

SYMPOSIUM PROCEEDINGS

Control Technology in the Plastics and Resins Industry

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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CONTROL TECHNOLOGY IN THE PLASTICS AND RESINS INDUSTRY

Held at the Atlanta Hilton Hotel Atlanta, Georgia

February 27-28, 1979

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Cincinnati, Ohio 45226

January 1981

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DHHS (NIOSH) Publication No. 81-107

PREFACE

NIOSH is concerned with prevention of occupational hazards through the application of control technology as a logical sequence to the traditional Institute activities of hazard recognition and evaluation. The study of control technology in the plastics and resins industry was part of this effort and it has in addition, special significance as a model being the first of such studies to be published. NIOSH is naturally concerned that best use be made of the projected studies in control technology.

NIOSH's present position is that the published report on the plastics and resins industry entitled, "Engineering Control Technology Assessment for the Plastics and Resins Industry" (NIOSH Report 78-159), is a starting point and that attention during this symposium should not be focused on this report but on the objectives of generating new information and stimulating the exchange of information. A properly structured national symposium backed by active participation, especially in interaction of those present of the core group of uniquely qualified experts, can be an effective means to reach these objectives.

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ACKNOWLEDGEMENTS

The success of the conference is due to the support given by industry, particularly Mr. Jerry Schroy of Monsanto and Mr. Nicholas Wheeler of Union Carbide who provided ideas and advice on the agenda.

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SESSION I:

OPENING REMARKS AND
PRESENTATION OF THE NIOSH CONTROL TECHNOLOGY
ASSESSMENT OF THE PLASTICS AND RESINS INDUSTRY

SESSION MODERATOR:

WALTER HAAG

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH CINCINNATI, OHIO

WELCOME TO THE SYMPOSIUM

Walter Haag National Institute for Occupational Safety and Health Cincinnati, Ohio

Good Morning. I am Walter Haag, Director of the Division of Physical Sciences and Engineering at the National Institute for Occupational Safety and Health. I would like to welcome you to the NIOSH-sponsored symposium on control technology in the plastics and resins industry.

To begin this morning, I would like to emphasize three underlying themes to keep in mind for the symposium over the next two days.

Perhaps the most basic theme of this symposium is simply that of change due to new technology and evolving national needs and priorities. Such change is not new, nor is the foreboding which accompanies it. The industrial revolution, for example, caused substantial trepidation and polarization as it effected a transformation of society in the 1800's. Viewed from one perspective, a large loss of traditional jobs seemed imminent. Viewed from another perspective, new and better job opportunities loomed on the horizon. Which viewpoint proved to be correct? In some respects, both did. However, on the balance, the lens of history permits us in 1979 to appreciate the enormous positive impact which the industrial revolution has had on quality of life through increased productivity and applied technology.

A more recent example involves the advancing computer age of the late 1950's and early 1960's. Again, a polarization occurred--potential loss of jobs versus new opportunities. History records, that in this case as well, better jobs and an improved quality of life were the result.

No industry better exemplifies the rapid pace of technological change in post-World War II America than the plastics and synthetic resins industry. Virtually the entire industry has grown since the second World War. U.S. synthetic polymer production (excluding rubber) has gone from 54 million pounds in 1940--to 6.3 billion pounds in 1960--to 34 billion pounds in 1977. This industry has been a leader both in promoting and in permitting change through the development of innovative products and processes. The pace of technological change in society as a whole is now increasing at a dazzling rate, sparked in no small way by the polymers industry.

Today, as in the past, change is viewed by some as a danger or threat, and by others as an opportunity. In the face of increasing economic competition from overseas, it is clear that America has no tenable alternative but to forge ahead with technological changes which will permit our nation to remain strong, productive, and competitive in an increasingly competitive world market.

The second basic underlying theme of the symposium is an emphasis on prevention of problems through proper design. As new and more efficient technology is implemented, one constraint in the design of this new technology must be the prevention of negative side effects such as damage to occupational or environmental health. A nation is composed of people, and the implementation of a technology that has a debilitating effect on those people who work with it is indeed shortsighted.

During the course of this symposium, we will hear how innovative technology is being applied to the "problem" occupational health areas of conventional polymerization plants (such as reactor cleaning, monomer stripping, or maintenance procedures) in order to maximize process effectiveness and to avoid unacceptable hazardous exposures to workers. Our intention is that participation in the symposium should extend not just to the speakers, but to all other interested individuals who can contribute to a constructive exchange of information of these areas through floor discussions and a special open discussion session that is planned for this evening. Such a cross-fertilization of ideas can often lead to significant progress, and we hope that each participant here will return with new and innovative ideas for solving problems with which you are faced.

At least as important as the application of technology to solve problems in existing plants is the design of new plants with built-in, integrated control systems. We will also hear how new plants are being designed, with the latest technology harnessed both to maximize productivity and to control occupational hazards.

The third underlying theme for the symposium is that of cooperation. The government will not achieve a safe workplace merely by promulgating regulations. Employers, employees, and academia--none is in itself able to achieve a safe workplace. All must cooperate with one another. Management must be committed to preventing occupational illness as it performs its function of investing in growth and sustaining a profitable enterprise. Employees must exercise a greater degree of individual responsibility. The government must strive to be a stimulus rather than a burden and to be a critical element in maintaining a free democracy and in protecting the rights of its citizenry. Underlying all of these is academia's role in developing new knowledge and skilled manpower to implement it.

At the fall oversight hearings before the Subcommittee on Labor of the Senate Committee on Human Resources, Dr. Bruce Karrh, the medical director of the DuPont Company, urged a stronger emphasis on effective coordination between the government and the private sector. He indicated that "cooperation between employers, employees, and OSHA is the key to a successful attack on industrial injury and illness". Also, he indicated that the only way to affect all workplace injuries is through a program that begins with management commitment.

In summary, one of the most important investments in America's future is a cooperative effort among employers, employees, the government and academia to implement new and innovative technology which will both increase our effectiveness and protect our health.

* * *

MR. HAAG: Our first speaker this morning giving what we have titled the keynote address is Mr. Richard I. Bergman. Mr. Bergman is just finishing up an assignment as the Executive Director of the Interagency Task Force on Workplace Safety and Health. I think most of the audience is familiar with the establishment of that Task Force, which is an outgrowth of the August 1977 memo from President Carter directing the Secretary of Labor and the Director of the Office of Management and Budget, to study the use of various incentives to supplement the traditional roles of Government regulations. Also, the Task Force was charged with evaluating the effectiveness of the present regulation of workplace safety. Mr. Bergman, with his considerable background of involvement in the health and safety area was selected to this post. He has two Chemical Engineering degrees, having graduated from M.I.T. He worked for Princeton Chemical Research and Systemedics Inc. and has served as an adjunct Professor of Chemical Engineering; he holds a number of U.S. patents. He has authored several papers on chemical and biomedical engineering and medical information systems. He is listed in Who's Who in the East and is currently finishing up the work of the task force, which has essentially ceased to be a full-time effort, and has returned to his previous company, now a part of Equifax Inc. of Atlanta. We are indeed happy to have him share his insight in working with the White House and his role on the Interagency Task Force.

KEYNOTE ADDRESS

Mr. Richard I. Bergman
Interagency Task Force on Workplace Saftey and Health
Washington, D. C.

The topic of this symposium is of great personal interest to me, because during the 12 years that I was a practicing chemical engineer, I was involved in processes to develop vinyl chloride, maleic anhydrides, and other related monomers.

Over a year ago, President Carter established the Interagency Task Force on Workplace Safety and Health. In establishing the Task Force, President Carter said he wanted to be sure that Federal programs actually did improve the safety and health of American workers and helped employers make any necessary adjustment.

The President directed that the Task Force be chaired by the Secretary of Labor and the Director of the Office of Management and Budget (OMB), and that a number of other Federal agencies be members of the Task Force. These included the Department of Commmerce; the Department of Health, Education and Welfare, the White House Domestic Policy Staff; the Small Business Administration and the Council of Economic Advisers. The Task Force was staffed primarily by detailees from other agencies with a very small core staff. I took a leave of absence from my company to serve as Executive Director. The Task Force was brought into existance to do a job and then go out of business on March 31, 1979.

In looking at the Federal role in workplace safety and health, the President gave us three tasks. One was to look at the use of economic incentives to supplement direct regulation. Another, to look at ways of improving the overall administration of safety and health regulation; and the third task was to look at the Federal Government's own safety and health program for its employees. We developed a work plan which we distributed for public comment in January 1978. Our work plan included a large effort of going out and talking to concerned people in the field to find out what they thought the problems were and what should be done.

For example, we held regional meetings in five parts of the country; we published a notice in the Federal Register asking for people's ideas; we held meetings sponsored by various concerned organizations, such as the AFL-CIO, the National Safety Council, the Small Business people and the Business Round Table. We had personal or telephone contact with over 1000 people in the safety and health business. Our report containing first recommendations was distributed last April, and over 1500 people requested copies. Many of them then communicated with us. A draft of our final report, titled "Making Prevention Pay," was released in December 1978 for

public comment. The public comment period closed last week. (Over 3000 copies of the draft final report were mailed out.)

What I am here to talk about this morning is a portion of our report. Very much in keeping with the theme of the symposium, the report contains a chapter titled Cooperative Programs. The Task Force found that there are many causes of workplace injuries and illness. One cause is improper design of equipment; another cause is behavior, either on the part of management or of workers. We also found that usually safety on the job is tied into what the company makes and how it is handled. By and large, companies which are unsuccessful or poorly managed will not have good safety programs. We also found that safety and health on the job seems inextricably linked with the quality of labor management relations.

If you take any industry and any size class of firms within that industry, there typically is a factor of five to ten times the injury rate, between the best 25% of the firms and the next to worse 25 percent of the firms. This clearly suggested that some firms in every industry do a much better job than others. All those findings led us to conclude that the improvement of workplace safety and health cannot be solely the Federal Government job, since many factors are outside the control of the Federal Government by direct regulation. We looked at what type of cooperative programs could be initiated by government, industry and labor and I would like to focus this morning on three of those possible programs.

The first program, again very much in keeping with this symposium concerns diffusion of proven control technology. The second program involves improved research and development, and the third program addresses organization factors, specifically worker-mangement Safety Committees.

Consider first the diffusion of information on control technology. One of the things we found is that because not many companies have workplace safety and health as a product, the information that is available on control technology is often kept proprietary to an individual company or if not proprietary, no particular arrangements are made to get that information out to the industry. Basically, there is no incentive for many companies to do that. There are exceptions, of course; for example, we talked to some large chemical companies who have as part of their operating philosophy programs to keep their customers aware of safe handling of products they manufacture.

Another finding is that a great differential seems to exist in access to information on control technology between large and small companies. Small companies often do not have full-time safety professionals and very often the owner or proprietor is doing so many things at once that even when appropriate information is made available, he or she has difficulty assimilating it. The kind of safety standards which Government imposes, in fact, can be anti-competitive in themselves, because big companies can comply with them more readily than the small ones. It is a real problem.

Based on these findings, one of our conclusions was that one appropriate role of Government is to act together on an improved system to disseminate information on control technology to those firms who do not have their own resources to obtain it. We saw this as a cooperative venture between the Government and the private sector, with participation from both labor and management in a three-phase sequence.

The first sequence would be surveying what is now available in control technology. The second phase would be setting up the information retrieval mode, keeping it updated. The third phase would be to identify gaps in information. We also recommended that such a program be tested for about three years, and assuming it is successful, consider spinning it off solely to the private sector. I want to emphasize that this recommendation, and the others in our report are in the drafts for public comment. They are not formal recommendations to the President from the Labor department or OMB at this time. (As the disclaimer on our draft report says, the contents have not yet been approved by any Government agency.)

There is resistance to an idea like our draft recommendation on control technology. There are many people who feel that Government can't disseminate information of this type economically. But like most things, we found examples where the Government has done very well indisseminating information and where it has done very poorly. We believe that as a proposed program a cooperative venture with the private sector will help its effectiveness.

The second program I want to talk about with you today is R&D. It is to improve workplace safety and health. The problem is that large companies are very active in R&D, many smaller companies do not have the potential for doing it. The capacity for creative innovation is really very disparate. One option which is open is for smaller companies to form consortia to do the R&D. It is generally thought that consortia type activities run afoul of anti-trust regulation and in fact, companies told us they had been advised against going into consortia for R&D and control technology information dissemination.

As part of our workplan, the task force developed guidelines for joint R&D. These have been received by the Anti-Trust Division of the Justice Department and are as follows:

Guidelines

1. Participants.

Joint research ventures among firms in noncompeting industries will create far less antitrust concern than ventures among direct competitors. Similarly, a venture whose participants are smaller competitors will have fewer anticompetitive effects than a joint project among the larger, dominant firms in an industry. Industry-wide joint ventures that effectively eliminate all competition in research within their scope should be avoided.

2. Scope and Duration.

The narrower the scope of, and the shorter the time allotted for, the joint research, the less anticompetitive effect will be created. More specifically, a venture that is limited to basic research raises fewer antitrust problems than a joint attempt to develop new commercial processes or products.

3. Ability of Participants to Conduct Similar Research Individually.

If participants can show that the cost and risks of the research are so great that they would not have undertaken the project individually, then the venture may have the effect of increasing rather than decreasing competition. In this situation, there is likely to be no antitrust objection to the formation of the venture, especially if it is limited in scope and duration and there is continuing competition in research and development from nonparticipants.

4. Access by Nonparticipants to Benefits of the Joint Venture.

The results of a joint research project may give the participants a major advantage over nonparticipating competitors. Where research and development efforts cannot be undertaken except through a joint venture involving major competitors, then, in order to avoid antitrust problems arising from this competitive advantage, participation in a joint venture should be open to all firms in an industry, or the results of the project should be available to competitors on reasonable and non-discriminatory terms.

5. <u>Collateral Restraints</u>.

A joint venture that is otherwise legal may nevertheless violate the antitrust laws if it imposes unreasonable collateral restrictions on the participants. For example, restrictions on the participants' right to use patents or information developed by the joint venture may raise antitrust problems. Similarly, an agreement by the participants not to engage in independent research, or not to use technology developed by others outside the venture unless the technology is available to all participants, tends to restrain competition in research and development and therefore raises serious antitrust concerns.

6. Exchanges of Information.

Sharing of confidential information about costs, productivity, prices, and similar matters among participants to a joint venture could lead to the reduction or elimination of competition among them. To minimize antitrust concerns, a joint venture should avoid such exchanges. If such information is necessary for the research project, an independent entity could be used to collect the data so that information exchange among competitors can be avoided.

7. Review of Proposals by Antitrust Agencies.

The plans for a proposed research and development joint venture may be submitted to the Antitrust Division of the Department of Justice or to the Federal Trade Commission under their respective Business Review Procedures for a determination of this enforcement intention under the antitrust laws with respect to the proposed venture. These statements are, of course, not binding on the agencies, but should provide an indication of any antitrust problems raised by your proposal. Naturally, before such a statement is to be of any use, all pertinent information concerning the venture must have been submitted to the reviewing agency and the actual operation of the venture must be consistent with the plans originally submitted.

We found that there is a mechanism available for companies to group together to do R&D to improve workplace safety and health even when individual companies might not be able to fund by themselves. The study paper discusses our findings in more detail.

The third program involves joint labor-management safety committees, an organizational change which could be funded in part by government. In those companies that have unions, there has been a dramatic increase in the last five years in the number of contracts which contain provisions for worker-management safety committees. There are two basic types of committees, one at the plant level, and another at the industry level. An example of the latter is the Advent Labor Management committee of the food industry. One could well imagine that the agenda of such joint labor-management committees would include items on improving control technology. (I might mention that NIOSH has funded one of the excellent reviewer studies in this area.) It has been suggested that such joint safety committees be made mandatory as is done in other countries.

The Task Force looked at this option and concluded that joint committees work best where the circumstances and environment are already favorable for them to work. In those circumstances where the situation is not favorable, there is relatively little chance that they are going to work. Our draft recommendation was that committees be encouraged by Government in those industries and situations where it was most likely that they would succeed. In the case of the food industry, for example, aspects of Federal Government regulatory programs coupled with the wage and price controls at the time were equally troublesome to labor and management and indeed, motivated them jointly to set up the committee and approach OSHA for changes together. The plant situations tend to vary as much as the individual companies and labor groups who participate in the committees, and there may not be any hard and fast rules generally applicable to all situations.

In regard to industry/government cooperative programs, I got a call from the Workplace Safety and Health Sub-Committee of the Labor Relations Committee of the Business Round Table, one of the groups we talked to

during the course of the fact finding activities. They said I could share with you today, that this subcommittee, has put together a group to develop proposals for sponsoring cooperative improvement programs. They are considering several options for inclusions in this type of activity. One program option is a system for diffusion of control technology information to smaller companies. I think that is a very positive step.

In addition to the cooperative programs I have discussed this morning the Task Force complete report had draft recommendations on the use of incentives, and on ways to improve the present regulatory process. In concluding sections we added some thoughts on how to take into account the cumulative impact of regulations on individual firms (i.e., environmental control and equal opportunity employment together with workplace safety and health). There are copies of this report available from the Task Force.

* * *

DISCUSSION:

DR. NARESH K. CHAWLA: What is your reaction to the proposal of different regulatory guidelines for small businesses and large businesses?

MR. RICHARD I. BERGMAN: In the last session of Congress, there was a bill introduced by Senator Culver to take into account differential regulatory impacts on small business. My personal feeling for safety and health granting that the process may be different for large and small businesses, is that one can't set different goals. To say that if someone works for a small business, that he or she can be exposed to a greater safety or health risk is unreasonable and also unfair. On the other hand, I think that small business may have more trouble in reaching those goals than larger businesses with more resources. In one part of our report, we made a draft recommendation for a specific type of assistance to small businesses to help them meet workplace safety and health goals.

MR. WALTER HAAG: We will move on to our next speaker, Dr. R. Hays Bell. He is currently the Director of the Directorate of Technical Support for OSHA. Dr. Bell has his Ph.D. in Chemistry from Ohio State University. He's worked for a number of years in the industry doing chemical research in the plastics and resins field. He is the holder of at least eleven patents in the industry. He has taken some advanced post-doctoral studies in toxicology, and then returned to the industry and worked as the head of a safety laboratory. He assumed his current role as the Director of the Directorate of Technical Support for OSHA almost a year ago in May of 1978.

Dr. Bell and myself and my staff have been trying to develop a more open dialogue within the Government sector with industry, and looking in a positive fashion to what we could do together. We are indeed happy to have Dr. Bell, who is familiar with their interest in control technology and its application, and other programs as well as economic assessment of the OSHA.

OSHA ROLE IN IMPLEMENTATION OF CONTROL TECHNOLOGY

R. Hays Bell Occupational Safety and Health Administration Washington, D.C.

This is a pleasure for me to represent OSHA at the Symposium on Control Technology in the Plastics and Resins Industry. I have been associated with this industry for a number of years before joining OSHA last May. As a Director of the Technical Support Directorate, I particularly liked the outline for the symposium, certainly the aspect of cooperation. Being the Director of a relatively new organization, I can use all the help I can get. Walter Haag supplied a lot of that in the past few months, and I hope that I can depend on him for that in the future.

Polymers have received little attention as a focal point of toxicological studies in the past. The monomer catalyst additives and the solvents have been the focal point and have been given considerable attention in the past. Macromolecules, because of their size, have been considered as biologically inactive, and therefore pose little danger to health. The hypothesis may be true, but there are no data to support it. We have seen the toxic effect of agents such as silica, cotton dust, and asbestos, just to name a few. For the most part, we simply do not have the answers, and will not have them for several years.

The smaller chemical molecules will continue to be the primary target of toxicological study. We should attempt to minimize exposure to them through toxicological study of exposure to catalysts, dusts, fumes, and fibers from the polymers as they are formed into products for sale to the consumer. Let me make one thing clear. In no way am I saying that polymers are going to be the cause of fibrotic lung disease or additional problems. We simply have very little data to support the hypothesis one way or the other. A lot of data are missing in the area as well as in many other areas of chemical exposure. I am a firm believer in the wonderful world of chemistry and the many wonderful things that chemistry can do. Man is exposed to many new chemicals each year, and for the most part, the exposure is not detrimental. Of particular concern is the severity of the problem with occupational disease and illness which is directly related to the work environment. Over the last decade, there has been an incredible increase in the availability of toxicity

information. The reasons for this are many and complex. They include increased investment by corporations and Government in toxicological studies, a greater public awareness of the environmental and occupational hazards, and more sophisticated analytical and statistical techniques for evaluating data. The threat of liability in third-party and worker suits certainly must be counted as positive here. We must also count the impetus from the control agencies. For all of these reasons, we have a virtual explosion of information which the Government must now learn how to handle. Only a few years ago, we were concerned with concentrations of acutely high level exposure hazards, where it did not demonstrate an acute effect. In the last decade, we have discovered long-term low-level exposure effects. The issue of carcinogens has done a lot to focus our attention. We are finding that the mistakes we made as long as 25 years ago are now just beginning to catch up with us, and to be evident. We do not know the total effect of the exposures we have experienced, and we won't know these at least until the year 2000, and maybe a little later.

I spoke earlier about possible disease from chronic exposure to polymer dust, fumes, and/or fibers. I did not do that to malign your industry, but to emphasize the point that we have few studies to substantiate or refute. We know little about your past exposures. Even if some polymer dusts and fibers cause chronic lung disease, this would not, most likely, be your major occupational exposure in the industry. It would be of concern to a relatively unique group of workers in a specialized industry who would handle the polymers and resins. Therefore, since we do have a work group for consideration, I would consider the topic worthy of study for the future. Until we know the answer of the toxicity of a given chemical, it is important to minimize exposure through control technology.

Basically, we have the monomers and we have employees synthesizing the monomers, and as we look back in the industry, your industry is a relatively new one, too, and in the field of chemistry the toxicity revolution has just occurred in perhaps the past decade. What I am trying to say, not to single out any particular phase or process of the plastics or resins industry, is that we know very little about toxicity information, even though we have volumes on it.

Now, for interpretation, especially in the area of chronic and sub-chronic exposure, it takes a long time before the results are known. For example, in the past year OSHA was involved in the discovery of 24 unknown occupational illnesses associated with the foaming agent used in production of polyurethane foam for car seats and other consumer products. This catalyst first came into commercial use approximately three years ago. It is relatively new. The catalyst is a product of a major U.S. chemical firm, and was produced under a controlled system at the plant so that the possiblity of human exposure was minimized. The company producing the catalyst did some routine toxicological tests, and the tests were primarily for determining acute hazards relating to the catalyst. They found no significant acute hazard, and the preliminary

toxicologic tests were done prior to selling the compound to the producer. The tests would not be considered adequate by today's standards, but at that time they failed to reveal the hazard that was later found in workers exposed to it. The manufacturer had received no report of ill health effects associated with the catalyst or the client either from their own workers or the people using the product in the usual fashion. In the past, the requirement had been such that the foam had been allowed to cure for a period of 24 hours. Production demands increased, and subsequently the curing time for the foam was drastically reduced to increase production. Workers that handled the foam, began to handle the foam in a less cured state. They found they had difficulty in urinating. There was a natural reluctance to talk about these symptoms with each other for a long time. When the workers went to their private doctors, their symptoms were diagnosed as prostate problems and bladder infections. After this, a number of affected workers did discuss their symptoms with each other, and realized a number of them were suffering from what appeared to be the same problem. The natural question arose, then, could that be associated with the job, exposure to something that they were all related to in terms of work. A complaint was made to the local authorities, and OSHA was called in to help out with the problem.

