M	6
SOLUTION	.1 M	

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END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>BUILDING AND CONSTRUCTION</u>		
PIPE, CONDUIT AND FITTINGS	29	1,345
FLOORING	9	440
WIRE AND CABLE INSULATION*	8	365
SIDING, PANELS	2	90
WALL COVERING	2	90
OTHER (WINDOW FRAMES, TRIM, GASKETING, SEALANTS, MISC.	<u>2</u>	<u>90</u>
	52	2,420

*INCLUDES SOME WIRE AND CABLE USED IN
COMMUNICATIONS EQUIPMENT.

R&S 136484

END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>HOME FURNISHINGS AND HOUSEHOLD GOODS</u>		
FURNITURE (MAINLY UPHOLSTERY)	7	320
SHOWER CURTAINS, TABLE COVERS, ETC.	2	105
APPLIANCE PARTS (INCLUDING HOSES, GASKETS)	1	40
GARDEN HOSE	1	35
OTHER (E.G., WINDOW SHADES)	<u>1</u>	<u>45</u>
	12	545

END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>CONSUMER GOODS</u>		
PHONOGRAPH RECORDS	3	145
FOOTWEAR (SHOES, RAINWEAR)	3	140
TOYS, DOLLS, AND GAMES	2	75
OUTERWEAR (E.G., APPAREL	2	70
SPORTING AND ATHLETIC GOODS		
(E.G., BALLS, BICYCLE GRIPS, MISC.	1	65
OTHER (INCLUDING HANDBAGS, WALLETS,		
LUGGAGE)	<u>1</u>	<u>55</u>
	12	550

END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>TRANSPORTATION EQUIPMENT</u>		
(MAINLY MOTOR VEHICLES)		
UPHOLSTERY AND SEAT COVERS	4	180
WIRE AND CABLE INSULATION	1	50
AUTO TOPS, HEADLINERS, TRIM,		
FLOOR MATS, OTHER	1	<u>45</u>
	6	275

END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>PACKAGING</u>		
FLEXIBLE FILM (FOR FRESH MEATS AND PRODUCE)	3	135
RIGID SHEET (FOR COOKIES AND CANDY, UNIT PACKS, BLISTER PACKS)	2	105
COATINGS (E.G., CAN LININGS, CAP LINERS, GASKETS)	1	50
BOTTLES, OTHER	2	<u>85</u>
	8	375

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END USE BREAKDOWN OF PVC RESIN
1973

	<u>% OF MARKET</u>	<u>MILLION LBS</u>
<u>ALL OTHER USES</u>		
MEDICAL PRODUCTS (E.G., TUBING, BLOOD BAGS)	1	45
STATIONERY SUPPLIES	1	35
AGRICULTURAL PRODUCTS (E.G., RESERVOIR LINERS, TUBING)	1	30
NOVELTIES (INCLUDING ADVERTISE- MENT ITEMS)	1	30
CONVEYOR BELTING	1	30
MISCELLANEOUS (TOOLS AND HARDWARE, CREDIT CARDS, BOOK BINDERS AND COVERS, OTHER)	4	<u>265</u>
	9	435
GRAND TOTAL	99	4,600*

*DOMESTIC USE ONLY; EXCLUDES EXPORTS OF ABOUT 145 MILLION LBS.

HEALTH STANDARDS

<u>YEAR</u>	<u>TYPE</u>	<u>STANDARD</u>
1950's	ACGIH	500 PPM TWA
1961	Dow	50 PPM TWA
1963	ACGIH	500 CEILING
1970	OSHA	500 CEILING
1971	ACGIH	200 TWA
1974 (4-5-74)	OSHA	50 CEILING
1975 (1-1-75)	OSHA	1 PPM TWA 5 PPM CEILING, 15 MIN.

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