At two plants, the medical people investigating the problem compared a list of the products used, and each of these plants discovered that one of the products used in common was the polyurethane foam catalyst. When this was established, the product was immediately taken off the market and supplies nationwide were recalled, and a nationwide hazard alert was issued by OSHA to each of the customers involved, as well as all regional offices. Subsequently, a bulletin was released to notify the occupational health community. Most of the effect has diminished, and symptoms have gone away. At this point, no one knows if there will be a long-lasting effect. It was caught in time.

I have given you this case for several reasons. It shows the need for control technology in the production of a chemical through its use in processing a polymer. Secondly, it demonstrates that industry, OSHA and NIOSH can work closely together in solving a problem.

Thirdly, it demonstrates that some of the effects can be missed when put through a minimum toxicological screen. Further, it shows the necessity of better and quicker reaction on preliminary information than we had in the past, not only action but action in the proper and correct way.

This brings me to the Technical Support Directorate of OSHA. This is relatively new. The organization was founded in 1976, I became Director in May, and we are just now beginning to fill some of the key positions. The Directorate was created to provide the Agency with added expertise in scientific and technological areas. Our office includes the Office of Science and Technology Assessment. In the Office of Science and Technology, we have an engineering feasibility group, or the beginnings

of one. We are trying to put together a group of competent engineers, people with whom you can discuss situations and people who have a better understanding of what you're doing. I think it is essential to develop this line of cooperation.

We also have an industrial hygiene group which we are continuing to staff to a greater number than we have now. I hope that I can continue to hire, and will hire those people who can better understand industry problems and occupational problems. We have added a physician to that group in the past six months, his name is Dr. Victor Alexander. He has been a great help to us as well as all of OSHA, and he also advises the other Directorates in OSHA on the medical field. We have hired, in the past two weeks, a toxicologist, I think a very essential and capable person to a group of this type. We hope to continue to build this group to get it to a considerably larger number than we have now. We also have a health response team, which is located in Salt Lake City, Utah. The team consists of seven people. Most of the group have degrees in engineering as well as degrees in industrial hygiene, and can work very closely with our science and technology assessment group to lead the field in a more effective manner. We also have the Technical Data Center. This center provides expertise to our compliance officers within the Technical Data Center and to other Directorates and officers within the agency, and to our field compliance people.

The Technical Data Center also serves the area libraries throughout the United States. Again, the focal point is trying to get the cooperation and understanding to better solve the problem. We have the environmental impact group, a statistics group, and a maintenance and calibration laboratory in Cincinnati, Ohio. I think these groups are self-explanatory. As I mentioned earlier, we believe that one of the keys is the science and technology group. We have hired, and will continue to hire first-rate scientists, as needed. We will draw on consultants from Government and private industry and any other available source.

You people know, and will continue to know, more about solving the control technology problem. You're the experts in your industry. We will support a common-sense approach for aiding those workers in the plastics and resins industry. I will be glad to attempt to answer any questions you have.

* * *

DISCUSSION:

MR. ARTHUR SPIEGELMAN: I would like to get some idea of your control technology dissemination program, whether this group which is apparently acting as a consulting group for OSHA, will also become part of the enforcement group of OSHA at the same time they're doing this

consulting? It seems to me to present some problems for a consultant to talk about means of solving the problems and at the same time go out and policeman the problem. It is hard to be a priest and a policeman at the same time.

- DR. R. HAYS BELL: As you know, OSHA is mandated by law to carry out certain activities. It is very difficult to separate compliance functions from consulting functions. We, at this time, are primarily serving as consultants to our compliance people, and we rarely go into an industry on our own without compliance people involved. The exception to that would be for a variance investigation, and in this sense, I believe our people could serve not in a compliance mode. It is a difficult question. It is one I have answered as best I could. What we are trying to do is give as much advice as we can, and we must stay within the confines as mandated by law.
- MR. R. NICHOLAS WHEELER: It seems the very existence of your group at OSHA is going to be more specifications oriented than performance standards oriented. Would you comment?
- DR. BELL: Those decisions will lie directly with Dr. Bingham and the directors of the Health and Safety Standards group. I gave you my opinion, a opinion as a scientist. I am interested to hear that you are very much in favor of further specifications. Did I understand your question?
- MR. WHEELER: It boils down to the fact that the existence of your group may signal that OSHA is going to write specification oriented standards, or does this mean performance standards?
- DR. BELL: That is how I thought you would have asked the question. I think that we need to get the job done, as apparently you do. It will be done in the best manner that we can do and still leave room for improvement. Consequently, today this could change, of course it is focused toward getting the job done, and I have stated in my speech that I felt that you in the plastics and resins industry knew more about the processes than I did. I did work in the industry for some time, but even so, I consider you the experts and I consider us specialists in the engineering feasibility function of the science and technology assessment group. More in the line of consultants and more in the line of interpreting the regulations to get the job done. Have I answered your question?
 - MR. WHEELER: I think you avoided my question.
- DR. BELL: I prefaced the question by saying the answer to that would have to come from Assistant Secretary, as well as people who write the standards? Anyone else?

DR. KEN BRIDBORD: One of the things that Mr. Haag and myself have been doing, at least in a philosophical way, is to try to think of the concept of technology, not so much in terms of specifically how you do that job, but in terms of setting goals for the future that may be much more effective in reducing exposure. Part of that reflects on what Hays said. He doesn't have all the information he needs. Many of the standards on the books today are based on the information we have, and have little, if any, margin for safety, so this creates opportunities in terms of new technology, new processes, and replacement of existing equipment, and in the participation, in part, of some of these experiences as to what has happened on the environmental health side, where people have tried to force the technology and the new processes to do a much better job. I think one will find, perhaps, in the future years, the same thing will happen on the workplace side.

MR. RICHARD I. BERGMAN: There were a number of relevant recommendations in our report. One was more flexibility in the meeting of regulatory requirements. Another was changing the emphasis of the OSHA compliance effort, even to the extent that firms whose performance was above a certain performance level would not be inspected at all. A third was to test assigning individual high injury rate establishments to individual compliance officers, and evaluating the compliance officer in part by the performance in reducing injuries, not the number that he gave. While there are many considerations here, I personally have come to feel that the specification standards versus performance standards issue is actually a non-issue. If you inspect based on performance and firm injury rates are low enough it doesn't matter what they are doing to accomplish low rates even using a ouija board.

There is a great deal of thought being given to more flexible regulations, and escalating to where the Government is going to look at the cumulative impact of regulation in an integrative fashion. There are over 100 agencies that can put regulations in the Federal Register. There really is a lot of thinking going on about the flexibility issue.

MS. MARYELLEN SWEDENBORG: What is a flexible regulation? What does more flexible mean?

MR. BERGMAN: For example, we recommended more flexible abatement procedures. We recommended that OSHA begin to keep lists of acceptable abatement procedures, and have a hotline system to disseminate them. By the way, it is a lot easier to see how to do that in the workplace safety area than in the health area. For example in health the effects of chronic low-level exposure is a very complex issue, obviously. Again, I want to emphasize that the recommendations to which I refer are still just draft recommendations. There are a lot of things going on in the administration to make regulation more effective yet less burdensome. I have had an opportunity to see a number of public opinion polls, sponsored by industry and Government, they indicate the same thing, the public is very definitely in favor of the Government's role in protecting workplace safety and other "social" regulatory areas. The polls also

show, however, that there is a great deal of confusion about who should pay for that. There is also a popular perception that Government is not doing its job well enough. Trying to make regulation more effective yet less costly I have found is one of the excitements of working for the Federal Government on this project.

MR. LAWRENCE KELLER: You addressed the gap of information in toxicology. Is your group going to interface with the toxic substance people?

DR. BELL: Our group is interfacing with the toxic substance people in a couple of ways. For one thing, we have set up an IRLG, interfacing as a group, and we work very closely with the other agencies. Secondly, I have just taken on a known toxicologist form EPA who understands their processes and what is going on there, and am attempting to get, not only some additional toxicological help from OSHA, but to liaison better as to things that are going on in the interagency group.

MR. KELLER: One of my specific concerns is looking at the parts per million informational requirement as it applies to the plastics and resins industry. I wonder what might be the relevancy of a lot of that information that is requested. What I am really concerned about, is the allocation of resources and time. This is going to drain off a great deal of energy, compliance energy, and we are talking about putting in control technology before the concrete is poured. We don't have the information base yet to make wise decisions, I don't believe.

DR. BELL: In terms of compliance time, in a number of cases, we will be told of a problem and we will go into a given worksite with very little knowledge, other that there is a problem. We go there and use a hunt and peck system in attempting to identify a chemical, if that's what we're looking in terms of, and related chemical exposure. Certainly, it would be helpful if we could get the cooperation and the knowledge, of all the toxicity information on each and every chemical, as I indicated earlier. We are now being deluged with toxicity information, and certainly there will be a lot of information from the system I just discussed. I am under the impression that the more knowledge we have, the better we can carry out our jobs. I am talking as a scientist, and I think I just gave you a scientific approach to the problem solving. The law says we do have certain functions in OSHA. We are carrying out that function.

MR. HAAG: The remainder of this session includes a brief overview of the NIOSH Report (DHEW-NIOSH Publication #78-159) on the Control Technology Assessment for the Plastics and Resins Industry; its objectives, procedures and results. Participating in this session are three of the principals directly involved in the technology assessment. The first speaker, James A. Gideon, was the NIOSH Project Officer for the control technology assessment project. Jim has Bachelor's and Master's degrees in Chemical Engineering from V.P.I. He has, in addition, six years experience in the organic chemical industry. Jim will be discussing the background to the study, NIOSH's objectives, and other related matters dealing with the assessment.

NIOSH CONTROL TECHNOLOGY ASSESSMENT OF THE PLASTICS AND RESINS INDUSTRY:

BACKGROUND AND NIOSH OBJECTIVES

James A. Gideon
National Institute for Occupational Safety and Health
Cincinnati, Ohio

To begin, I would like to define the concept of control technology as it is being used by NIOSH. We have broadened the definition of the term to include many types of measures (such as engineering design and controls, work practices, protective equipment, monitoring devices, etc.) which may be used to prevent worker exposure to occupational health hazards. It is possible to consider a hypothetical occupational hazard as having a source of emission into the workplace, a means of transmission in and through the workplace, and a point of contact with the worker. This concept is shown in Figure 1. With this concept in mind, control measures can be divided into those which are applied to the source of emission, to the general workplace environment, or to the individual worker. Other control measures can be regarded as adjuncts or modifications to these three types of control. Table I shows a listing of control types broken down in this manner.

The objective of the NIOSH control technology program is to promote the application of effective control measures in order to prevent occupational illnesses and injuries. As Mr. Haag mentioned earlier, our intention is to work cooperatively both with industry, labor, and academia toward this end. The talent which exists in many major companies such as those represented here constitutes the greatest pool of technical resources available to solve occupational health problems. Even though this pool is responsible for many other important tasks (such as producing a product within specifications while maintaining a profitable market position), occupational health problems depend on the technical community which is represented by the group.

The study of the plastics and resins industry is the first of the NIOSH control technology studies to be completed. The contract to perform the study was awarded to Enviro Control, Inc. (ECI) in July 1976, and the study was completed in November 1977. A number of factors dictated that the plastics industry would be studied. Perhaps one of the most significant factors is the series of widely publicized health effects among workers in polymerization plants--primarily polyvinyl chloride, but also including styrene-butadiene rubber (SBR) and (sometime afterward) acrylonitrile. A second major factor is the innovative nature of the plastics industry in developing and implementing control technology, and the potential for transferring this technology to other organic chemical processes.

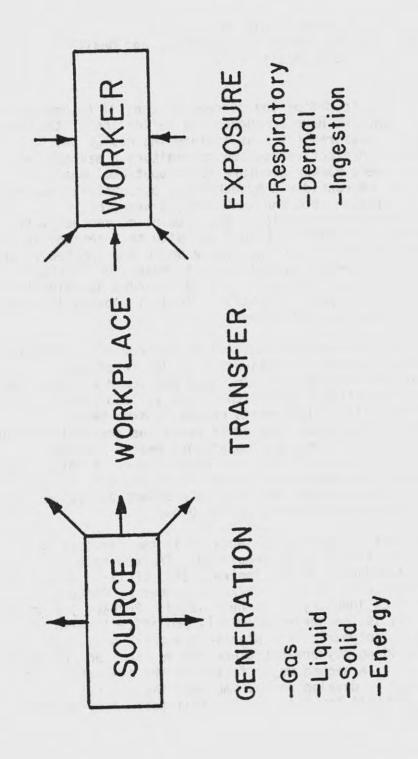


Figure 1. Generalized occupational exposure.

Table 1. Principles of controlling the occupational environment.

POINT OF APPLICATION OF THE CONTROL MEASURE	CONTROL MEASURE
At or near the hazard zone	Substitution of non-hazardous or less hazardous material
	Process modification
	Equipment modification
	Isolation of the source
	Local exhaust ventilation
	Work practices (housekeeping)
To the general workplace environment	General dilution ventilation
	Local room air cleaning devices
	Work practices (housekeeping)
At or near the worker	Work practices (housekeeping)
	Isolation of workers
	Personal protective equipment
Adjuncts to the above controls	Process monitoring systems
	Workplace monitoring systems
	Education of workers and management
	Surveillance and maintenance of controls
	Effective process-people interaction and feedback

You have been given a copy of the final report from the study entitled, "Engineering Control Technology Assessment for the Plastics and Resins Industry." The objective of this morning's session is to briefly review the study, and then to have an open discussion of its merits and weaknesses, and of ways in which other control technology studies could be improved as a result. We need your feedback in order to direct future studies in areas that will meet the real challenges which we all face.

It has been interesting to note how the study has been used thus far (particularly by younger hygienists without engineering backgrounds). The work permitted both NIOSH and Enviro Control to provide substantial input to OSHA at the acrylonitrile hearings. Numerous industrial hygienists have found the report to be particularly useful as an educational aid. OSHA staff have also made use of the report in conducting plant inspections. We will be interested in the comments of this group concerning your perception of the report's usefulness.

Clearly, there are some gaps, which Ken Schoultz will touch on. Also, we were able to draw some definite conclusions, as Julius Bochinski will discuss. The important thing for us all to realize, however, is that the study is only a first cut at describing control technology at a point in time for a complex and changing industry. The present symposium will add significantly to that study. The production of reports and the conduct of symposiums should not be regarded as an end in itself, however. The proper goal is the implementation of effective control measures to prevent worker exposure. We also support the promulgation of effective regulatory standards. That is why we are here.

* * *

MR. WALTER HAAG: Our next speaker is Kenneth Schoultz, who served as the principal investigator for the plastics and resins control technology assessment. Ken is an industrial hygienist with extensive experience in control systems and technology. He left Enviro Control to manage the industrial hygiene programs of LFE Environmental, a consulting firm located in the San Francisco and Boston areas. While with Enviro Control, Mr. Schoultz participated in numerous studies for the NIOSH as well as for OSHA and the National Cancer Institute. Ken's discussion this morning will deal with the study methodology, the industry coverage, and some of the advantages as well as the weaker points we found in undertaking this study.

NIOSH CONTROL TECHNOLOGY ASSESSMENT OF THE PLASTICS AND RESINS INDUSTRY:

METHODS AND APPROACH

Kenneth S. Schoultz LFE Environmental Research Laboratories Richmond, California

As background for the upcoming open floor discussion, I'd like to review how the study was conducted, describing the significant problems encountered and how they were overcome.

The primary objective of the study was to assess and document engineering control technology used to reduce worker exposure to toxic chemicals and harmful physical agents in the plastics and resins industry. The assessment was to be accomplished primarily through in-plant survey of 9 polymerization processes selected to best represent the industry relative to criteria such as common unit operations, maximum number of workers and best control technology. The scope of work encompassed all processes used to manufacture the polymerized materials listed in Standard Industrial Classifications 2821 and 2822, including thermoplastic and thermosetting resins, elastomers, and synthetic rubber. All operations from receipt of raw materials through compounding of polymerized materials were to be included in the assessment.

Prior to selecting the 9 survey sites, it was first necessary to broadly determine the types of processes to be included. We soon recognized that the plastics and resins industry is extremely diverse and complex and therefore not easily characterized by a single parameter such as process type. There are at least 20 distinct polymerization processes used to produce many hundreds of different polymerized products. Rather than develop meaningless statistical techniques to select optimum process categories for site surveys, we decided it was preferable to use a common sense approach based on our understanding of the objectives of the study. Our logic was as follows:

- 1. The seven additional polymerization processes used to manufacture thermoplastic resin, elastomers and synthetic rubber make up a much larger percentage of the industry output and number of workers than do the 13 condensation polymerization processes used to produce thermosetting resins. Thus these processes were emphasized in the study.
- 2. Polyvinyl chloride is commonly produced by four of the seven addition polymerization processes, Also, because of the very strict OSHA regulations for vinyl chloride, these plants were known to possess effective, sophisticated control technology. Therefore PVC plants were subject to a far disproportionate number of surveys.

- 3. During the study, NIOSH was very interested in processes using styrene, particularly styrene butadiene rubber plants. For this reason, we decided to include three processes using large amounts of styrene, including a polystyrene and ABS-SAN resin process and an SBR process.
- 4. Even though the three addition polymerization processes for polyethylene and polypropylene comprise a large percentage of the industry output and number of workers, none were included as survey sites. We concluded that these processes do not use large quantities of toxic materials, and are thus not good subjects for assessment of control technology.
- 5. Many polymerization plants also possess compounding operations. It was thus decided not to select compounding operations for specific surveys; rather, we would evaluate these operations while at a given plant to survey a selected polymerization process.

In retrospect, I feel that this common sense approach to process selection yielded a very representative and useful assessment of control technology in the industry. It is strongly felt that other process selection techniques based primarily on process or material production rates or number of workers would have diminished the effectiveness of the study. I do, however, regret the omission of a solution polymerization process using large amounts of a solvent such as benzene - frankly, we did survey such a process but determined that the controls were not sufficiently effective to be included in the study.

Once we had determined the types of processes to be surveyed, it was necessary to locate and gain voluntary access to well controlled plants using these processes. This turned out to be a very difficult and time consuming task because we could not identify an industy-wide organization or association to assist us and, since this was the first study of its type, plant personnel were somewhat reluctant to cooperate at first. There were many concerns about proprietary information, and skepticism relative to the end use of the study. However, after several months, we were able to obtain a sufficient number of plants that were willing to cooperate in the study and possessed effective controls. Two other factors were important in the selection of the survey sites. First, it was determined that it was best to include an equal number of batch and continuous processes. Second, we also felt that it would be most useful to concentrate on retrofit controls, such as those implemented in PVC plants after promulgation of the OSHA standard for vinyl chloride. Our reasoning was that the most consequential control technology problems and need for information occur in existing plants following the passage of new standards, such as the recent standard for acrylonitrile. We also believe that, in most cases, the ability already exists to design and construct new plants to comply with existing standards. Furthermore, evaluation of controls in new plants may not generally be applicable to existing plants.

A major impact on how the surveys were conducted was the level of funding for the project, equivalent to an effort of slightly more than one man-year. To put this in perspective, it should be noted that NIOSH is currently funding similar studies with budgets several times larger than this. The study objectives were quite broad in scope, incorporating controls for all potential toxicants and physical stresses in both polymerization and compounding processes. Clearly, priorities had to be established to focus the effort on the most important issues; otherwise we would have either run out of money long before the project was completed or else ended up with a final document that covered all possible areas, but was too diluted to be useful. After studying the industry, we decided to concentrate on evaluating control technology used to minimize worker exposure to toxic monomers such as vinyl chloride, styrene and acrylonitrile. Controls for minor process additives and other potential toxicants used in small quantities, and for noise and heat stress were not neglected, but were relegated to a position of secondary importance. Essentially, the same was true for compounding operations, although a sufficient number were observed to allow an evaluation of needed improvements. The relatively small budget also limited the number of in-plant air samples that could be collected and analyzed. This constraint had two major effects on the surveys: First, it was necessary to use existing plant sampling data wherever possible to evaluate the effectiveness of control systems. All of the PVC plants we surveyed possessed exhaustive monitoring data that we were able to use to full benefit. However, most other plants had not collected extensive sampling data, and control system effectiveness had to be evaluated based on a limited number of samples. Second, we did not have sufficient funds to allow a large amount of investigative type sampling needed to evaluate the effectiveness on individual controls on overall worker exposure. However, since most plants utilized a systems approach to control exposures, it was generally sufficient to evaluate the effectiveness of the control system as a whole.

Although there are many issues concerning the conduct of the study that I'd like to discuss, there is only time to briefly touch on one additional item, i.e., the problems associated with proprietary technology. In most plants, sophisticated controls were developed requiring extensive research and development, as exemplified by monomer stripping operations in PVC processes. In all cases details of these technologies were considered proprietary and at best we were only able to describe them relative to performance criteria. Due to the extreme importance of such technologies, it is strongly suggested that procedures be developed in the future to allow dissemination of this information, while protecting the interests of the companies who develop it.

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MR. HAAG: Our next speaker, Dr. Julius Bochinski, is the Manager of the Industry Study Group of Enviro Control. He was also deeply involved with the project. He is a chemical engineer from Iowa State University and the University of Detroit. During the past year he has worked in the area of control technology. Dr. Bochinski will be discussing the conclusions of the study and some of the significant findings in outlining some recommendations.

NIOSH CONTROL TECHNOLOGY ASSESSMENT OF THE PLASTICS AND RESINS INDUSTRY

RESULTS, CONCLUSIONS AND RECOMMENDATIONS

Julius H. Bochinski Enviro Control, Inc. Rockville, Maryland

Since all the attendees have been given a copy of the report (DHEW-NIOSH Publication No. 78-159), I will discuss only the highlights of this study. The areas I will address are:

- The need for a systems approach
- Recommendations for research
- Conclusions

Reduction of vinyl chloride levels in the PVC plant was achieved after a substantial effort to identify and reduce or eliminate emissions from all sources in the plant. In other words, you have to use a systems approach. Also, with a continuing effort by management in identifying and correcting problems with compliance with the vinyl chloride standards, compliance would not be possible. In my opinion, the most effective means of reducing emissions was stripping the monomer from the resins as soon as possible.

The problems presented for consideration for research by NIOSH were selected on the following basis: Resolution would result in a significant reduction of worker exposure; the problems are common to various segments of the industry; and the effort and cost involved would be commensurate with the expected results.

We have the following five general recommendations:

• The safety work practices are often the most cost effective investment. However, long-term success in the area depends on educational level of the worker and attitude of management, physical appearance of the environment, house-keeping practices and age level of the workers, and engineering controls operating effectively.

- Real time monitoring instruments are needed that are more reliable and simpler to operate and less expensive.
- Computer control of processes further automation will reduce worker exposure, reduce human error. Automation with monitoring instruments of work procedures that have a high incident of worker exposure is needed.
- Better mechanical designs of certain equipment would reduce maintenance problems. Better seals and better materials of construction are most important. Improved seals on rotating equipment would substantially reduce worker exposure. Early failure could be the result of construction, poor preventive maintenance or improper installation.
- The additives were not evaluated. Many of the thousands of common though minor ingredients used may not have been subjected to toxic analysis and evaluation. Many of the additives are purchased as trade name products, so the users do not know what they really have.

In conclusion, reduction and exposure levels requires three things:

- Technical expertise
- Time
- Financial Resources

You must have sufficient technical capability, and you must have adequate time and financial resources to integrate your activities with the other activities in the company. Extrapolation of control technology must be done with care. Attention must be paid to physical and chemical properties of hazards you intend to control.

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MR. WALTER HAAG: At this time we will have a critique of the study report by John Barr of Air Products and Chemicals, Inc., followed by an open discussion of the study from the floor.

NIOSH CONTROL TECHNOLOGY ASSESSMENT OF THE PLASTICS AND RESINS INDUSTRY

A CRITIQUE OF THE STUDY REPORT

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

I will limit my remarks to the area of polyvinyl chloride, which is the only place I have enough expertise to make any comment. First, the good news. This is not the worst report I have ever seen. That's a compliment, because I have seen alot of awfully bad reports in the last few years, since the regulatory agencies became active. Some of these reports are a disgrace. This is not one of them. However, it does have some problems. Many of them have already been recognized by the people who put it together, and some of the reasons for these have been touched on. But, to put it briefly, this report didn't do much for me when I read it. There are several reasons for that. It is superficial, it is not critical in its evaluation of what was seen, and it didn't give me anything new. Let's talk about why these things happened.

This is not a problem which is unique to this report. I would say that the study was initiated about 1976 and we are now into 1979, and we're beginning to talk about it. Let's get this done. Why is it so slow? A part of that has to be the fault of the way the contract was handled, first by the funding Governmental agency, and then by the contractor who states he was seriously impeded by the low funding, which was less than one man year, or something like that. It has a date on it of March '78 and here it is February '79. Government moves too slowly to help us. If we wanted help from this document, we would have been in tough shape. It is superficial, because the people who did this work didn't know enough about the industry that they were working with. It is not their fault. They can't look at an industry for that short a period of time and expect to know more than those who have been living and working in it. That's part of the problem. We need to find a way to get better input. That's the principal reason it didn't tell me anything I didn't already know. I wasn't asked to participate in this, but had I been, I wouldn't have told you any secrets, either. There is a financial problem, and there is no way to get around it; that inherently is going to limit the quality of these kinds of reports in the future. I am not going to tell you secrets and you're not going to tell me, and we're going to learn by hiring each other's employees.

Finally, there was very little downstream study done. Again, limited funding, limited opportunity. Despite these difficulties, it seems to me that the recommendations and conclusions that came out of this study were proper. I particularly want to agree with and emphasize several of them.

First, there is no question that retrofitting an old plant is the most serious problem industry has. Given enough time and money, we can build a plant that will do anything. But to try to keep industry in operation is a serious problem. Waiting for the development of a technology that will come some day - how do you keep industry going? Regulations have to approach that problem. The research recommendations, of course, speak to this quite adequately. I want to emphasize that safe work practices are probably the most important part of reducing worker exposure. However, the report did not adequately provide for the place of the operator. The operator can simply make or break any program. He serves as a source of ideas. In our experience with vinyl chloride, the most serious problem we had was convincing those guys that had been there for 20 years that they weren't supposed to have those exposures now. They could see no reason whatsoever why they should pay attention to this new law that interfered with the way they worked. We must get the worker on our side, give them enough education, and if it's there, give them enough scientific basis of the regulation to convince them it is a sound regulation. We do have a little difficulty conveying that idea sometimes. But the worker is extremely important in this, and we must bring him into it. Computer control is another way to minimize exposure. We'll never have zero exposure, but we will have less exposure in the future as the new plants are built with remote operated computer controls; there is somebody sitting half a block away punching buttons; large reactors cut down on the frequency of exposure or pipeline plugging, and when you have to open one and have that unstripped resin streaming out in order to get a pipeline unplugged, you have probably your major source of exposure, rather than pump seal failure. If anybody knows how to do that, it will be a blessing to the industry.

The other major disagreement is that the study has totally ignored the effects of other agencies. One of the reasons it did not receive any better reception in the industry was that in 1976 we had just gone through the first round of OSHA work. We picked a bad time to make a survey on vinyl chloride, particularly when these two agencies, OSHA and EPA are both putting out regulations, as they will continue to do, on the principal organic materials. The cross effects of these regulatory agencies must be understood, and we cannot afford to do the job two and three times. We must do it once.

Finally, I was disappointed that nowhere in the document did I see a mention of the Vinyl Chloride Safety Association. It has been in existence almost ten years. The sole purpose is for the vinyl chloride - PVC people to get together to discuss safety. I think it has done more for safety than any single organization to this day.

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DISCUSSION:

- DR. NARESH CHAWLA: I have listened to John Barr's comments with great interest. I would like to add a few more comments. One of the things which has very much been omitted in this symposium and some of the previous ones is the management technique. The U.S. Department of Energy for instance, has come up with a management oversight and risk-free concept, and I am sure many of you are aware of this concept. I would like to see a lot of work done in this area, and this be accepted as a control technique in all industrial programs.
- MR. JAMES A. GIDEON: Does the safety association do any better at finding out more of the real facts than this report did?
- MR. JOHN T. BARR: Does the Vinyl Chloride Safety Association do any better finding out the real facts or do other organizations?
 - MR. GIDEON: Government included?
- MR. BARR: We do not discuss proprietary suggestions. Nevertheless, the discussions are so detailed that a great deal of information is exchanged. It's sole purpose is to talk about safety, and the rules prevent us from discussing anything else. No, we don't exchange proprietary secrets, but it is a meeting group where we exchange working information.
- MR. JOE LEWIS: I am also in the PVC business. Could you comment on the cost and advantages of retrofitting your older plants, versus the impact of building a new highly automated plant, the advantages and the disadvantages of both?
- MR. BARR: Well, let me tell you what we did. We decided at our Calvert City plant to build a new one, rather than try to retrofit it to suit OSHA and EPA standards.
- MR. JOHN JANOUS: I guess as a taxpayer I am also interested in getting more for my money. I was formerly in the steel industry, and now in the chemical industry and have had in the past four or five years an opportunity to praise NIOSH publications in general, and certainly would agree that many of them are not of much value. I think that potentially, this type of an approach or an assessment of control technology in a given industry is one of the better things that NIOSH could be doing. I think their resources should be dedicated to these ends. I would further recommend that assessment of other industries, perhaps, should include the important areas of human factors. I think we go in plants, we see health effects, but then we see dramatic injuries from the relationship of people and the machines they work with.
- MR. HAAG: We will adjourn now and return after lunch. This afternoon's session will be on control of emissions at the source.

SESSION II CONTROL OF EMISSIONS AT THE SOURCE

DONATO R. TELESCA

Enviro Control, Inc.
Rockville, Maryland

MR. DONATO R. TELESCA: Welcome to Session II. In the first session this morning, you heard the reasons for the control technology in plastics and resins. The speakers discussed the background for the study, the methodology, and the overall nature of control technology. This symposium is built around four sessions. For this second session we will discuss control of emissions at the source. The third session, which will be tomorrow morning, will be on the control of the workplace, and session four will be on implementation of controls and conclusions.

In this session, we will be discussing more specifically the methods and procedures of preventing exposure. The technology for the plastics and resins industry; the subject of monomer stripping procedures; process stream sampling; maintenance problems; up to the role of the insurance and promoting preventive measures.

The first presentation this afternoon will be by Fred Krause, a graduate of Purdue University with both a B.S. and M.S. in Chemical Engineering. He started with B.F. Goodrich Chemical Division in 1959, where he has served in a variety of technical and management positions in the polymer process, product and product application R&D before assuming his present position of Director of Plastics Materials Research and Development in 1976. He was directly responsible for B.F. Goodrich's program on VCM containment.

Mr. John T. Barr, whom you heard this morning, received his B.S. degree in Chemistry from Arkansas College and his M.S. from the University of Arkansas, and has further training at the University of Tennessee and Murray State University. His 31 years of industrial experience include 24 years in polyvinyl chloride and related processes. Mr. Barr's talk will be on solvent cleaning of PVC reactors and on the selection of a particular solvent to be used, important decisions applicable to existing equipment and processes.

THE PREVENTION OF PVC REACTOR FOULING

Fred E. Krause B. F. Goodrich Chemical Division Cleveland, Ohio

B. F. Goodrich is the largest PVC producer in the U.S.A. As such, we have been very involved in the vinyl chloride toxicological, manufacturing and regulatory actions during the last five years. Simultaneously with our disclosure of the relationship between vinyl chloride monomer and angiosarcoma in humans, B. F. Goodrich mounted a major program on vinyl chloride monomer containment to eliminate exposure to our employees and our customers and to minimize emissions to the atmosphere. I would like to report today on two technology developments which were an outgrowth of this program: The prevention of reactor fouling and later reducing vinyl chloride monomer in PVC resins.

Opening a PVC polymerization reactor has been one major source of vinyl chloride exposure or emissions. The openings are required primarily to remove polymer buildup. Reactor fouling or buildup historically has been a problem in PVC polymerization. There are basically two possible approaches to this problem:

- 1. Elimination of reactor fouling
- 2. Removal of the buildup either mechanically or chemically

We investigated both of these approaches. In fact, in the 1960's the industry encountered problems with acro-osteolysis, a deterioration of the bones in the fingers of some of the workers who entered to clean PVC reactors after each batch. At that time, we developed th hydraulic reactor cleaning (HRC) technology which uses a high pressure (4000-6000 psi) water jet. The nozzle is inserted into the reactor and programmed to rotate so that it cleans the entire reactor surface. This approach was very successful. Vessel entry was reduced to once every 25-30 charges using the HRC and the equipment is still used in some of our PVC reactors today.

We also looked at chemical cleaning but found this added several additional processing steps and also required handling and treating of another chemical or solvent. Therefore, we turned our attention to the prevention of reactor buildup. There is a myriad of approaches to buildup prevention as indicated by the heavy increases in the patent literature today and over the last several years. Some parameters to be considered are polymerization recipe and raw material, operating procedures and even reactor design. Significant attention was addressed toward understanding the mechanism of buildup formations, i.e., how and why it occurs so we could more productively address its prevention. I won't attempt to go into these studies today. Suffice it to say after addressing all of these concerns, we have developed and implemented

commercially a system we believe is both simple and effective. As you can see from Figure 1, the system outwardly is very simple, consisting only of a chemical feed tank, a pump and a feed nozzle used in conjunction with existing reactors in which vinyl chloride monomer is polymerized to PVC. The key to the system is the coating solution and method of application. The process consists of carefully water rinsing the loose resin from the reactor interior to the slurry stripping system after each polymerization and then spraying a coating solution onto all the internal surfaces of the vessel.

These operations can be performed simply with a hose through an open manway or more preferably by spraying through a permanently mounted nozzle inside the reactor. The latter approach permits ease of automation and operating the reactor in a completely closed mode.

When this procedure is followed after every polymerization charge, reactor fouling is eliminated and significant reduction of vinyl chloride emissions can be attained. Our results to date have shown we can run well in excess of 500 polymerization batches without cleaning reactors. We have also run in excess of 50 batches without opening the polymerizer. The technique eliminates vinyl chloride emissions and operator exposure due to reactor downtime, reduces labor, and improves raw material efficiency. Reactor entry is now required only for normal maintenance.

The benefits of this technology then are:

- Closed reactor operation entry only for normal maintenance
- 2. Reduction in worker exposure to VCM.
- 3. Reduction in VCM emissions to the atmosphere.
- 4. Reduction in reactor downtime due to cleaning and a result increase in productivity.
- 5. Savings in labor.
- 6. Polymer buildup lost as scrap is eliminated.
- 7. Reduction of rupture disc changes due to polymer buildup.
- 8. Constant and maximum process side heat transfer coefficient in the reactor.
- B.F. Goodrich presently uses this technology in all of its PVC plants both foreign and domestic. In addition, the technology is available for license and has been licensed here in the U.S. and overseas.

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VCM Reduction

Clean Reactor System

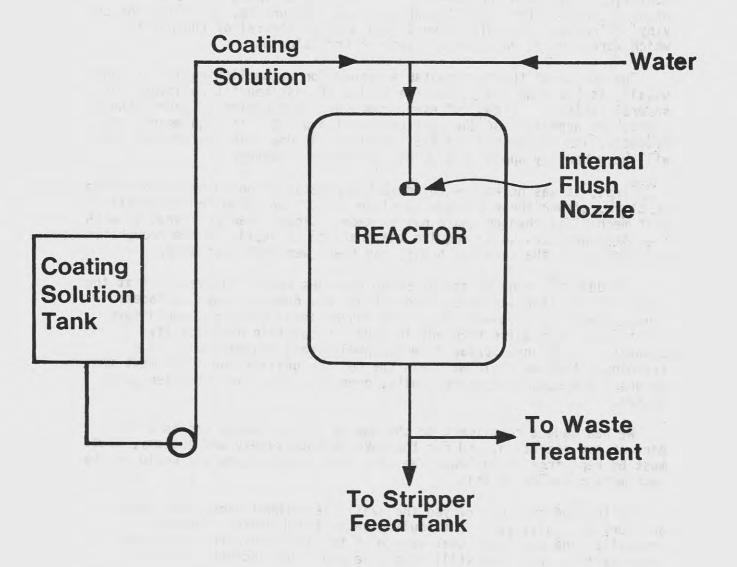


Figure 1.

SOLVENT CLEANING OF PVC REACTORS

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

Air Products has chosen solvent cleaning of its PVC reactors as being the most suitable method of completing one step toward the major goal of achieving closed-reactor operation. This mode of operation is one of our major objectives for reduction of employee exposure to, and emissions of, vinyl chloride. This afternoon I will discuss several of the points which were considered in this choice of technologies.

The choice of the most suitable method for accomplishing a given goal usually is based on a balance of a series of cost/benefit decisions for several factors. Seldom, if ever, can a proper decision be made without a detailed appraisal of the particulars of a plant - its equipment, its products, its processes, and its location. No one rule can be made that will be generally applicable across an entire industry.

First, it was necessary to adapt the process to be chosen to existing reactors, either those already in place, or so far along in construction that mechanical changes could not be made. Closed reactor operation with high pressure jets would require the presence of nozzles large enough for the passage of the rotating heads, and these were not available.

In addition, many of the existing reactors were relatively old at the time this decision was made, with extensively damaged inner surfaces. Thus, polymer buildup was rapid, and conventional cleanings would have had to have been quite frequent in order to maintain high quality product. It did not appear from our preliminary evaluation of this techniques that we could maintain the desired quality and still meet the proposed EPA reactor-opening limits, even with an efficient water purge system.

We had made a commitment to the use of reflux condensers in a large part of our operation, and for the sake of both safety and economy, these must be kept free of buildup. We felt that solvent cleaning would be the best method for doing this.

At this point, we surveyed the available technologies, both domestic and foreign, relative to antifouling methods and other clean wall processes, and concluded that even with the assistance received from these systems, we would still need a reactor cleaning method from time-to-time.

Thus, having decided to utilize solvent cleaning, we had to decide on which solvent. A variety of materials was available, and several which have been used or recommended are listed in Table I. These range from poor solvents such as ethylene dichloride, which must be used with high

Table 1. Comparison of cleaning materials.

REMARKS	Toxicity	Volatility	Potential corrosion	Peroxides, volatility	Very difficult to recover	
EASE OF RECOVERY	High	Medium	Medium	Medium	Very low	
SOL VENT POWER	Low	Medium	High	High	High	
MATERIAL COST	Low	Low	Medium	High	High	
SOLVENT	Ethylene Dichloride	Ketones	DMF	Tetrahydrofuran	NMP	

frequency before the buildup becomes very thick, but which can be recovered very simply and quickly, through the ketones which are intermediate in solvent strength to the very good solvents such as tetrahydrofuran, methyl pyrrolidone, and dimethyl formamide. These latter materials are quite good solvents, and can remove very heavy buildup under the proper conditions.

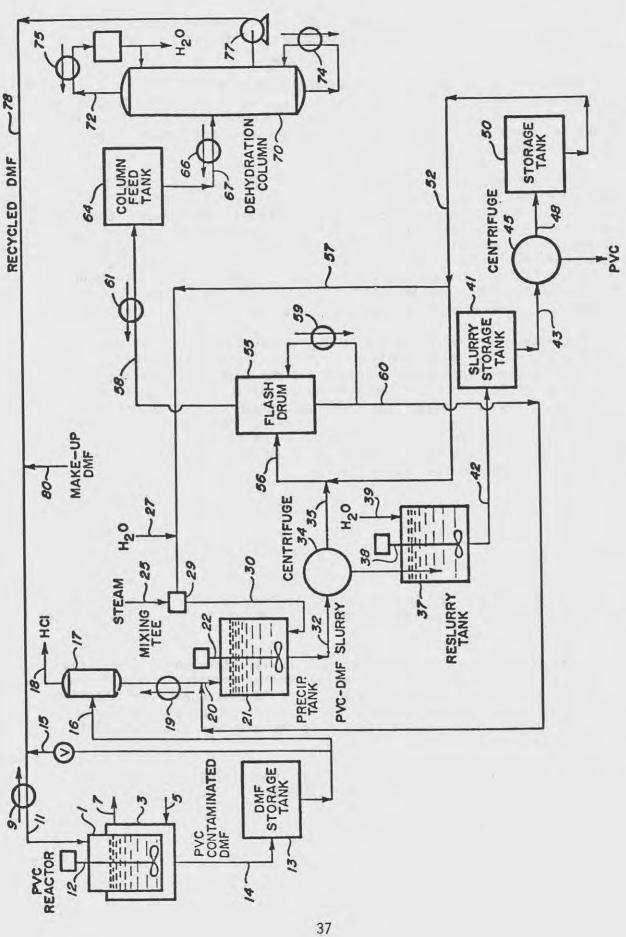
After consideration of the type of polymer deposits we expected to see in the future, the type of equipment we intended to build, and our own experiences, we chose dimethyl formamide. One important factor in this decision was that we manufacture this material and therefore are familiar with its characteristics. Just as those who manufacture vinyl chloride and are familiar with ethylene dichloride have chose it for their reactor cleaning solvent, and even for the end of the pipe abatement scrubber in place of an incinerator, we felt more comfortable committing our resources to develop a process using a familiar material.

Another important factor was its good solvent power. We manufacture substantial quantities of acetate copolymer, and this system is subject to occasional partial or complete failures of the suspending system, which can result in severe fouling, or even in a phenomenon known as a "set-up". We felt we needed the availability of a strong solvent as we moved toward the manufacture of these products in 24,000 gallon vessels.

We therefore began development of a process to utilize this solvent. The actual reactor cleaning operation is simple. When a reactor is to be cleaned, the residual vinyl chloride vapor is displaced by the water purge system, and the water is displaced with an atmosphere rich enough in nitrogen to avoid the possibility of explosive mixtures in subsequent operations. The reactor is filled to overflowing with the solvent, the vapor being displaced to the storage tank, and the reactor is heated and stirred for the required time. A small flow of solvent is maintained in order to sweep the reflux condenser with warm solvent through the cycle. The solvent is then returned to the storage tank, and the reactor rinsed with water. The first rinse is directed to a solvent-rich storage sump of gradual release to the biological treatment system. The reactor is then ready for evacuation and recharge.

The solvent regeneration system is more complicated. The point at which regeneration is needed is an economic balance between recovery cost and cleaning time. Both the accumulated solids and the water concentration are a factor in the solvent power. Thus the regeneration is done so as to maximize the overall efficiency, bearing in mind the type of wall deposits that are being removed.

Figure 1 is a drawing from U.S. Patent 4,009,048, which describes our process. Spent solvent is mixed in precipitation tank 21 with recycle water of suitable temperature. The flocculated solids are separated in a centrifuge, reslurried in tank 37 to remove entrained solvent, recentrifuged, and sent to disposal. The organic phase is flashed to reduce the acid content and distilled to separate the solvent and water.



The system is now in operation in our plants manufacturing both homopolymer and copolymer, and has found application in our emulsion operations.

Commercialization has not been without difficulties. The formate-chloride combination can lead to severe corrosion problems if not handled properly. Copolymer precipitates are more difficult to process because of their more tacky nature. Nevertheless, the system is now operating successfully in our plants.

One by-product of this technology, above the goals of reduced employee exposures and emissions, has been improved life of our equipment. Reactor manways are no longer damaged from frequent openings and contact with ladders, tools and buckets, and interior surfaces are not subject to mechanical harm. One glass-lined reactor that is over eight years old and has been cleaned only by solvents still has a near-perfect glass surface, and thus fouls at a much slower rate than others that have been mechanically cleaned. Polished stainless steel surfaces are similarly protected from mechanical damage.

In summary, we have found that many factors must be considered before the "right" process can be chosen. It is the accomplishment of the end goal that is important in the long run and the means of achieving that goal should be left to the ingenuity and capability of the individual companies. This will ensure that most satisfactory solution for each situation, and provide a diversity of technology for the future. The successful development and commercialization of this process is an example of just such a result, which would not have occurred if technology had been frozen by regulation.

* * *

DISCUSSION:

- MR. D. G. IRWIN: Mr. Krause, you listed several ways of improving your reactor design, reducing the fouling. Can you tell me which was the most effective?
- MR. FRED KRAUSE: I am not sure I can really state which is exactly the most effective. It is fairly obvious in the industry if you looked into a PVC reactor, or any place where there is a stagnant spot, fouling will build up and continue to build up in subsequent polymerizations. Minimizing those points in the reactor is the only way to reduce that buildup.
- MR. IRWIN: You had to complete all of these things to be as effective as you were in eliminating buildup?

- MR. KRAUSE: Yes. Eliminating buildup is a combination of things. It is not strictly one thing, as anybody in the industry who is familiar with it knows.
- MR. ARTHUR SPIEGELMAN: I would just like to make a comment. Both Fred Krause and John Barr have show us two ways in which to apply control technology without changing the materials involved, and without putting greater stress on instrumentation and things of that naure, and I think that I can show you a few other ways when I get up to speak, but I think it is very important for us to realize that the design of the equipment and the method of operation are just as important, from a control technology standpoint, as examination of the original raw materials.
- MR. R. NICHOLAS WHEELER: Mr. Krause, I am a little bit curious as to whether this particular chemical procedure would be adaptable to other monomers?
- MR. KRAUSE: We have, obviously, looked at that. I think it is very important as to what the chemical nature of the product is and the chemical of the coating in general. It is not applicable to other products.
 - MR. WHEELER: I thought it might be a little bit specialized.
- MR. JAMES A. GIDEON: Would either of you care to comment on what additional options you have open if you were putting in a new polymerization line, over and beyond those which are available for existing lines?
- MR. KRAUSE: John and I will both comment a little on that. We're not going to say too much, because be both have installed new plants within the last several years. Sure, we have taken advantage of everything we could.

We use these coatings to minimize reactor fouling, and as I said, it is part and parcel of the total technology when you design these systems to do that. This is on the edge of properietary information and I don't think we are going to say much more than that. There are obviously things that can be done.

- MR. JOHN T. BARR: I agree entirely with what Fred says. The two methods we have discussed here are not mutually incompatible. If you have a workable anti-fouling system, we use the solvent less frequently. The kind of plant you build and the kind of products you build are dictated by the market, and these are not necessarily totally interchangeable.
- MR. DONATO R. TELESCA: Fred Krause will now come back and talk to us about monomer stripping. Reduction in monomer content reduces worker exposure in the PVC production operations. This technology is currently commercialized in the United States and licensed to a number of PVC producers world-wide, and I am sure it is available to license to others that may be interested.

VINYL CHLORIDE MONOMER STRIPPING OF PVC RESINS

Fred Krause B. F. Goodrich Cleveland, Ohio

As mentioned in our earlier discussions on reactor cleaning, the two major sources of vinyl chloride emissions in our PVC manufacturing plants were from reactor opening and residual vinyl chloride in the PVC resins. Although both were important, the foremost problem we faced commercially was to reduce the residual vinyl chloride monomer (RVCM) in our PVC resins. The high levels of RVCM (10-30,000 ppm) at various points in process was a major source of worker exposure and emission to the atmosphere. In addition, the RVCM in the final dried resin was sometimes high enough to expose our customers during subsequent melt processing.

When we embarked on our program it was immediately apparent that we needed to supplement our basic information on vinyl chloride solubility and diffusion in PVC. This was necessary not only to define how best to eliminate the vinyl chloride monomer (VCM) but also to define the levels at which RVCM would no longer be a hazard to handle by both our customers and our own workers. The basic data was obtained by A. R. Berens of our Corporate Research group and is well documented in the literature (1-8). Simultaneously, exploratory studies on paper and in the laboratory were initiated on various approaches to reduce or eliminate RVCM. These approaches included postpolymerization to remove the vinyl chloride in-situ. This was quickly abandoned when our kinetic data indicated very high levels of initiator would be required, thus increasing costs significantly not to mention the negative impact on resin properties.

Beren's early work immediately showed that VCM followed normal Fickian diffusion and was, therefore, strongly influenced by temperature and particle size or in the case of suspension PVC - particle structure. His work oriented our program in two directions: engineering - mechanically stripping the RVCM out at higher temperatures and, polymer chemistry - modifying the basic PVC polymer structure to permit more rapid RVCM removal. Although both approaches were aggressively pursued we rapidly zeroed in on stripping, either batch or continuous, as likely the best and most rapid solution to the problem. While batch stripping was pursued on a pilot scale and in our production plants, a small pilot plant stripping column was installed at our Brecksville R&D Center. Although batch stripping at higher temperatures significantly reduced the RVCM levels, the pilot stripping column work quickly indicated this would likely be the most efficient route.

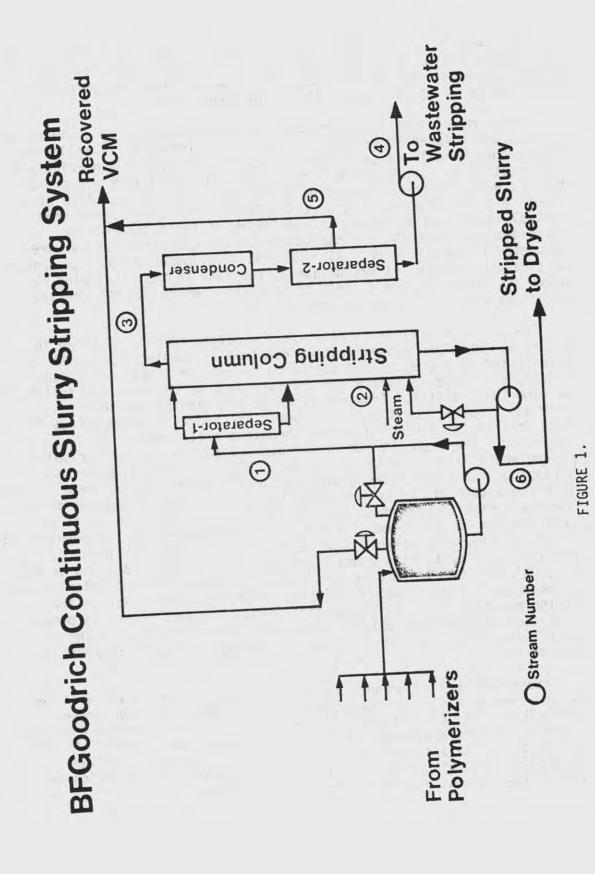
As a result of this work, a prototype unit using a modified distillation column was constructed and installed at our Avon Lake, Ohio production plant. Engineering data, resin quality data, and RVCM levels at various stripping conditions were obtained from this unit for design

of the commercial units. This unit is still in operation today in one of our polymerization lines at Avon Lake, Ohio. Again, data verified the favorable results of the pilot plant stripping column and permitted optimization of operating conditions and procedures.

The commercial stripping columns were designed so they could be skid-mounted and shipped to each of our plants for immediate installation. This technique allowed each plant to do their own pre-engineering and construction so that when the unit arrived only utilities and process tie-ins were required. Stripping units were built for all five of our plants and installed as they were completed. The development from initial laboratory stripping to completion of final design took approximately 10 months. Installation of the commercial units were completed 12 months later. Although the development and design appear to be straight-forward, it was unique at the time in that stripping PVC above its Tg was generally felt to be highly harmful to PVC thermal stability and particle structure.

The stripping column is relatively straight-forward as shown in Figure 1. When the polymerization reaction is complete the batch is transferred to a pressurized stripping column feed tank. This tank functions to release excess VCM pressure back to the recovery system and to form the transition from the batch polymerization reactors to a continuous operating stripping column. PVC slurry is pumped from the feed tank to the stripping column through a small vapor-liquid separator. The vapor stream is directed to the top of the stripping column where it exits with the stripped VCM. The slurry enters the stripping column and flows downward counter-current to the steam injected into the bottom of the column. Counter-current contact between the two streams strips the residual VCM from the slurry and forces it to exit from the top of the column. The vapor is passed through a condenser into the vapor-liquid separator. The vapor from the separator which is primarily VCM containing a small amount of water vapor is piped to the conventional VCM recovery system. The liquid from the separator, which is water with a small amount of soluble VCM, is pumped back to the stripping column for additional stripping. Stripped slurry is pumped from the bottom of the column to a blend tank or directly to the centrifuge, dryer and storage bins for packaging or bulk shipment to customers.

There are obvious methods for improving energy utilization in the design, and we have now incorporated some of these into our present operations. The conventional VCM recovery system as shown in Figure 2 is a series of compression-cooling steps to condense and recover the VCM. The vent from this system can be handled by incineration, solvent absorption-desorption, or activated carbon absorption. Goodrich has chosen the solvent absorption-desorption system.



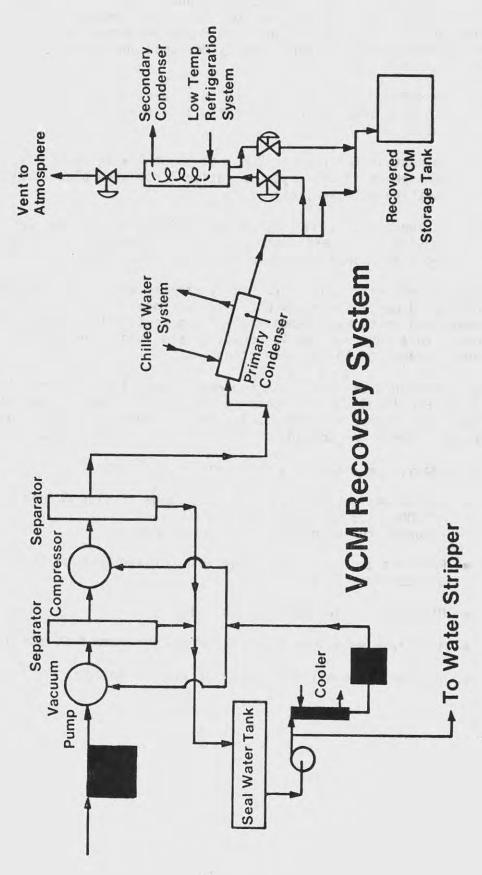


FIGURE 2.

Figure 3 shows an installed Goodrich continuous counter-current stripping system. The two tall structures are stripping columns. As I noted earlier, these were a prepiped package design skid mounted for direct shipment and installation. Utilities and process streams could then be piped directly to the unit for rapid shakedown and startup. The slurry stripping process when properly designed and operated fulfills our three-fold objectives:

- To reduce RVCM in PVC slurry to a level so that the dried finished product resin contains less than 1 ppm RVCM (dry resin basis).
- To contain and recover VCM that is otherwise vented to atmosphere in the dryer operation (from open blend tanks, centfigure, dryer, etc.).
- To operate continuously so as to afford better and more consistent process control (as to temperature, residence time, etc.) and hence result in better quality resin.

This process will handle PVC slurry streams with a wide range of RVCM (200,000-5,000 ppm) and resins with a wide range of particle structure. Our production units have demonstrated on a routine basis that RVCM can be removed to a very low level, normally less than 1 ppm, without any apparent degradation to PVC properties.

As I mentioned earlier, this process is operating commercially on suspension PVC in all of our domestic PVC plants. The process was made available for license in 1975 and is presently being used by a number of PVC producers here and abroad.

In summary, the continuous PVC stripping process:

- Can be designed to handle a wide range of slurry feed.
 - 5,000 200,000 ppm RVCM
 - Porous to non-porous particle structure
- Provides an energy efficient means to reduce RVCM to <10 ppm without harming PVC resins
- Minimizes worker exposure to VCM
- Minimizes emissions to atmosphere downstream from stripping
- Improves recovery efficiency of vinyl chloride

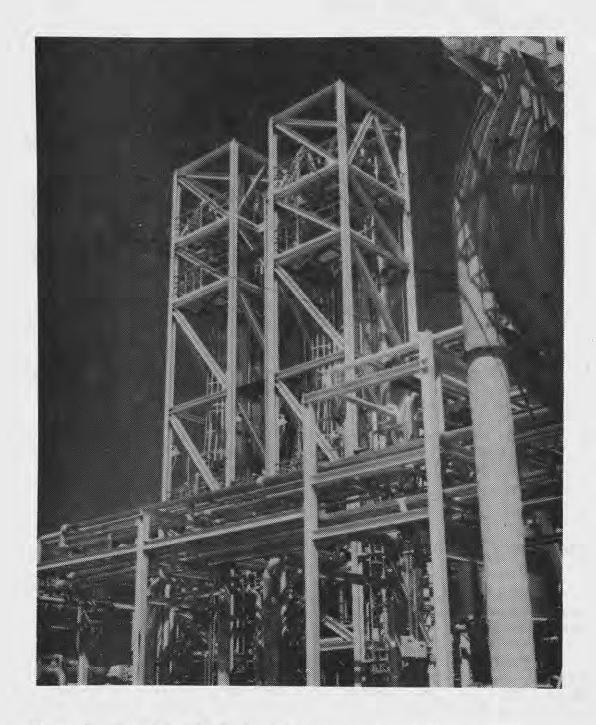


Figure 3. Installed B. F. Goodrich continuous counter-current stripping system.

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DISCUSSION:

MR. JOHN T. BARR: Is this correct that this can be obtained over all types of polymers or limited to certain molecular weights? Have you worked on copolymers on this?

MR. FRED KRAUSE: In general, the answer is yes for all molecular weights. We have done work with copolymers. We do not domestically manufacture a copolymer commercially. We have work based on the data there and we feel that we can design systems to handle copolymers. We

have also worked with a very nonporous resins, blending resins, and those that we could use the technique to do that. The design of the system itself has to be looked at fairly carefully--because these types of resins are more difficult to strip.

- MR. JAMES A. GIDEON: Could you comment on what your experience has been with licensing this technology. Has it proven to be profitable? What factors figure into the licensing of technology rather than keeping it to yourself?
- MR. KRAUSE: I cannot directly answer the question of profitability, because you have to balance out what we have gotten out of licensing versus development. It should be a profitable venture for us because of the number of licenses. It was very early when the decision was made by Goodrich to offer this technology to the industry because of the severity of the problem. I think there may have been some question as to whether or not prior to the vinyl chloride problem, we would have necessarily gone out and licensed the technology. It was done specifically to address a problem.
- MR. GIDEON: Do you have any thoughts on any way that the Government might serve to encourage more licensing of proprietary technology like that by technically advanced companies?
- MR. KRAUSE: It is a difficult question to answer, because any company that's in a commercial business looks at their technology on a basis in terms of what it can return to them. A licensing decision is based on business in general, and you only license because it looks like it is going to be more profitable than if you kept it to yourself. It is a competitive business, and I guess other than incentives I don't have a good answer about how the Government can encourage that.
- MR. BARR: Industry has been accused of being as bad as the special interest groups, running to the Government and saying, do things to protect us. But, here's one case where perhaps that could be justified, in that if it were considered to be enough of a social benefit that all society wanted to pay for this, then you could make the revenue from licensing proprietary information tax free; that would encourage the license process. That's sort of a socio-economic decision the Government has to make. That is one way to encourage it.
- MR. RALPH C. BARLEY: I would like to offer an opinion. First, I understand that the stripping is directly connected with compliance. In other words, it stems from EPA findings which by now are part of the Federal Register and Federal law. Stripping represents compliance with those regulations. I think the industry would be very much encouraged to license technology which they have developed in this kind of connection, and to directly relate it to something that John said near the end of his talk, namely, that Government should not restrict industry too much so that it can't develop new technology. Am I on the right track?

- MR. JOHN BARR: So far you sound good.
- MR. GIDEON: In the course of NIOSH control technology studies such as the present one on plastics and resins, it has really been frustrating to see that much of the most innovative and effective technology for protecting workers cannot be widely used because of proprietary concerns. In my opinion, resolution of this area in order to permit technology sharing for purposes of providing improved worker protection is one of this most important issues which we all face.
- MR. KRAUSE: I certainly agree with you, and I would like to reiterate that in the case of stripping, particularly, and to some degree from the reactor coating technology, the criticality of the problem and the exposure to employees dictated Goodrich's decision to offer licenses. Again, it is at some point, it had to be a business decision, because your whole industry is based on profit.
- MR. ROGER HALL: My company is concerned with reducing levels of the monomer to the lowest level. I am asking the speakers and anyone else about acrylonitrile. We tried stripping it in the lab, and we're hunting for other methods.
- MR. KRAUSE: I can't speak directly on acrylonitrile. Again, we found the diffusion of monomers in polymers is relatively close to the same. There are some monomers that have a high affinity for polymer itself, and as a result do not want to leave.
- MR. TELESCA: Our next speaker will be Tod Delaney on leak prevention, proper selection and maintenance of equipment, seals, et cetera. Dr. Delaney obtained his degree in Environmental Engineering from the University of Texas at Austin. He is associated with the Environmental Consulting firm of Fred C. Hart, as manager of the Air Quality and Environmental Engineering Group, concerned with fugitive emission sources which are coming under tighter regulatory control. This regulatory control initiative requires that plant managers and employees must be aware of the characteristics of fugitive emission sources. His paper provides information and data dealing with the rapid detection of hydrocarbon leaks. The statistical division of the leaks, which will be used in determining total plant leak rate, and the potential of fugitive emission reduction, due to the aggressive maintenance programs.

FUGITIVE EMISSIONS - DETECTION, DISTRIBUTION AND REDUCTION

B. Tod Delaney Fred C. Hart Associates New York, New York

Introduction

There are many sources of volatile organic compounds (VOC) within the resins and plastics industry. Many of the VOC's associated with processes in this industry have been determined to be deleterious to health (e.g., benzene) in very small concentrations. VOC emissions also can play a signficant role in air quality degradation, especially through the formation of photochemical smog. The types of emission sources in the resins and plastics industry, as in the petroleum-petrochemical sector, can be divided into two categories: point sources (stack and vents) and non-point sources (fugitive emission sources comprised mainly of pump seals, valve seals, compressor seals, etc.). This paper will address fugitive emission sources and will use valves as a representative type of fugitive emission. The paper will generally cover the following three major areas:

- Leak detection and sampling.
- · Distribution of leaks.
- Maintenance and reduction of leaks.

Leak Detection and Sampling

A fugitive emission can best be described as an atmospheric emission from an industrial operation that does not emanate from a process stack or vent. This definition includes such emission sources as leaking equipment, valve, pump and or compressor seals, storage tanks, loading/unloading facilities and cooling towers. Because fugitive emission sources do not emanate from an enclosure such as a stack or vent they have been difficult to quantify. Industry and EPA have generally accepted emission factors for these sources that were developed more than 20 years ago.(1)

In recent years, however, fugitive emissions have come to comprise a larger percentage of overall plant emissions due to improvements in industrial process emission controls. This increased importance has led recently to many studies. (2, 3, 4, 5) These recent studies have used screening techniques such as soap solutions sprayed on equipment as well as sensitive hydrocarbon detectors such as the J. W. Bacherach Instrument Company "TLV Sniffer" and the Century Systems Instruments "Organic Vapor Analyzer" (Model OVA-108) for leak detection. The process of detection, sampling and analysis can require a considerable effort in both manpower and time to acquire statistically significant data to be used for the determination of emission factors. After the leak is detected the source is enclosed usually by plastic or other suitable material and a sample is obtained for analysis.

Plant managers and industrial toxicologists are not primarily concerned with the development of emission factors but with the rapid detection and quantification of emissions within a processing area. The ideal instrument for survey work should be intrinsically safe, portable, provide rapid response, and provide both qualitative and quantitative information. Century Systems' Portable Organic Vapor Analyzer (OVA), mentioned earlier and shown in Figure 1, meets all of these criteria. The instrument was designed to measure small quantities (1-10,000 ppm) of organic material in air. The OVA can be used to obtain reliable data above the 10,000 ppm limit to almost any desired level with the use of a dilution system. The OVA uses a hydrogen flame ionization detector (FID) which has been used for many years as a detector for organic compounds. The portability of the OVA coupled with its intrinsic safety classification makes it an ideal instrument for field survey use, especially in areas where potentially hazardous concentrations (above the lower explosion limit) exist. The inclusion of a gas chromatographic (GC) option within the instrument increases its usefulness as a monitoring and detection instrument. With the GC option, not only can the magnitude of the leak be measured but composition can also be determined in the field. thus aiding in the location of the source.

The FID system used in the OVA (Figure 2) consists of a diffusion flame of pure hydrogen which is free of ions and is thus nonconducting. However, when a sample of organic materials is introduced into the flame, ions are formed and the flame becomes conductive. The conductivity of the flame can then be measured. The amount of conductivity that the flame exhibits with the introduction of organic compounds is related to many parameters, but is thought to be primarily based on the number of carbon atoms present and the efficiency of combustion.

In the typical laboratory FID (Figure 2) the sample to be analyzed is introduced and entirely mixed with the hydrogen prior to introduction to the burner. This premixing of sample with the hydrogen does not occur in the OVA. In the OVA, the sample is brought in with the combustion air (Figure 3). The sample contained in the combustion air is introduced into the combustion/detection chamber through a porous bronze filter which disperses the air and organic compounds around the hygrogen flame.

The method used in the OVA to introduce the sample to the hydrogen flame modifies the typical ion formation process and consequently changes the OVA's FID response to various compounds from that of a conventional FID. In the usual laboratory FID, a normal C_3 would have a response of three times the methane response (for the same $100~\rm ppm_V$) and a normal C_6 would have a response of six times that of methane. The OVA FID, however, has a response for nearly all commonly encountered hydrocarbons of between 50 percent and $150~\rm percent$ the response of methane. Table 1 provides a sample of OVA responses for $100~\rm ppm_V$ samples of common organics encountered in the petroleum petrochemical industry.

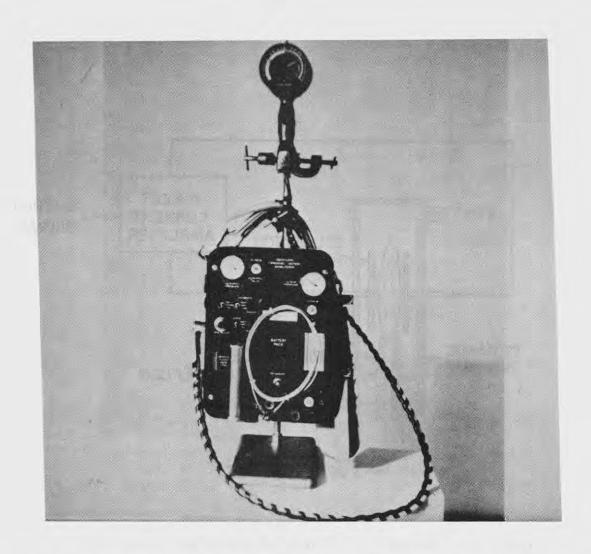


Figure 1. Century System's portable organic vapor analyzer (OVA).

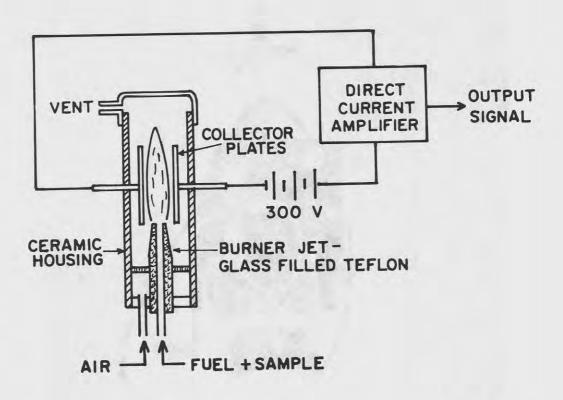


Figure 2. Flame ionization detector hydrocarbon analyzer burner-detector - standard type.

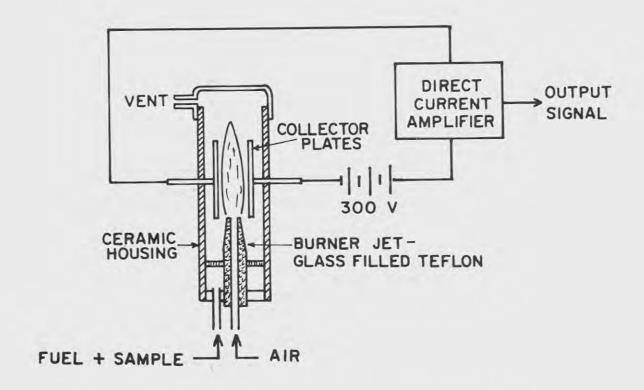


Figure 3. Flame ionization dector hydrocarbon analyzer burner-detector - OVA type.

Table 1. Relative responses at 100 ppm (V/V)

Compound	Meter Readout		
Methane	100 (calibration sample)		
Propane	85		
Propylene	75		
N-Butane	100		
N-Penthane	100		
Ethylene	65		
Acetylene	225		
N-Octane	150		
Benzene	235		
Toluene	150		

The precise reason for the difference in response between the OVA and other FID's has not been completely determined. One hypothesis is that the size of the reaction envelope and the energy available from the hydrogen flame are altered by introducing the sample at the periphery of the flame reaction zone. This allows for less contact time, which reduces the number of ions formed, and consequently changes the response mechanism.

The Century Systems Organic Vapor Analyzer (OVA) will respond to almost all organic compounds. But since the responses of the OVA to the various compounds differ, it is necessary to calibrate the instrument with the organic compounds that are expected to be encountered in the field. Once the expected mixture of organics has been determined, a calibration curve for the mixture can be developed in the laboratory. The basic method for developing a calibration curve consists of recording the response of the OVA to a range of concentrations of the expected gas mixture. The OVA responses to the known hydrocarbon concentrations are then plotted to obtain a calibration curve for the test mixture. (An example of the curve is shown in Figure 4.)

After the calibration curve has been developed the OVA can be used to determine emission factors, the emission rate for a specific piece of equipment, or the concentration and composition of the ambient plant air. The test program can take many forms, such as a simple walk-through of the plant with the instrument or a detailed survey of each possible source of fugitive hydrocarbons in a specific process area. The level of effort is directly related to the data desired or required.

The GC option of the OVA greatly expands the instrument's analytical capabilities. With this option the OVA can obtain the concentration of specific compounds during field sampling in approximately 20 minutes. As with the total hydrocarbon analysis, a calibration curve has to be made. For GC operation, however, a curve has to be made for each compound tested. The curves are developed by measuring the peak heights from the portable strip chart recorder. Table II is an example of repeated measurements of benzene. Table III is the compilation of data from Table II, and Figure 5 is an example of a calibration curve of peak height and the test gas concentration.

Distribution of Leaks

Emission factors for valves and other sources of fugitive hydrocarbons which are of general use to agency officials and industry representatives have to be based on statistically valid data. Most fugitive emission factors published to date except for the valve data published by Exxon Research and Engineering(5), were not well grounded on statistical test programs or parameters. The general assumption had been that fugitive emission leak rates were normally distributed and that the arithmetic mean was the best descriptor of the population and would thus provide the best emission factor. This was not found to be the case. For valves and most other sources (for some sources the data base is not large enough as yet to make a definite statement) the log-normal distribution should be used.

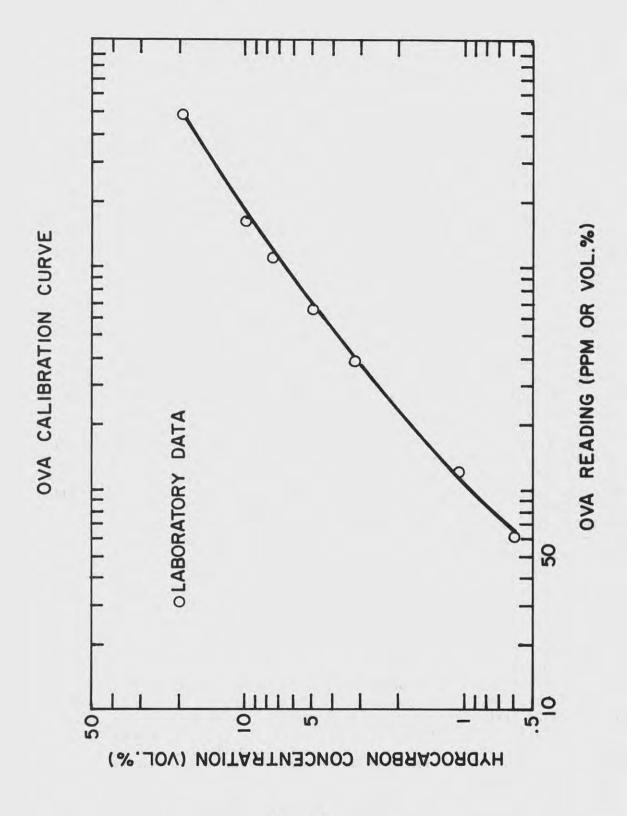


Figure 4.

Table 2. Tradewell Corporation benzene data.

Concentration	Peak Height	<u>(mm)</u>
2 ppm	6.25	
- FFW	6.20	
	6.22	$\tilde{\chi} = 6.238$
	6.22	$\sigma_{n-1} = 0.039$
	6.30	
4 ppm	12.06	
- 100	12.10	$\tilde{\chi} = 12.062$
	12.12	4
	12.05	$\sigma_{n-1} = 0.054$
	11.98	11-1
5.33 ppm	16.46	
1,444, 10	16.37	$\tilde{\chi} = 16.452$
	16.52	
	16.45	$\sigma_{n-1} = 0.054$
6 .	16.46	11-1
8 ppm	24.82	
	24.80	$\tilde{\chi} = 24.884$
	25.51	
	24.72	$\sigma = 0.363$
	24.57	
10 ppm	30.72	
	30.46	$\chi = 30.292$
	30.45	
	30.36	$\sigma_{n-1} = 0.479$
	29.47	n=1

Table 3. Benzene Data Courtesy Tradewell Corporation

Concentration	Mean Peak	Height
2 ppmv	6.238	mm
4 ppmv	12.062	mm
5.33 ppmv	16.452	mm
8 ppmv	24.884	mm
10 ppmv	30.292	mm

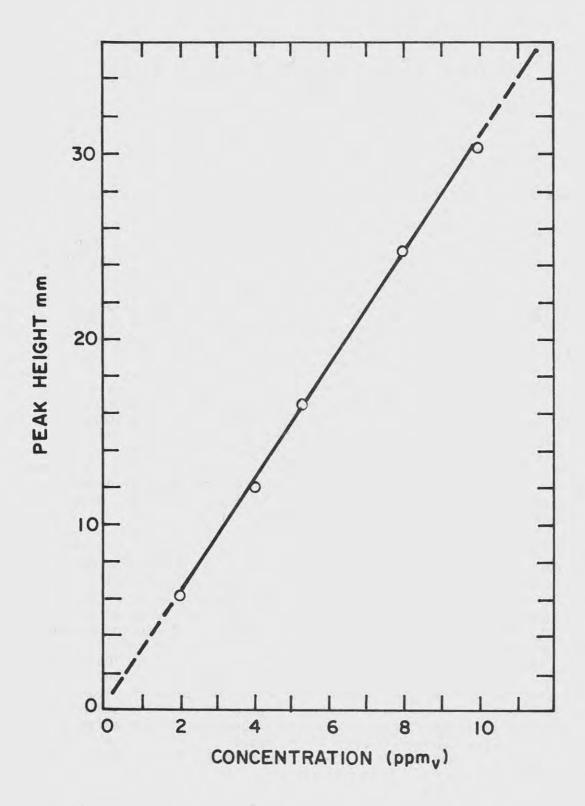


Figure 5. Peak height vs. concentration benzene (0-10 ppm)

Data Courtesy Tradewell Corporation

This conclusion can be best illustrated by briefly describing the test program I conducted for Exxon (referenced earlier). The objective of this test program was to verify and/or update emission factors used to estimate fugitive losses from valve stems, pump and compressor seals and atmospheric safety valves at a petrochemical facility. Valves are used as a representative source type. A stratified random sampling procedure was developed to assure that the pieces of equipment selected would provide the required statistical data base.

The sampling program was divided into two phases:

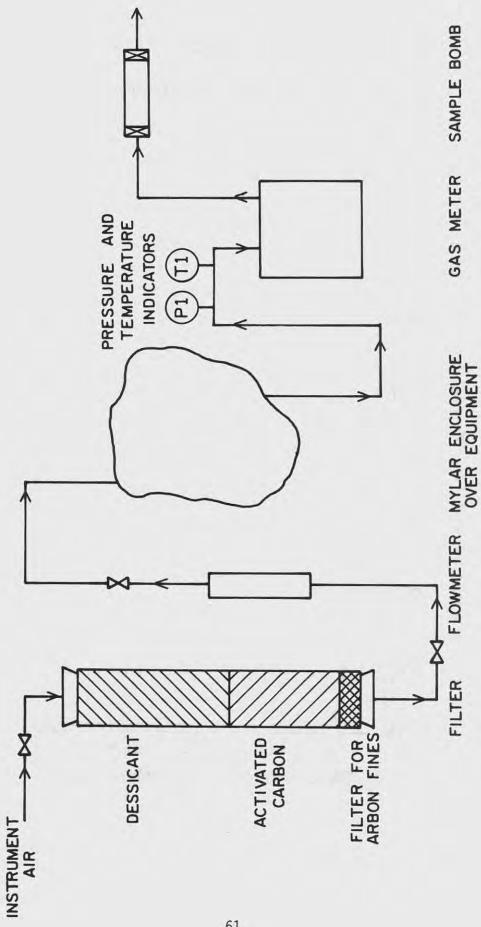
Phase I involved quantification of the number of valves in the plant. A random selection of about 10% of the total valves were then screened to determine the presence of leaks and an estimate of magnitude.

Phase II involved the stratified random sampling of a number of valves from the total data set developed under Phase I. The valves were bagged (enclosed in a plastic enclosure) and sampled. These valves reflected the same proportion and magnitude of leaks as determined from the initial screening.

The bagging involved enclosing the individual emission source with a plastic or aluminum foil enclosure. Figure 6 shows the equipment used. Plant instrument air was then passed through a dessicant and a charcoal filter at a predetermined flow rate. The flow rate was maintained so that a slight positive pressure would be maintained inside the enclosure. A sample of the air/hydrocarbon mixture was withdrawn from the enclosure outlet to a stainless steel cylinder for analysis by gas chromatography. The leak rate could then be easily calculated from the known flow rate and measured hydrocarbon concentration.

The initial approach for the analysis of the data was to calculate an average emission rate based on the arithmetic means of the entire data set. This preliminary analysis indicated that the number of small leakers far outnumbered the moderate and large leakers. In order to obtain a quantitative description, the measured emission rates were divided into 10 classes based on the total difference between the maximum and minimum emission rates measured. Figure 7 is a plot of the 10 classes. The preponderance of data falling in the first class indicated that the measured emission rates might not be normally distributed. Consequently, statistical tests were undertaken. The tests coupled with the positive skewing of the data indicated that a log-normal distribution would better describe the data. The natural logarithm of each emission rate was obtained. Figure 8 represents the result of using the natural logarithm for each emission rate. These transformed valued resemble very closely the familiar bell shaped curve.

A computer program was developed to convert the field data (flow-rate and concentration) to emission rates; the emission rates were then used to determine the geometric mean and standard deviation. The geometric mean and standard deviation were then used to obtain a population mean. This population mean then represents the emission factor for the component in question.



Fugitive emissions sampling train. Figure 6.

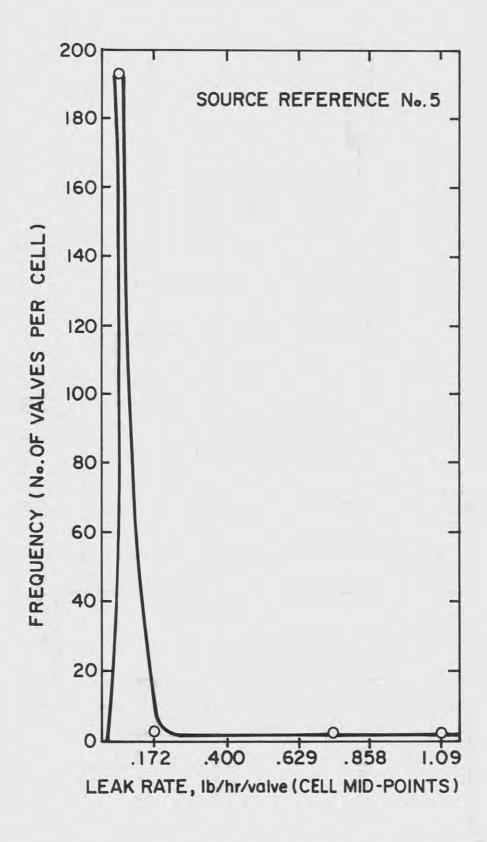


Figure 7. Frequency distribution of valve leak rate data.

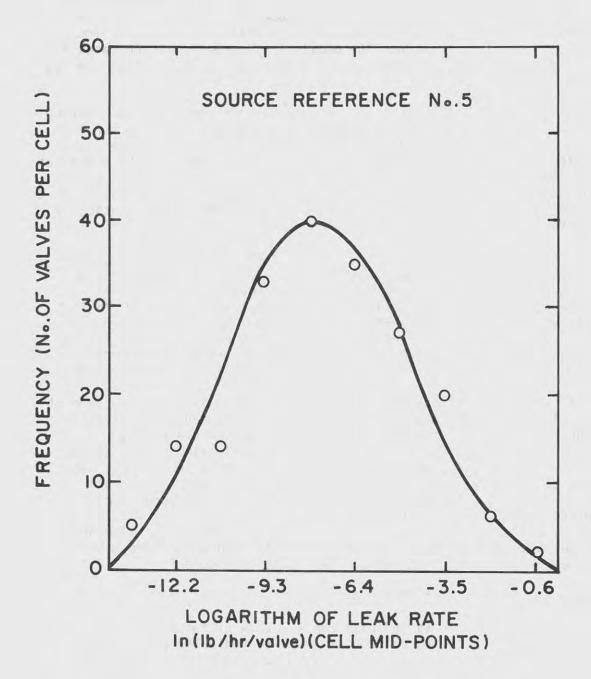


Figure 8. Frequency distribution of logarithms of valve leak rate data.

Table IV contains the emission factors obtained by following the above procedure for three different product lines at the petrochemical plant. When all of the data from each product line are used as single data set, a value of .64 lb/day per valve is obtained as an emission factor. This value represents the population average emission rates for leaking valves in the petrochemical plant during the period that the test program was conducted.

This emission factor has to be adjusted by the percentage of leaking valves in the plant to obtain a plant specific emission factor for valves. The initial screening of 10% of the total valves in the plant indicated that 15% leaked. Adjusting the emission rate for the number of valves leaking one obtains an overall emission factor for valves of approximately .11 lb/day. When used with the total number of valves at a plant this valve would provide an estimate of the total contribution by valves to the total fugitive emission burden.

The .11 lb/day compares well with the AP-42(6) emission factor for valves of .15 lb/day. But the .11 lb/day valve is considerably larger than recent values obtained by Meteorology Research, Inc.(MRI), at Atlantic Richfield's Elwood California Gas Treatment Facility. MRI's results were based on a very small size and the use of the arithmetic mean. Also, recent Radian results employing the geometric mean with a large data base obtained from their petroleum refinery measurement program compare well with the results obtained during the Exxon study.

Before any of the emission factors contained in Table IV are used at a specific plant, data has to be obtained on the percentage of leaking components. This data can be obtained by use of the OVA or soap solution. Once an estimate of the percentage of leaking components has been obtained, an estimate of the total quantity of material lost can then be calculated. For most calculations of this type the overall emission rate of .64 lb/day per leaking value should be used since it is supported by the largest data base. The result obtained by this precedure will provide a good indication of the quantity of hydrocarbon loss, but age, amount of maintenance, chemical composition and other variables will influence the actual leak rate considerably.

Maintenance and Reduction of Leaks

The values in Table IV indicate considerably different emission factors for each of the three product lines tested. These differences are a direct result of variations in individual maintenance programs. The maintenance programs for each line varied from routine maintenance to a special program designed to reduce unacceptable losses of a costly chlorinated hydrocarbon. The results show that a significant improvement in both the emission factor and the percent of leaking components can be obtained through a conscientous effort and desire to reduce losses.

A concise definition of what constitutes a good maintenance program is currently not available. Also the cost associated with maintenance

Table 4. Valve emission factors.

	Leaking S (Factor (1	Leaking Source Emission (Factor (1b/hr/valve)	Percentage	Plant Product Line Emission
Source Sample Size	Mean Value	30 Confidence Limits	of Leaking Components	Factor (lb/day/valve)
Total Plant Valves (197)	0.031	0.017 - 0.057	15	E.
Product Lines:				
A-Routine maintenance (100)	0.032	0.014 - 0.076	17	.13
B-Improved maintenance (49)	0.019	0.008 - 0.047	16	.07
C-Special maintenance (48)	0.008	0.002 - 0.026	80	.014

programs has not as yet been developed. But the data indicates that inspection and maintenance of valves has the potential for considerable reduction of fugitive hydrocarbons in plants.

The magnitude of the reduction can be illustrated by assuming that a plant has 1000 valves. If the plant had a routine maintenance program, the amount of hydrocarbon lost per day would be approximately 130 lbs. If this same installation has a well executed maintenance program, this loss could be reduced to 14 lbs. Assuming that all 1,000 valves are located within a building having a volume of 100,000 ft³ and that the leaking compound is benzene the 1,000 valves would contribute approximately 600 ft3 of benzene per day to the plant atmosphere. If the air were changed 10 times per hour this would result in a daily concentration level of 25 ppm for a routine maintenance program and about 2.5 ppm for a well-executed maintenance program. Thus, the initiation of a valve maintenance program could be expected to reduce fugitive emissions by up to a factor of 10. Reduction by this magnitude could be sufficient to reduce the need for additional, more costly controls which may be required to meet some of the newer standards being proposed and instituted.

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- 5. Hanzevack, K. M. "Fugitive Hydrocarbon Emissions Measurement and Data Analysis Methods", Paper presented at Symposium/Workshop on Petroleum Refining Emissions, Jekyll Island, Georgia, USEPA, April 26-28, 1978. (Note: The planning and analysis of the test program described in this paper were performed by Dr. Bernard T. Delaney and Paul H. Woods, Jr. Their contribution and that of others at Exxon were not recognized in the Authorship or in an acknowledgement at the time the paper was presented due to Exxon policy.)
- 6. "Compilation of Air Pollutant Emission Factors," AP-42, Third Ed. Plus Supplements, EPA, OAQPS, Research Triangle Park, NC.

* * *

MR. DONATO R. TELESCA: Mr. Ralph Barley will be giving the next talk. He is a Chemical Engineer with 25 years' industrial experience in operation and engineering design. He was recently involved in the redesign of an existing suspension PVC plant to bring it into compliance with the Federal regulations. His talk will be on the reduction of worker exposure during on-stream maintenance in a PVC plant.

REDUCTION OF WORKER EXPOSURE DURING ON-STREAM MAINTENANCE IN A PVC PLANT

Ralph C. Barley Catalytic, Inc. Philadelphia, Pennsylvania

Introduction

The purpose of this brief talk is to highlight a few ways in which worker exposure during on-stream maintenance can be reduced. We have chosen as a background a composite manufacturing facility for polyvinyl chloride.

Reactors

Reactor cleaning procedures have been the subject of the talks by Fred Krause and John Barr before the break. These procedures are an example of a way to reduce exposures to maintenance workers. There are a few additional procedures which can be highlighted relative to reduction of worker exposure during on-stream maintenance.

One of these procedures involves changing out the double mechanical seal on a reactor agitator shaft. Worker exposure can be minimized during on-stream replacement of the shaft seals by two principal approaches. One is to provide an agitator shaft, coupling, seal and gear drive assembly design which permits supporting of the agitator from outside the reactor during seal replacement. Opening of the reactor to atmosphere or entry by workers in connection with agitator support during seal replacement is thus rendered unnecessary.

The other principal factor in agitator shaft seal changeout is the provision of cartridge type double seal design. The mechanical seal cartridge can be removed as an integral assembly. It is therefore possible to replace the seal cartridge in its entirety with a new or reconditioned cartridge. The worker time at the reactor is minimized. And the cartridge which was removed is simply delivered to the maintenance shop for repair.

The working atmosphere during cartridge removal and replacement is checked by a portable detector and personnel are trained to make use of proper respiratory protection, as required.

Another procedure required for on-stream reactor maintenance is replacement of rupture discs. Let us assume for this example that the disc has begun to leak. Now, the reactor must be taken off the line and made safe relative to replacement of the defective disc. By following well defined regulation procedures, the reactor is made safe so that when the disc assembly flanges are broken there is no pressure under the disc, and therefore no leakage to atmosphere.

Worker time at the reactor can be further reduced by using complete disc assemblies in the design, so that the new disc is already fitted into the replacement disc assembly when the new disc is delivered to the reactor location. As in the case of the mechanical seal cartridge, the disc assembly which was removed is delivered to the shop for fitting with a new disc.

The use of complete disc assemblies also improves the reliability of rupture discs, since seal damage and misfit which can occur during field replacement of a disc are eliminated.

Equipment Evacuation

As prescribed in the regulations, equipment can--under certain circumstances--be safed by connecting it to an evacuation path. An example of this approach will illustrate the procedure.

There are usually two large-size filters in parallel on the discharge of the high capacity pumps which transfer liquid vinyl chloride from storage to process. The filter which is on-stream will eventually need to be taken off the line as the pressure drops through it rises toward the maximum operable value. The clean filter can be valved into service and the fouled filter blocked off. The blocked-out filter can then be vented to the gasholder. This filter can then be filled with displacement water. Final removal of vinyl chloride from this filter prior to opening can be done with reduced worker exposure by connecting the filter to the evacuation system. All of these steps are performed by operators.

On-Stream Flow Totalizer Calibration

Flow totalizers on liquid vinyl chloride batching into reactors can require on-stream maintenance in the form of calibration while the plant is running.

An example of a specific system will show that this on-stream maintenance procedure can be done with reduced worker exposure.

Two totalizer systems are installed in series on the same vinyl chloride liquid flow path. It is assumed that as long as both totalizers are in close agreement, there is proper reliability in their performance. If the totalizer loops develop a discrepancy, they can be checked by running water through them from nitrogen-padded weigh tank at a steady flow-controlled rate. Usually, one totalizer is found to be out of calibration and in need of service. The system is designed so that this totalizer can be by-passed, blocked-off, and removed after proper safing procedures have been carried out. The repaired item can be shop calibrated and reinstalled. Both totalizers (which are now once again in series) can be double-checked by the water weight vs. time method described above.

It may be worthwhile to mention a variation of the system just described. In some installations it is desirable not to put water through the meters. In this instance, vinyl chloride liquid can be run from a VCM weigh tank to and through the meters. The use of liquid VCM makes it unnecessary to run water through the meters to check or calibrate them.

Thermal Expansion Hydraulic Relief Valves for Liquid Vinyl Chloride

There are numerous lines in a PVC plant which carry liquid vinyl chloride. The vinyl chloride liquid can be blocked in so that as the liquid expands in a line because of temperature rise, the pressure tends to go up to undesirable high levels. If this tendency towards higher pressures goes unrelieved the trapped liquid can try to force its way past manual block valve stem packing, control valve stem packing, etc. At worst, the pressure rise could cause sudden failure at an unpredictable location; for example, a line could split open somewhere in the piping run in which the liquid is trapped. Events such as those above could result in worker exposure during on-stream maintenance.

The thermal expansion problem is relieved and avoided by providing hydraulic relief valves at places in the system where trouble from trapped liquid can arise. The discharge from these valves shall always go to a safe and captive part of the system, such as to an upstream surge vessel or to the recovery train.

Pinch Valves

Improvement in design is an on-going activity, which can be pointed up by citing an experience with pinch valves. In the original design the fingers which press on the boots to close off the valve were tearing the boots. Unexpected boot failures could have caused surprise exposure of workers to vapors from unstripped polymer slurry. The pinch valve fingers were modified and lengthened. The improvement in finger design plus routine turn around maintenance reduced a potential onstream source of worker exposure.

Incinerator Maintenance

Incinerator is often the final abatement step prior to atmosphere. Thermal incineration equipment must be capable of running at temperature and space velocity conditions which insure complete reaction of the vinyl chloride component of the vapor stream to hydrogen chloride, water, and ${\rm CO}_2$.

The incineration step provides a means of taking nonconforming residual vapor streams as feed, and discharging innocuous effluent to the atmosphere. The incineration equipment must incorporate necessary interlocks for safe operation, and must perform on a demand basis with complete reliability at all times. Therefore, two incineration paths are

provided in parallel, with each parallel system sized for the full process vapor flow capacity. One incineration equipment line is kept at the ready, while the parallel line is on-stream. This continuous 100% stand-by provision affords a planned and routine scheduling of on-stream maintenance activities with reduced worker exposure. The entire stand-by line can be checked, inspected, maintained, and put back into the at-the-ready condition while the parallel on-stream line is effectively ensuring full reliable compliance with the regulations.

Rotating Shaft Seals

Rotating shaft seals are required to be double mechanical seals with either pressurizing so that leakage is solely into the process equipment and not to atmosphere, or with ducting so that leaking is to a control system.

The kind of maintenance program which can be followed with excellent results and minimum worker on-stream exposure is typified by the following description. This description is based on actual experience.

In the installation described below, the mechanic or millwright foreman in the plant maintenance group keeps a detailed and comprehensive list called a "mechanical seal survey". This man has an itemized list showing operating time, repair or replacement, and exact specifications for every seal on every pump, agitator, and liquid-ring compressor or vacuum pump in the plant.

There is a principal seal vendor whose representative lives in the area. Through a mutual effort between plant and vendor's representative, and the cooperation of the plant management, a duplicate and up-to-date copy of the mechanical seal survey is kept by the vendor. This situation results in the following two kinds of effective maintenance:

In the first instance, a seal of size and type used in several locations in the process needs to be replaced promptly. Because it is a commonly used replacement item, it is kept in stock in the plant. A work order and shop requisition procures the seal from stock and the pump is fitted with the seal. Routinely and automatically, the plant man duly notes this new seal usage in the mechanical seal survey, and the vendor's representative is sent a copy of the updated survey. Based on a standing order arrangement with the plant purchasing department, the vendor at once orders a seal to be delivered to the plant to replace the old seal.

The seal which was removed can be repaired in the plant shop, or if necessary, returned to the vendor's company for credit value.

In the second instance of effective maintenance, a seal which is relatively expensive and is used in limited service application fails, so that it requires a complete replacement in kind. This seal is not in the plant stock. However, it has been determined in

advance by plant and vendor that this seal can be promptly delivered out of the vendor's distribution warehouse at any time on short notice. The plant contacts the vendor, refers him to the specific item on the mechanical seal survey, and the vendor has the new seal on its way in short order.

The following practices described above, and given the excellent current state of mechanical seal technology, the experience factor with seals in the PVC plant is good, and seldom the cause of worker exposure, loss of production, or unwanted emissions. We should note here that experience in general shows a seal life expectancy of up to three years operation, with a statistical average life of about six months without maintenance.

General

A few general observations will indicate practices which are of proved effectiveness in reducing worker exposure during on-stream maintenance.

- 1. There is an indoctrination of all involved workers so that they are informed about regulations, precautions, etc., which are specific to working in the PVC plant where exposure must be reduced.
- 2. As a part of a formal program, workers about to become active in the area are shown how to use the NIOSH approved breathing air appurtenances. This training includes instruction in both the plugin apparatus which permits a man to access breathing air from a permanently piped system, and self-contained apparatus (often called "air packs") which can be worn by a worker who is making his way out of an area on a emergency basis.
- 3. Well established procedures and parameters established by NIOSH and implemented by OSHA ensure that breathing air qualifying under the "D" quality requirements is available; and that this air can be accessed during normal conditions, and also for prescribed conditions of emergency such as a general power failure.
- 4. For detailed additional information, one is referred to sources such as 29 CFR Part 1910, amended as of January 1, 1977, and the NIOSH publications of approved equipment listed by manufacturer and exact model number.
- 5. In conclusion, the most important factor in reducing worker exposure during on-stream maintenance is perhaps also the most obvious factor, that is, planning for most major maintenance work to be performed when the plant is not on-stream.

* * *

DISCUSSION:

- MR. THOMAS A. ROY: You mentioned breathing air systems that are available suitable for breathing quality air for, I assume, PVC plants.
- MR. RALPH C. BARLEY: I was attempting to highlight some points relative to composite PVC plant, yes.
- MR. ROY: Do you know of a way that meets a D or B quality air requirement, I'd like to know about it.
- MR. BARLEY: I am not directly connected with those two kinds of processes, but I have a feeling that with all these people here, there is probably someone who can answer that kind of question.
- MR. NATHAN W. CLAUSS: In your discussion on totalizers, I believe you said that you installed those in series, and I got the impression that this was to provide some redundancy I am confused.
- MR. BARLEY: This isn't suggested as a practice to be used in each and every installation. However, in one installation it was proven to be useful. There were meters installed in series, and if one of the meters started to drift, it could be blocked out and the other meter would still be performing properly and the blocked out meter could be shop maintenanced and calibrated and put back into service after this, which is a sort of redundancy in the actual practice. After a reconditioned or a new totalizer is put back in, they can again have either the water or the PVC run through them and the calibration can be checked further. Is that what you mean?
 - MR. CLAUSS: Yes, sir.
- MR. BARLEY: There are, obviously, other ways of doing this. These meters have been coming more into prominence, and hopefully, the degree of reliability will come to a point where the redundancy of putting two meters in series, which has been designed by some of our clients, will become unnecessary.
- MR. ROY DEITCHMAN: Your emission rate at the valve, how does an individual valve the emission rate vary over time?
- DR. B. TOD DELANEY: Before we could get the sample of a line, we like the system to flow for approximately 20 minutes. After 20 minutes checking with the OVA, things usually lined up and we got a constant reading. For each sample we took, we took multiple samples and if the sample were not within a certain percentage of each other, we would then throw that valve over.

- MR. JAMES A. GIDEON: Ralph, it seems like much of the state of the art in industrial hygiene is directed toward respirtory protection. I wonder if you also require protective clothing or gloves for use with vinyl chloride and other materials?
- MR. BARLEY: That is a good question, and I wasn't really attempting to get into that aspect of it. I was trying to highlight some points about items of equipment maintenance. However, part of the answer to your question is answered in OSHA 29 CFR, Part 1010, relative to protective clothing. Yes, very definitely if a man is about to enter a reactor, he is required to wear protective clothing. Is that what you mean?
- MR. GIDEON: I guess the question was do you have any data on permeability of different materials or protective fabrics to various monomers or other chemicals? Would you like to have this kind of data in the design of maintenance procedures?
- MR. BARLEY: We surely would like to have it. Your question reminds me of many years ago when I was involved in working with hydrogen fluoride and boron trifluoride. We were told to wear protective clothing, which consisted of coveralls impregnated with paraffin. As soon as the supervisor had their backs turned, we took them off. In my recent observation, there has been tremendous improvement in the comfort and utility of protective clothing.
- NIOSH does have a rather comprehensive list of breathing apparatus, and they call out the exact manufacturer, the exact model number, right down to the last detail. Does that help at all?
- MR. GIDEON: I guess I am fishing to see whether you see the need for more work in terms of the permeability of different types of protective equipment for specific materials.
- MR. BARLEY: Yes. One important thing is to convince the workmen that they need to use this type of item. If a man has been going into a reactor, and a few years ago he was indeed doing it, and either not objecting to the results, or perhaps even enjoying them. It is difficult in some cases to convince the men to use items such as protective clothing. I think that anything that NIOSH could do toward greater comfort and greater ease of donning the clothing would be in order.
- MR. JOHN T. TALTY: I know ASTM has recently established a committee on chemical protective clothing that is trying to come up with standardized test procedures for permeability and such. Hopefully, they will be coming up with some useful methods in the future.
- MR. BARLEY: In some other industries, they have gone into this double change room concept for workers. They come in from home, must strip down completely, and they're given a complete change of clothes,

including underwear and outerwear. On the way back from the plant into the work area, they must go through a shower area. The change room is designed so they cannot avoid it. They dispose of their clothing in the proper receptacle. Until better materials are found, that is one possible way of avoiding the contact problem.

- MR. R. NICHOLAS WHEELER: Have you ever run into a case where a volatile material was absorbed out of the air into the clothing?
 - MR. DONATO R. TELESCA: Can't say I have.
 - MR. WHEELER: Thank you.
- MR. JEREMIAH LYNCH: Ralph, in your two valve system, have you found that it's necessary to have a dead spot about halfway, or do you find that you can have that system working properly without such a dead spot?
- MR. BARLEY: You have your two valves that you turn simultaneously. At one point the process is going through them, and in the other operation the sample is being taken.
- MR. LYNCH: Do you find it necessary to have a dead spot to prevent cross flow, or is that not necessary to your system?
- MR. BARLEY: We have preferred to use a valve that has a dead zone or dead spot in the center, simply because we feel very strongly about making sure there is no possibility that process conditions could be discharged through the sample ports. This is why we feel very strongly about it. We have run into a problem where the people have used the wrong valve and found that there was a discharge during the actual procedure. This is one of the reasons we are very particular about those type of valves. We have had installations where instead, the valves were being operated by two separate air drive actuators. The problem we encountered was that both actuators did not stop the area at the same time. Again, one valve turned faster than the other and allowed some leakage where there were none expected.
- MR. DONATO R. TELESCA: The next speaker is Bruce Lovelace, who received his B.S. degree in Chemical Engineering from Webster Polytechnic Institute in Massachusetts. He joined Dow Chemical in 1968 as a Production Engineer involved with the production of styrene and related monomers.

His talk this afternoon will be on the safer design of manual sampling of liquid process streams. There is a large selection of sampling equipment that can be used, and no single piece of equipment is appropriate for all situations. Taking process samples requires an understanding of the hazards of the process material and the circumstances under which it may be sampled; sample size frequency in using special handling procedures and materials of construction. With this information, it is easier to choose a design that meets the criteria to obtain the desired process sample, and protect the individual during this procedure.

PROCESS STREAM SAMPLING SAFER DESIGNS FOR MANUAL SAMPLING OF LIQUID PROCESS STREAMS

Bruce G. Lovelace Dow Chemical Company Midland, Michigan

(Much of the information about to be given was developed from a paper of the same title written for presentation through the American Institute of Chemical Engineers. Requests for copies of the original paper should be handled through that organization.)

Taking process samples is one of the most common daily operations used in the chemical industry. It can be an activity which may pose a significant hazard to personal safety, if done improperly. Yet, it often received little attention in the design and operation of chemical processing plants. With increasing emphasis on industrial safety, coupled with a heightened awareness of the hazards of handling chemicals, process sampling can no longer be a haphazard or poorly planned operation.

There is a growing need to develop a reasonable approach to safer sampling which can cover a diversity of sampling situations. I will limit my comments to liquid line sampling, however the approach can be applied to other types of sample systems.

Safe sampling involves a careful balance of design and procedure. The design is important, for it can help reduce the potential risks involved. Design implies a systematic definition of the process requirements, and an understanding of the hazards and conditions under which the sample must be obtained. Only with this information in hand, can the proper equipment and procedure be developed to reduce the risk of exposure.

Whether designing for sampling in a new process, or an existing plant, the method is the same. First, the sampling needs of the process must be anticipated and understood. The reasons for taking samples can be grouped into four areas:

- to establish a material balance
- to evaluate process operations
- to trouble-shoot equipment
- to aid in product quality control

Often, by examining the need for a particular sample, we can establish the type of information the sample should provide.

The diverse conditions under which samples may be taken often compound the problems of safe handling of hazardous materials (Refer to Table 1). The interaction of these problems may greatly affect the complexity of the sampling equipment, and the procedures used.

The second step is to interpret each sample point as a distinctive piece of equipment - a piece of hardware which must provide two functions: to obtain the desired process sample; and to protect the individual during the procedure.

This is helped by the use of a specification or data sheet as shown in Figure 1, for each sample location. Each sample point in the process is assigned a unique equipment number, and has its own corresponding design document. On this sheet are summarized the operating conditions for each sample. The definition of these process conditions should be done with the same deliberation that would be used for a pump or a heat exchanger. The specification sheet is used to organize the thinking. It asks specific questions to assist in defining the needs of the sample equipment. The items on the specification sheet are by no means all inclusive, they are simply to act as a focus for evaluating some of the pertinent facts for each sample location. Let's take a closer look at some of its major areas.

This first section is used to help define the hazards asociated with a particular sample material. In it is noted whether the material is lethal, toxic at high temperature or pressure, or is flammable. Space is provided for key items of data. The limits as to the degree of hazard are completely arbitrary. They may be changed according to the interpretation of the engineer, or to reflect the practices of a particular production unit or company.

The second sector focuses on some of the specific conditions involved in taking the sample, such as why is it in, how much and how often is it to be taken. Sample size is very important - it should reasonably match the requirements of the end use. There is no need to take eight ounces of material if only five microliters are required for an analytical procedure. Oversize samples simply increase the potential for exposure, and may create handling problems when finally disposing of the excess. Likewise, the size and material of the sample container should be checked to be compatible with the procedure and process materials. Some materials may also warrent comments regarding environmental toxicity and related handling precautions.

The third major section summarizes some of the other special handling conditions which may be necessary to get a good, safe sample. Foaming, viscosity, chemical reaction, heat treating and ventilation are just some of the items which could have a significant impact on the overall design of the sampler system. At times, characteristics of the materials or the analytical procedures may impose further special handling considerations. All of these factors may require a specialized design that is unique to that particular process sample.

Table 1. Materials and conditions affecting process sampling.

Consider both type of material and physical conditions. Plan procedures to meet needs.

Solid	
Liquid	{ Type of Container
Gas	
Sensitizer	
Toxic	Isolate
Corrosive	
Flammable	Ventilate
	Inert Atmosphere
Hot/Cold	Isolate & Readjust
Pressure/Vacuum	to ambient conditions
	by special handling
Reactive Chemical	Quench/Inhibit
Contamination	Materials/Procedure

PLAN	TION		BLDG.	NO.		CHARGE N				
	FACTURER						/M NO.			
						P.O. NO.				
1	Lethal			Yes	No					
2	Hot - Gre	ter than 6	0°C (140°F)	Yes	No		°C			
3	High Press	Hot - Greater than 60°C (140°F) High Pressure - Greater than 30 psig			No		psig			
4 4	Flesh Burn	High Pressure - Greater than 30 psig					Paris			
5	Toxic Lin	Flesh Burning Yes Toxic Liquid Yes Toxic Vapor Fumes Dust Yes Flammable <140°F Flash Point Yes					-			
6 7	Toxic Vanor Fumes Dust			Yes	No No					
7 5	Flammable <140°F Flash Point Yes No						l °F			
8	Turismubic	1170 1 1	Tusti Tottic	1 163	110		-			
9							1			
10	Sample Typ	10	Solid	Liquid		Gas	Other			
11	Sample Si	76	00110	214010		945				
12	Sample Cor	tainer	Туре	Size		Material				
	Sample Fre	equency	/hr	/da	V	/wk		/mo		
14 3	Sample Fre	oint	*C	7 40		7.111		1.11.0		
15 2	Freeze Po	int	°Č							
16	Environmen	ital Toxici								
16	Freeze Point °C Environmental Toxicity									
18		I amount								
18	Other Samo	le Conside	rations:							
20	A. Foar	nina								
21	D C7-	hing								
22	C. Sub	lime								
23	D. Viscous E. Reactive Chemical									
24										
25	F. Quench Sample G. Heat/Cool Sample H. Ventilation (Positive or Negative) I. Inert Atmosphere J. Corrosivity K. Thermal Shock (Container) L. Pressure Limit (Container)									
26										
27										
22 23 24 25 26 27 28										
30 -										
30 -	U L Pres	L. Pressure Limit (Container)								
32 6	M. Other									
33										
34										
35	Item or Pa	rt	Ma	terial In	formati	on				
36	Process		110		- STIIIU GI					
37		Sample Valve(s)								
2000										
39	Sample Line Vent Line(s) Sample Fnclosure Sample Container Sample Support Plate									
40	Sample S	nclosure			33.3					
41	Sample (Container			72 1	-				
42	Sample Support Plate									
43	Overflow	/								
44		2 mg 2 mg					100			
45	Sample End	losure								
46										
47	Piping Ins	tallation:								
48	ro I						7			
49	St		1 Con 12							
50	5									
SPEC.	. BY							EQUIP. NO		
CHEC		SERVICE								
APP'C							SAMP	LED		
							PECIFIC	CATIONS		
DATE	1	REVISION DAT	EA	8	C	SPEC.				
VEND		ALL INFORMA				14.64.				

Figure 1. Process sampling specification sheet.

The last two sections deal with the details relating to the actual installation of the sample system. Most important are the materials of construction to be used, for both the process piping, and the various components of the sample system. Choosing the proper materials is usually influenced by the corrosivity of the process materials, but construction materials may also effect aspects of sample quality such as color or metals contamination.

Once the requirements or problems related to getting a particular sample have been identified, the job is only half done. There is a large selection of sampling equipment which can be used, no single design may effectively handle all situations. We need to understand the strengths and limitations of each system to choose the one that best fits the needs of utility and safety.

Despite efforts to establish and insist on the use of proper sampling procedures, there is no guarantee that the person in the plant will always wear the prescribed clothing and equipment, or always follow the procedures. Instead of isolating the man, it may be possible to reduce the risk of exposure by isolating the sample in an enclosure. This enclosure has to be simple to use, permit easy visual operation, and offer increased protection of the individual. If it does not fit these guidelines of being simple to use, it probably won't be used at all.

Figure 2 shows a plastic sample enclosure made up in one of our shops. It is a stock design and a few extra units are kept in inventory. It has a Plexiglas(R) window which provides good visibility of the sample inside the box. The window is easily removed for cleaning or replacement, and usually the plants keep extra precut windows on hand. Inside the box, the perforated floor will support a sample container, and allow any overflow or spills to drain into the bottom. This unit can be piped directly to a spill containment system, or the funnel could be outfitted with a collection bottle instead. In actual operation, the sample piping would extend down through a hole in the top of the box, with the control valves mounted outside. The valves should be positioned so that the person would stand in front of the window, away from the opening while taking the sample. Any splash or spray is deflected away by the sheild along the front edge of the opening. This design is very easy to modify with the addition of a door, exhaust ventilation, rubber gloves, adsorbent materials for spill, or any other features required by the process conditions.

A substantially less exotic design is the simple plywood box shown in Figure 3. The front and rear sliding plastic panels serve as doors. Units such as this are relatively inexpensive, but very effective when used properly.

The enclosure shown in Figure 4 was made from a steel Freon can. The plastic window is easily removable for cleaning or replacement. This enclosure also has a swing and bottle holder to place the sample bottle

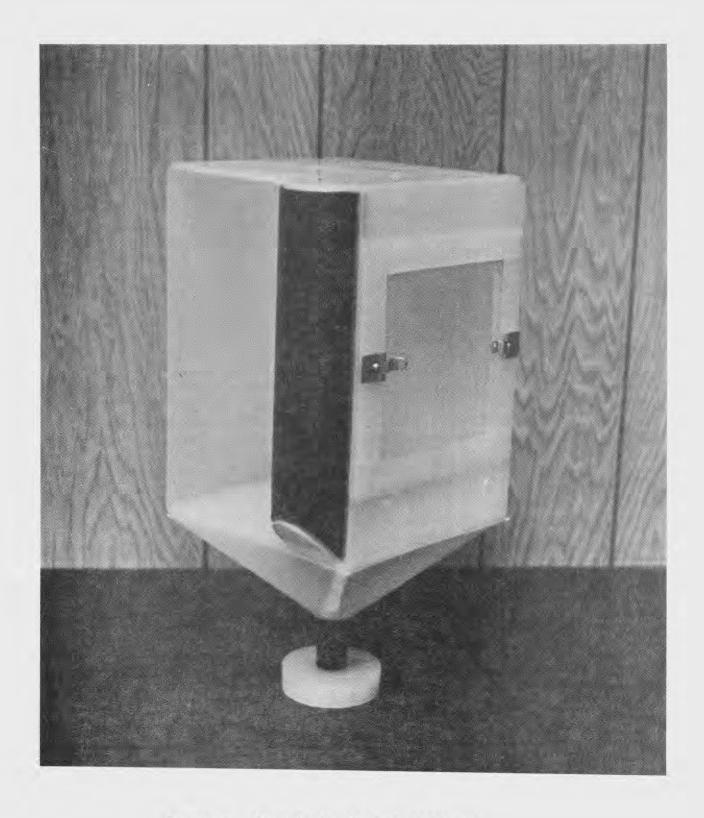


Figure 2. Plastic Sample Box Enclosure.

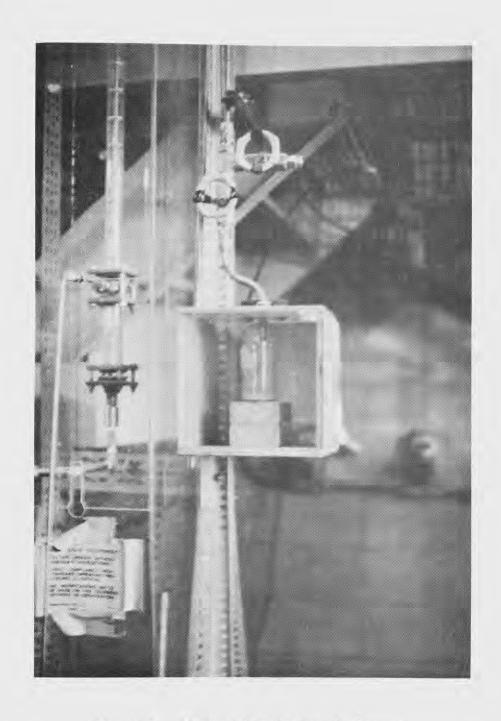


Figure 3. Plywood Sample Box Enclosure.

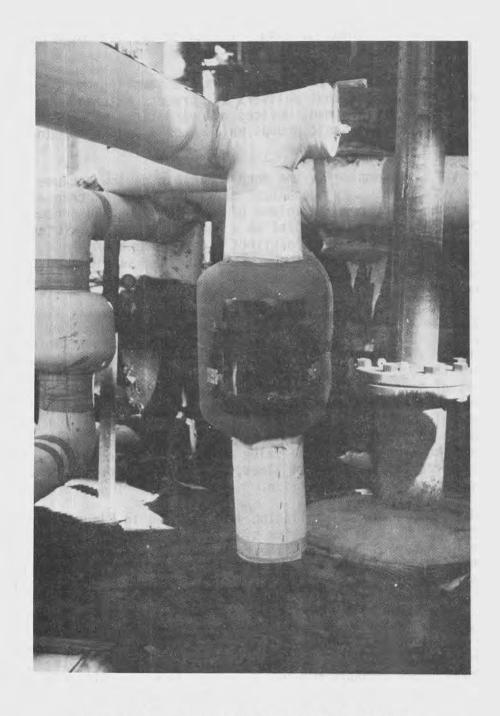


Figure 4. Freon Can Sample Box Enclosure.

in the proper position inside. Metal units such as this may be preferred when high temperatures or chemical solvents may damage plastic materials. The plastic units are effective in corrosive environments. The common key in all of these is simply reduction of risk exposure by containment.

The second part of the sampling system is the sampling device. This is the actual working piece that delivers the process material. Like the sample enclosures, there are many devices and variations which can be used. These fall into two basic groups which I call Direct and Indirect line samplers.

The Indirect line sampler is the more desirable device because of its inherent safety features. By mechanical means, these units trap and isolate a predetermined, precise volume of material from the process line, and then delivers this material to a sample bottle, within an appropriate enclosure. These two distinct steps prevent sample containers at full process conditions. Isolating the sample from the process and restricting the volume improves chances to anticipate and control potential problems.

The simplest of the Indirect samplers is the sampling plugcock shown in Figure 5. The plugcock valve has been modified by adding sample and vent ports to the valve body. In the normal open position the process material flows through the opening in the plug. As the valve is closed, a small amount of material is trapped within the cavity of the plug. When the valve is turned to the full closed position, the plug cavity is open to the sample connection, allowing the trapped material to drain out. This valve delivers a precise, predetermined volume of sample, depending upon the line size of the valve used. The valve may be installed in horizontal or vertical lines, in the main flow, or in a by-pass, in pressure or vacuum service.

An actual sampling plug installation is presented in Figure 6. The sample connection runs from the bottom side of the valve through the top of the sample enclosure. The vent line from the top side of the valve runs down behind the enclosure and connects into the lower part of the funnel, below the support plate. Any spilled or vented materials will be collected in a bottle to be placed under the funnel.

A somewhat more complicated system uses a pair of two position, three-ported valves. This arrangement allows more flexibility in obtaining larger sample sizes. During normal flow conditions, the process material flows through the two valves as shown in Figure 7A. The sample volume is the amount contained within and between the valve plugs. This volume is determined by the length of the piping between the valves. The sample is taken by turning both valves simultaneously. In the 90° position (Refer to Figure 7B), the sample is trapped between the plugs, and is isolated from both process and sample connections. Turning the valves through the full 180° opens the sample ports, and lets the trapped sample drain out.

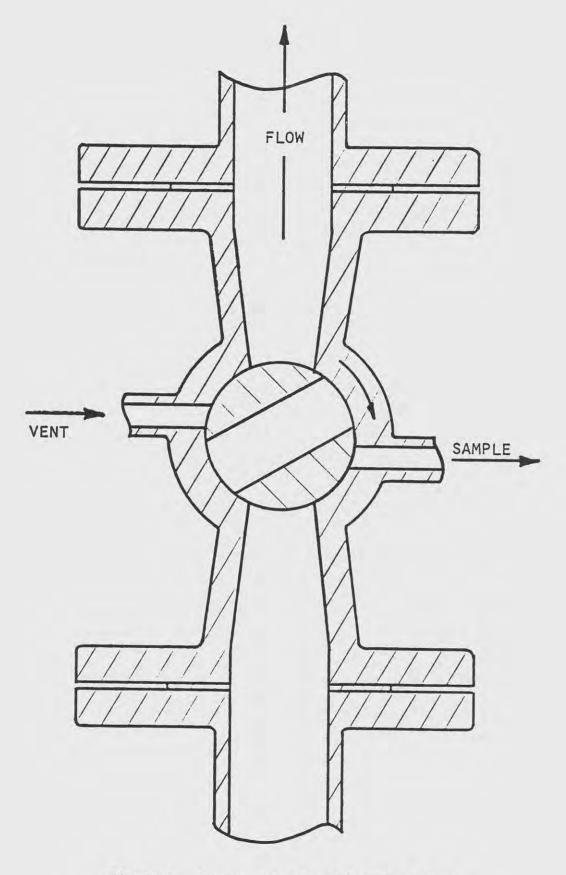


Figure 5. Diagram of a sampling plug valve.

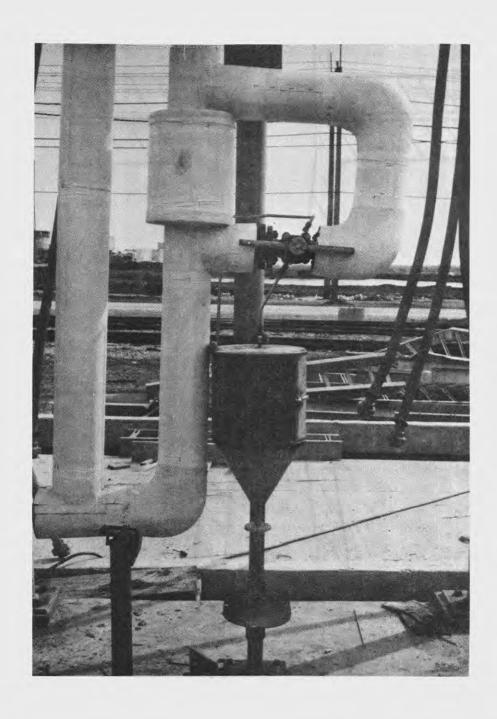


Figure 6. Sampling plug valve, used with a stainless steel sample box enclosure.

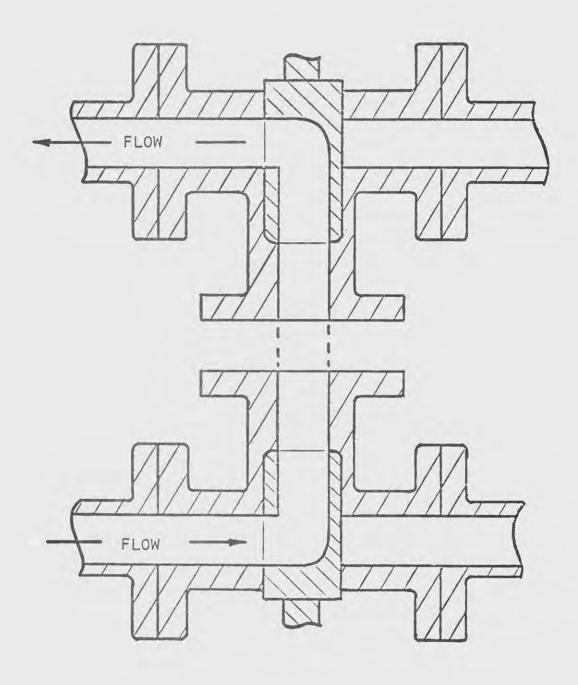


Figure 7a. Diagram of a double three-part valve arrangement normal flow position.

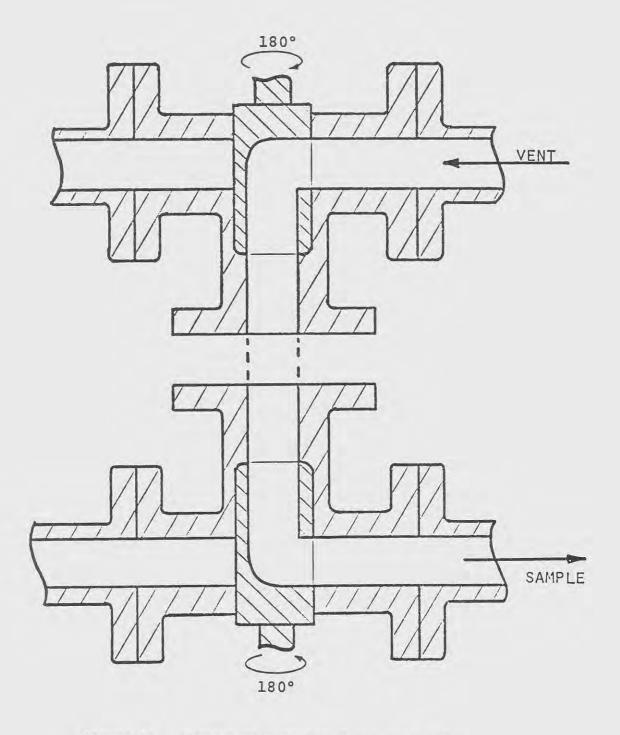


Figure 7b. Diagram of a double three-part valve arrangement - sampling position.

There are two important precautions to be exercised when using this system. The valves MUST NOT be transflow-type plugs, but must offer complete shut-off in the intermediate position. Second, the two valves must operate simultaneously. If both valves do not turn at the same time, full time pressure and flow could be discharged from either the sample or vent ports. There are various gear set and mechanical linkages which can be used to ensure positive, simultaneous movement. In this double valve system, under construction, the interlocking gear mechanism has been removed, and placed off to the side (Refer to Figure 8). When completed, the two valves will be operated by a single handle, and will deliver one quart of sample per cycle of the valves.

There are a number of companies which do manufacture liquid samplers like the ones shown in Figure 9. Typical operation of these units uses a air or hydraulic actuator to insert a hollow piston into a process pipe. As the piston retracts through the barrel of the sampler, a small, precise volume is trapped within the cavity of the piston. The piston stroke first seals the cavity from the process, and then opens it to the sample connection, to which a bottle may be attached. The sampling cavity within the piston usually has a capacity of only a few milliliters, so larger samples may require repeated cycling, either manually, or with automatic timers.

Another method uses a sample chamber attached directly to a process line as illustrated in Figure 10. Sample chambers can be designed to match process conditions and materials of construction, and may be sized for any desired volume. This particular arrangement uses a remotely operated control valve to admit a reaction mixture into a sample chamber. The chamber was preloaded with a quench solution to stop the reaction mixture from continuing. This system takes a good representative sample, but is somewhat difficult to use frequently. Furthermore, it may expose a person to potential chemical exposure during the step of breaking the union connection to remove the chamber from the system.

In the area of Direct line sampling, the piston ram type valve is finding increased use (Refer to Figure 11). This valve has a retracting piston which ensures that the process connection has no dead zone cavity, and that the valve is rodded out with each use. This makes the valve useful with process materials which could freeze or plug in the process connection. The disadvantage of this valve is that it is Direct line sampling - that is it has the potential to expose a person to full line pressure and flow. There is little positive control over the amount of sample discharged, and the valve may be difficult to close quickly. However, these potential drawbacks can be reduced significantly when this valve is used in combination with other sampling features, such as a sample chamber or sample enclosure.

Still another method of sample taking involves the use of a hypodermic type syringe to withdraw material through a septum attached to the process line (Refer to Figure 12). This method is restricted to

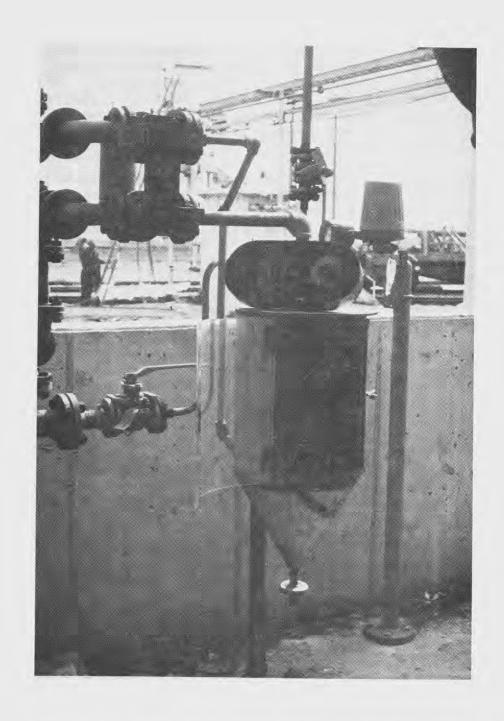


Figure 8. Double three-port valve installation with interlocking gear set removed.

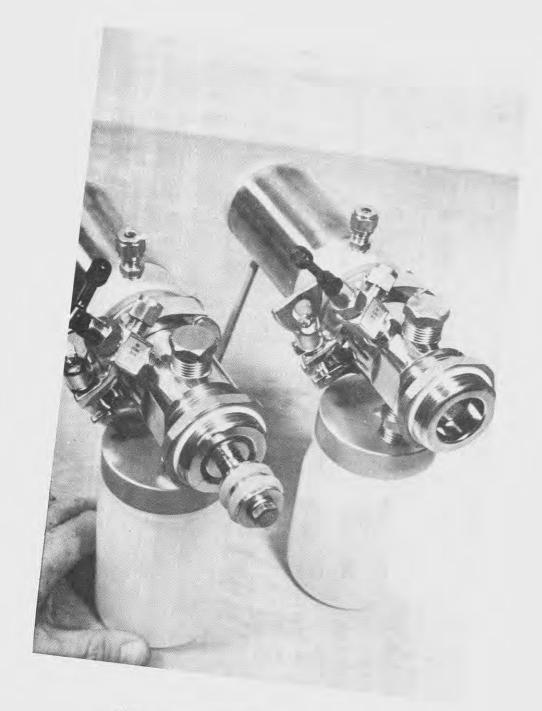


Figure 9. Isolok(R) liquid sampler. Courtesy of Bristol Engineering Company

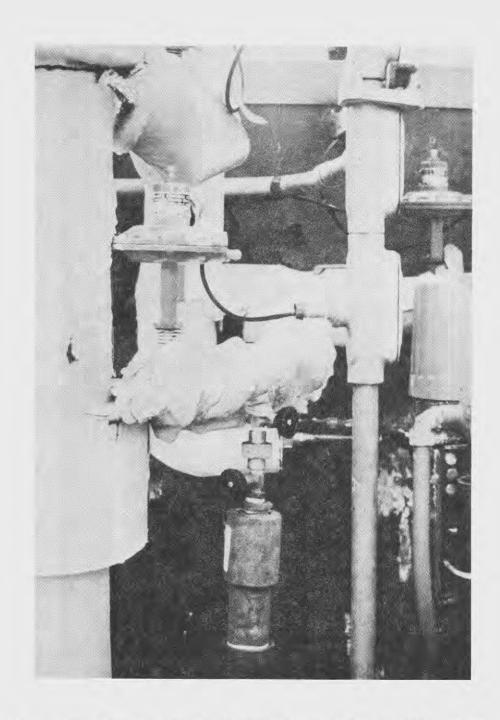


Figure 10. Sample chamber filled by remotely operated valve.

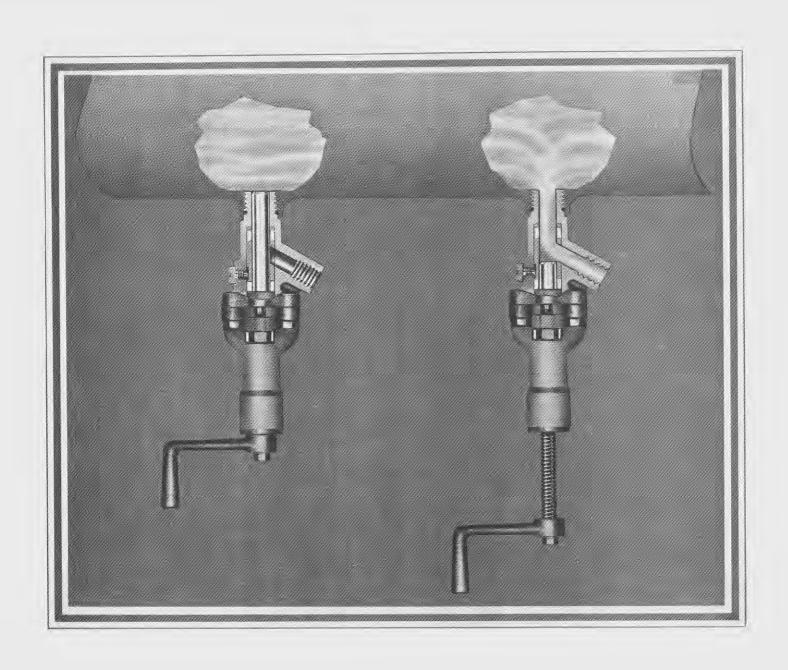


Figure 11. Strahman piston type sampling valve.

Courtesy of Strahman Valves, Inc.

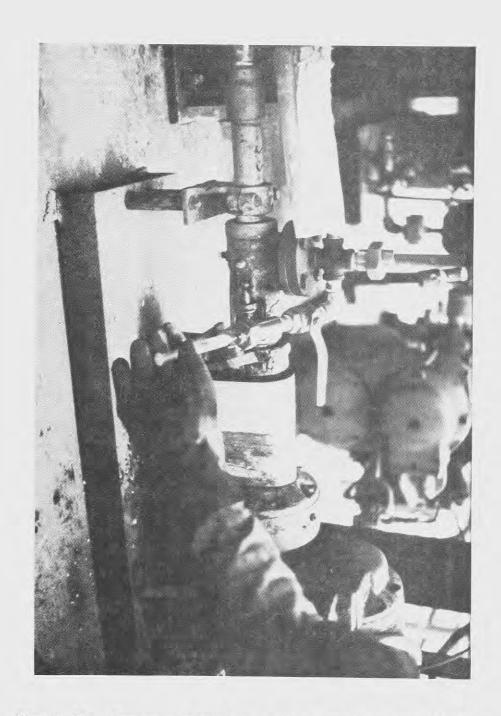


Figure 12. Septum and syringe method sampling installation.

conditions where the required sample is very small, the process material is nonviscous, nonfreezing, or does not contain solids which may clog the needle. Also, it should only be used with chemicals which will not attack or degrade the septum material. In this installation, the septum is at the end of the pipe stub, and can be isolated by means of the shut-off valve. However, this arrangement creates a substantial amount of dead volume. To manually bleed the dead volume out through the red handled bleed valve defeats the purpose of using the syringe to reduce personal exposure to hazardous chemicals.

An improvement on this method uses a three port, or a cross pattern valve shown in Figure 13. This valve is installed in a by-pass loop of the process line. The process material flows through the side ports, and the septum is installed on the bottom port. When the valve is opened, the needle may be inserted through the septum to extract a sample from the flowing stream. When the valve is closed, the septum is isolated from direct exposure to process conditions, and can be replaced with minimum interference and risk. The amount of dead volume within the valve is negligible, and the valve can be fitted with a needle guide to reduce damage to the syringes.

In conclusion, process sampling is a necessary facet of daily operation in the chemical industry. To be done safely, it can not be left to chance. The risks involved with sampling can be reduced by good design, and well planned and followed procedures. The sampling need must be anticipated and carefully considered; the sampling equipment should be uniquely identified, and selected or designed. The final design will be that sample system which best meets the requirements of process conditions, sample quality, safety, and costs.

* * *

DISCUSSION:

MR. JERRY SCHROY: What is the potential for leakage due to needle punctures or permeating simple diffusion through the organic material through the membrane. Is there any possibility of the process pressure enhancing leakage through a needle puncture?

MR. BRUCE LOVELACE: On this particular application we were using the septum in ethyl benzene process stream, the rubber that we were using was a silicone rubber and we would periodically change the septum whether it developed a leak or not. By using this particular valve, we only had the septum exposed process conditions at the time that we needed to get a process sample, the rest of the time it was isolated so that it wouldn't develop a leak. Care should be exercised in selecting the septum material both with regard to mechanical durability and chemical permeation.

MR. SCHROY: Have you ever reversed the situation, where you put the needle in the process and the septum in the sample bottle?

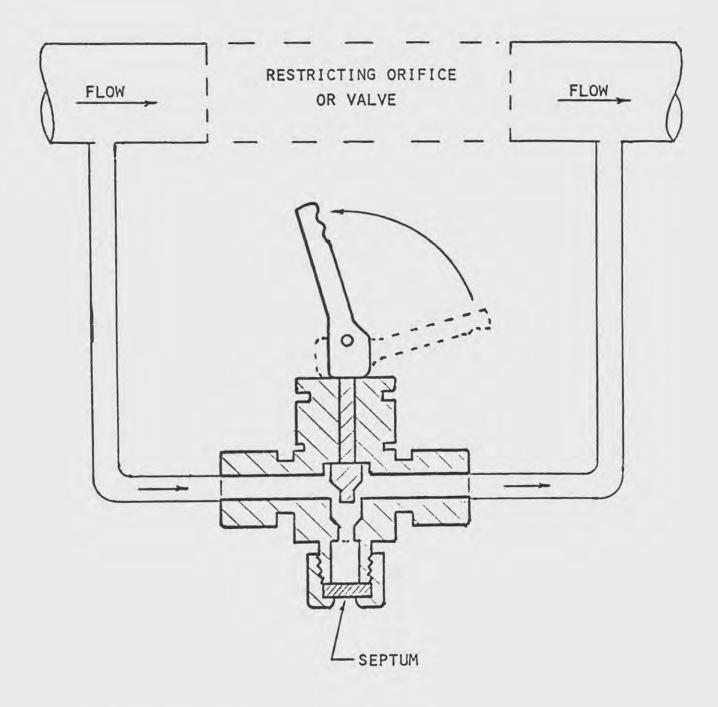


Figure 13. Diagram of syringe septum mounted on an isolating valve.

- MR. LOVELACE: No we haven't. That is something we would like to consider.
- MR. SCHROY: Your paper that was based on the AIChE paper, what meeting was it given at?
- MR. LOVELACE: The paper has been written for some time but will be presented at the 86th National Meeting in Houston, Texas, this coming April (1979). It will be part of the Safety and Loss Prevention Symposium.
- MR. SCHROY: You have two valves which turn simultaneously in one valve position, the process flows through the valve and in the second position, the sample is taken. Do you find that it is necessary to have a dead zone when the valve postion is changed from position 1 to position 2 to avoid process conditions being exerted on the sampling system to avoid cross-flow or is that not necessary in your system?
- MR. LOVELACE: Yes, a dead zone is necessary. We have preferred to use a valve that has a dead zone in the center simply because in these particular applications we feel very strongly about making sure that there is no possibility that process conditions could be discharged through the sample ports. There have been applications that ran into problems where people have used the wrong valve and have found there is discharge during the actual procedure of turning the valves. We have also had installations where instead of a hard mechanical linkage to operate the two valves, the valves were being operated by two separate air driven actuators. The problem that we encountered is that both actuators did not respond to the air signal at exactly the same time and again one valve turned faster than the other one and allowed some leakage through one of the ports where they were not expecting it, this is why we are going back to a hard mechanical linkage.
- MR. SCHROY: In dealing with a needle and septum sampler, have you ever reversed the position to put the needle on the process side and the septum in the sample bottle?
- MR. LOVELACE: No, we have not used this technique, in my experience, however I see no major problems in doing this. (This technique is highlighted in Chemical Engineering, March 12, 1979, Plant Notebook Section.)
- MR. DONATO R. TELESCA: The last speaker this session will be Arthur Spiegelman, who has his B.S. in Chemical Engineering from Cooper University. He is a registered Professional Engineer in New York and New Jersey, and has 25 years experience in the insurance industry. He was Vice President of Engineering of the American Insurance Association until he retired in 1979. At present he is a consulting engineer in all phases of loss control. Mr. Spiegelman's talk will be on the role of the insurance industry in motivating loss prevention measures.

THE ROLE OF THE INSURANCE INDUSTRY IN PROMOTING LOSS PREVENTION MEASURES

Arthur Spiegelman Professional Engineer Millburn, New Jersey

One advantage of being the last speaker on the program, the bugs have been worked out of the sound system and the taxis have all gone home with their noise. It is just you and me to talk this little problem over. I am going to try to give you an overview of the way the insurance industry looks at loss prevention.

A friend once taught me how to sell life insurance while I was going through college. He did something that I thought was interesting. He would take a dollar bill out and place it right on the table in front of the client, and he'd say, for every dollar you put up, I will put up a 500 dollar bill. If you die during the year, your family will collect the \$500. If you don't, we are going to keep the dollar bill. It was something that you could see and understand. This is essentially what the insurance industry is doing. Insurance is taking a smaller amount of money, for the cost of a premium. They're saying that if you sustain a loss, we'll pay for it. So, it is a business of risk evaluation. It is a business of trying to determine how much of an exposure exists, and how do we determine an adequate pricing mechanism.

While the work that we do is humanistic in the sense that we are trying to prevent loss of life and property, we are doing it with an economic factor in mind. If we sustain heavy losses, we are going to pay, and we sustain a loss in the rating column at the end of the year. We're in business, like any other organization, to make money. So, we're attempting constantly to try to evaluate the technical aspects of all insurable risks. We have been doing this for a number of years. At the turn of the century, we developed the first Building Code in the United States, which was followed by others. We turned out the first Fire Prevention Code, First Electrical Code, we started (U.L.), we started the National Fire Prevention Association (NAPPA).

The insurance industry Underwriters Laboratories are well-grounded in the field. They have people serving on over 200 technical standards-making committees. In the American Insurance Association, my former organization, we had some 240 insurance companies that bought technical consulting services from us. As an organization, we were very much interested in the job that they were doing. It was our job to keep their 10,000 engineers on top of their jobs. I use the term engineer loosely as they are not all engineers. Some of them work in the field of industrial hygiene, some of them work in the field of nuclear fission and fire prevention. All of these people work together in an attempt to prevent losses of every type.

Industrial health has interested us for a long time. The insurance industry has 15 large laboratories presently operating in the United States, and over 200 people working in the field of industrial hygiene. You should recognize that we are doing that in spite of the fact that at the present time, the losses due to occupational health only constitute three percent of our worker's compensation claims. So, we are looking at this in the long-range view. We anticipate that it may increase; we hope that it doesn't.

Half of the three percent are problems associated with noise. This has been with us for many years. One and a half percent of the health problems are actually due to people being exposed to various chemicals. One of the problems with worker compensation, as we see it today, it is like insuring a time bomb. You feel that some day it will explode. We are faced with the problem of attempting to evaluate it, and we certainly have been trying to do our homework to find ways that we can evaluate the size of the health problem accurately.

Consider a person who goes to work in a plant today, and is exposed to some chemical. He may not observe the onset of his occupational sickness for 20 years or more. Insurance companies have been insuring that man at today's rates, and with the present rate of inflation, receiving premiums at today's dollars. However when he finally does come down with the disease, the insuror will be paying him at an inflated rate of 20 years from now. This brings a great many problems to our minds that insurors never had to face in the straight accident type of worker's compensation. If a person fell and broke his arm, you saw the damage immediately, and you put in the proper amount of reserve. You could cover it, and you could tell at the end of the year if you were losing money or making money. This is not true for long term occupational disease problems.

The mission of the insurance engineer is to determine whether the proposed risk is insurable, and in that sense, he examines the risk even before any insurance money is placed on the line. The second mission is to advise his management as to what conditions are acceptable and what was required for the insured to minimize his exposure. Now, in no way does the insurance engineer accept the responsibility of the insured for safety. In other words, because one of these people has entered the plant and gone into it and looked at it and spoken to the management, management still bears the entire responsibility for any mishap that occurs.

For many years, insurance companies were pretty much alone in the safety field. Industry wasn't too interested in what was happening; government was just taking a passing interest in it. Anything that we did develop was passed on to industry. We have had hundreds of meetings with industry people on this very subject.

A major part of the current development of control technology, is to be sure that you make use of the private sector's expertise in developing acceptable standards. Unfortunately, if you look at the experience of some of the federal agencies, when they attempted to take standards and enforce them as regulations and laws, they found out that standards were not made to be laws or regulations. Most of our technical engineering standards were developed to guide engineers in the field, to assist them in producing a product and in carrying on the same job safety. When they were made into mandatory standards, they found that they were far too exact for enforcement. In addition, it required highly sophisticated personnel to spend a very large amount of time in going through a plant to see if every screw was turned and every nut was in the right place. Basic concepts should be sought.

I would hope that in the future, when NIOSH goes into the control technology business, that they heed the American Institute of Chemical Engineering, which has recently started a safety and health division and is in a position to bring together all of the facets of the industry, the federal establishment, state government, insurance industry, and all of the people who are interested, in developing a safer working environment.

About ten years ago, the insurance industry looked at the chemical industry with a pretty jaundiced eye. We suddenly found that no matter what we did we lost money. The industry was practically becoming uninsurable. What was happening to this industry? Well, it was going through a great many technological changes and loss control personnel were unable to maintain the pace.

First, the industry was moving ahead, into the single train plants, so that if you had four, five small lines producing a chemical, they were all combined into one large single train. The result was that when you developed a leak, it was a catastrophe. What we also had to insure was the continuity of their business. We found out that they couldn't replace huge compressors. When we tried to check the fires, we found that the fires were too large to be controlled by ordinary equipment. When a leak developed and a huge cloud of a flammable liquid came out as a vapor cloud, we simply did not have the technology to control it. Some tremendous losses have occurred over the last 20 years.

At the same time, the insurance industry was developing a new type of policy, something like your homeowners' policy, - "a multiple risk" insurance policy. In 1969, we had a premium of \$20,000,000 in this type of insurance. Last year, we sold \$4,000,000,000 of this type of insurance. This signaled the development of group engineering which covered all of the risks.

With this change in the offing, we decided to look at the chemical industry and find out what we could about it. We turned out a survey report ten years ago. It was a survey of the chemical and allied industries. This year, we came out with the second revision of this

book. After looking over about 3000 large losses ten years ago, we found out that these losses fell into nine major groups that we could relate the hazard factors to.

Hazard Factor	Number of times Assigned	Percentage of Total
(1) Plant Site Problems	16	3.5%
(2) Inadequate Plant Layout and Spacing	9	2.0%
(3) Structures Not in Conformity with use requirements	14	3.0%
(4) Inadequate Material Evaluation	93	20.2%
(5) Chemical Process Problems	49	10.6%
(6) Material Movement Problems	20	4.4%
(7) Operational Failures	79	17.2%
(8) Equipment Failures(9) Ineffective Loss Prevention	143	31.1%
Program	37	8.0%
Total	460	100%

Plant problems, was the site adequately investigated? Was there an adequate plant layout and spacing between equipment? Was the structure in conformity with use requirements and the chemical adequately evaluated? Was the chemical process hazard problem adequately considered? Was material evaluation during the unit operations properly considered? Were there operational failures and equipment failures? And finally, Ineffective Loss Prevention Programs exist essentially where top management isn't paying enough attention.

Ten years ago, most of our losses were in the fields of fire and explosions. Now, we have a number of boiler and machinery problems, an item that we didn't adequately cover in the 1960's. But, in 1968, very few were talking about the problem of occupational health. Inadequate site accounted for 3 1/2% of our losses, improper plant layout accounted for about 3 1/2% and improper procedures 1 and 1/2%. Material evaluation, which in 1968 was about 20%, has come down to about 10%-11%. Improper process evaluation, which remained pretty much at about 10-12%. Now, unit operation went from 4.4% to 13%. Operating failures from 17% to 28%, and equipment failure still was the major component. It went from 31% to 29%.

These facts are interesting to us, because from an underwriting standpoint, for many years we were underwriting on the basis of the nature of the material and very little else. The material was evaluated, to determine if it was toxic, explosive, flammable or was it corrosive

causing some damage. One of the things that we did notice in this survey is that we were finding a tremendous number of explosions reported, see Table below.

Study of the 317 case histories with regard to placing them in categories of (1) fires, (2) explosions, or (3) both fires and explosions, reveals the following:

(1) Fires	(only)	122	38.5%
(2) Explosions (only)		111	35.0%
	and Explosions	74	26.5%

Now, while we have about 18 volumes of standards for fire hazards, and we have many standards and criteria for chemicals, we have practically nothing written on explosion on methods of anticipating explosions, and methods of evaluating the amount of damage that will occur when we do have an explosion. Let's just go through these hazard factors. I would like to show you how they apply to the health problem as we consider it.

The Plant Site Problem. Poor location with respect to adequate water supply; unreliable emergency units; traffic problems for the emergency equipment, also, exposure to the public from the standpoint of pollution with the site of the plant too close to it; inadequate plant layout and spacing. Here, we ran into the problem of being unable to do proper inspection and maintenance, exposure of high value equipment that was very difficult to replace, lack of proper emergency equipment facilities in the event of an emergency. If you have a process that contains a very hazardous and toxic chemical, and it is located right next to some potentially explosive process, one explosion will open up the other tank, and you wind up with real problems.

Structures not in conformity with use requirements. The fact that you do put a plant into a building increases your exposure of your people who work in the plant. It also increases the explosion potential. The physical structure may not be in conformity to use, and we do find a great many plants are transformed from one type of chemical process into another. Too often, the major factor is that the plant and building is available at a site, that it is useful. The owner of the plant will therefore use it for that purpose despite the fact that the plant will not serve as a good building from the standpoint of explosion resistance.

Not too long ago, 47 people were very badly hurt in a factory in Long Island City. Some of these people died and 35 of them were severely burned. Material evaluation is probably one of the major things that we are concerned with. Insufficient evaluation from the health aspect has been with us for many years. NIOSH has a list of 2400 suspected carcinogens and is presently regulating 15 or 16 of them. We need to work to bring together the information to conduct an intelligent evaluation of the problems.

Much of the evaluation of fire hazards has been done over the years; very little on the health aspect. We need a great more on the explosion aspect of hazards. Some of the information that is required when one of our engineers goes into a plant is not just the name of the chemical, but we want to find out where the commercial grade chemical is, and what contamination factors exist when a quantity of the material is released. These are some of the basic things we are trying to find out. We also want to know what are the end products. We run into a great many problems. There is a lack of information on many of the processes, mainly because almost every single company considers its process a proprietary sort of information.

Over the last few years, many companies have started sharing this information. When you hire a man from company to company, he takes along a lot of that information with him. When a plant blew up in Tonawanda, New York in 1955, we were rather surprised when we went to investigate that explosion - we found out that many of the people who used the product had little knowledge as to the nature of the materials they were handling.

One of the things that concerns us is the operation and physical transformation of chemicals. Just naming chemicals and saying, we will rate this chemical with regard to toxicity or saying this is a hazardous item in itself is to miss the point. When changes in the physical form of the chemical occurs, such as venting it off as a fine mist, that chemical is no longer the same as it was originally. Fine powders are much more easily absorbed into the body, brought into the lungs and absorbed through the skin's pores. One of the things that has to be spelled out when we're talking about evaluation of the risk, is the nature of the material that we are handling. Not just the name of the chemical, how it is being handled and at what temperture? If a leak develops, is it possible for that material to form a gas or vapor, or will it remain in liquid form?

One of the items that I can see coming up for review is operational practices and training. As our technology changes, too often we don't change the training of the operators to keep pace with the technology. We find that a lack of detailed information on what is changing puts the operators in the dark. Subsequently, if an emergency develops, it can result in inadequate handling of the emergency. We would like to see a good operating manual that has a description of the equipment, of the process, the material properties, the start up and shut down procedures, normal operating procedures, and safety considerations. We would like to see what precautions to take. These are some of the items that should be every day knowledge, and all of these things together affect the safety of the operation.

Equipment failures are one of our biggest problems because the hazards are built into the design of the equipment. It has taken us a long time to get the "safety and health division" put up on a division level, so that we are on an equal footing with the equipment division and the design division in the American Institute of Chemical Engineers.

I remember when I first worked on this technical survey, I went to a number of larger consulting engineering concerns, and asked them, what standards they were using for various types of equipment? They showed me volumes that looked like the Manhattan telephone book. This is the design standard for one company, and no two companies used the same design standards for equipment. They had spent a lot of money to make that process work, they weren't about to give it away for nothing.

I think we have almost come to a point now where we have to share some of this knowledge. Otherwise, we are going to have some governmental agency come up and dictate to us that certain factors have to be in the equipment. I think it is about time that we recognize that we can afford to share safety knowledge with one another.

These are some of the considerations that should go into design of the equipment; the reliability of the unit, ease of operation, flexibility, provisions for the future, adequate emergency shutdown facilities, standardization. All of these things are essential. It might be interesting to note that in pollution control, we are not only interested in seeing that the operator of a particular tank of toxic chemicals has some means of warning that there is a leak in the tank, but we also desire air automatic shut down and alarm device. This is something which is still to come in many of our loss prevention surveys. If loss prevention comes as an afterthought, and I am talking about every kind of loss; fire, explosion, health, worker exposure, economic, pollution control and general liability, any of these losses, it will be more expensive and more of a job to sell to the top management of your companies.

If loss control is worked into the economics of the project, if it is shown that by running a safer plant, you're also running a plant that is economically sounder, than top management will look upon this with a much greater appetite. You can see, just from these items that we have detailed, that it is possible to conduct a lecture on parts of each of the subjects. After working in the business for 30 years, and working in the laboratory for ten years as a chemist, I saw many things that eventually drew me into the safety field. It is more important today than any other time in our history, as we have greater opportunities for achievement. Now, if I may wind up with just a few more thoughts that I scribbled while I was sitting here today, there are no such methods for anybody to prescribe a loss control technology that will guarantee loss-free or a risk-free industry. The total loss control concept which I just discussed here, is just one approach to the project. The reason that we're approaching it this way is that we feel that in too many instances, people think they can only control losses by laboratory testing of materials and "total loss control" is necessary. You have to touch all the bases if you want to hit a home run in this ball park.

One of the hardest problems that we have to face as a society today, is to determine what is an "acceptable" risk. In no way can you have a completely risk-free society. It is one of the problems that is being

faced by regulators. How far shall we go? One part per billion? How safe do we actually want industry to be? The insurance industry is constantly facing this problem. It puts money on the line to support its opinions. We feel that you should strive to be as safe as you can. However, that must be much safer than you are today. Unfortunately with some of the things that have come up in recent years, such as cancer, or suspected materials that produce cancer, the public wants to be entirely rid of them. We don't know enough about the subject to really guarantee that whatever we're doing in the field, we can completely rid the public of this entire problem. However we do know that we can improve on what we're doing, and so we should encourage all the people who are working in this direction to try to achieve an acceptable risk, one which we and society, through meetings like this can agree on.

* * *

DISCUSSION:

MR. D. G. IRWIN: You said that of the worker compensation cases, some were chemical, some were noise and that the chemical part was a time bomb with more claims in the future. Can you give us some example of settlements that have had to be given recently to workers due to chemical exposures?

MR. SPIEGELMAN: I don't have a list of those claims, but there is hardly a day that I can pick up the paper and see where workers in some plants have discovered that they have become sterile. Workers in one plant right near my home in New Jersey, recently went on strike. One of the major reasons was the health problem that they were experiencing at the plant. From our standpoint, the very fact that the insurance industry would set up 15 different laboratories and employ 200 people in those laboratories for hygiene purposes should give you some idea that we have become aware of the fact that if you work in a plant with a chemical, you don't die all at once, but die a little bit every day from that type of exposure. Therefore, it is hard to pick any particular moment when you should put your claim in. Sometimes it is at the end of a life. When doctors perform an autopsy and find out that the liver isn't there anymore, it is too late. I think we have come to a point where intellegent people are looking at this. We have lawyers looking at it as well as chemical engineers and chemists who see that there is a serious problem in the future.

MR. JOHN T. BARR: This is more of a comment than a question. The industry is perfectly aware that insurance companies are pretty much in agreement with the regulatory agencies. There is no limit to the money that our industry has spent to reduce our risks. We are here by mutual consent. So the record need not go uncorrected as to a misapprehension that has been expressed here today, the NIOSH list of some 2,750

suspected carcinogens. Flatly, there has not been a list of suspected carcinogens, but materials which will be investigated to see if they could be carcinogens. This is what it says in the preface of the book. Now, OSHA hired people to write carcinogen standards. They hired them to go through that list of carcinogens, suspected, possible carcinogens to see how many of them would be classified as carcinogens. Something like 85 turned up. There is another laboratory study in addition, and they have come up with a different number of different ones which shows the confusion, but their number is something less than 300. That is something different than 2750. Three hundred is enough. Let's don't exaggerate the problem.

MR. SPIEGELMAN: Before you accuse people of exaggerating, I think you ought to be accurate as to what I said. I said there were 2450 on the list, the NIOSH suspected list and we're presently regulating 15 of them. Even taking your figure of 85, that would be 15 out of 85 and I think we ought to be concerned about the other 70 of them that are not being regulated as to our writing insurance for the people exposed to them.

MR. BARR: The point I want to make is we should do the things which we do with a sense of perspective so that we understand the actual problem. We understand what we have available to us; we understand where we are going. We are doing it in the light of the best numbers that we have available.

SESSION III CONTROL OF WORKPLACE

MODERATOR

JULIUS H. BOCHINSKI

Enviro Control, Inc. Rockville, Maryland DR. JULIUS H. BOCHINSKI: Good morning and welcome to Session III of the Symposium. I am substituting for Mr. Lou Belizsky of the United Rubber Workers, who could not participate as a moderator and speaker because of very urgent business matters. The first part of the session will cover three automatic monitoring systems in use in industry for determining concentrations of hazardous materials in the workplace. A question and answer period will follow the presentation of the papers.

Our first speaker this morning is Mark Soble. He is the Commercial Development Manager of the Hooker Chemical Corporation. He has a B.S. in Chemistry from John Carroll University, and an M.S. in Environmental Health from Temple University. Presently, he is with the Hooker Ruco Division Industry Task Force for both OSHA and EPA relations.

AUTOMATIC MONITORING SYSTEMS FOR DETERMINING TIME WEIGHTED AVERAGE WORKPLACE LEVELS:

PROCESS GAS CHROMATOGRAPHS

Mark Soble Hooker Chemical Corporation Burlington, New Jersey

Uncle Sam brings you this program because if it wasn't for Uncle Sam, I don't think that Hooker Chemical would be involved in the control technology we're going to discuss. We got started in the program of monitoring because of the OSHA vinyl chloride regulation that came into effect in 1974. I am not going to review the history of the B. F. Goodrich discovery of the VCM problem. What I do want to say is that we were put into this position and we had to react to an industrial hygiene problem.

At that time we chose a gas chromatography system, specifically the Bendix System. We wanted to monitor a PVC resin plant; this is where the polymerization of monomers into polyvinyl chloride takes place.

Figure 1 is a picture of our control room. It is important to notice that there are many gauges and gadgets in it. If a company is going to put in a monitoring system, it must be capable of reacting in some way to let people know there is a problem.

I am not going to stand here and recommend what columns to use with your chromatography system. There are experts in the field who could do a better job. I am going to try to explain what we did with a system to make it work better. What we have is a control room and a GC monitoring system that is going to react. Our chromatography system is a Bendix Model 3000. We have six individual units and each unit monitors ten points; each point is monitored every minute and a half.

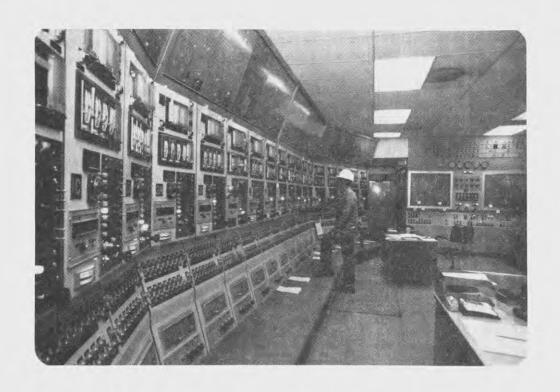


Figure 1. Control room.

Our plant is divided up into four sections. We have integrated systems for every section. We have set up a panel in the control room, which indicates how each of the 60 points looks at any particular time. It gives the control room operator—and by the way, the room is always monitored by someone—the ability to know where a leak may be severe or whether it is a mild leak and where exactly it is located.

We set up the system in our plant. The actual monitoring and the actual gas chromatography is done in the reaction areas, via a waterproof, explosion proof type system. The signal is fed back into a data acquisition system, but the actual system is located right in the plant. We wanted it right there in the plant for less potential dilution of stream.

How did we decide where to put the sensing points? To say that it was easy would not be accurate. We had to put our sensors in 60 specific locations. It is important to make sure the lines are portable lines, because as soon as you think you have a point well located, you then think of changing the location because other factors change. We also put in a ventilation system which changes the air in the plant about 39 or 40 times per hour. After we put the ventilation system in, we found that the air vents carried the leaks to different locations. What we then had to do was readjust our monitoring in the different areas.

Figure 2 illustrates exhaust stacks coming from our plant. We have gas chromatography unit detector points at the exhaust points. If there is a sizeable leak in the process area, somehow the stream goes right to the exhaust and the gas chromatography system can then trace the problem leak. We can then work on the leak.

We have also been able to modify the system and bring the sensor points outside the plant to monitor unloading of VCM railcars. We have also tied our system into our EPA unit so we can monitor the stacks to help determine what the emissions are. Our data acquisition system, is a Hewlett-Packard computer. The chromatography system works well, and the printer works well. However, they don't always work well together. It is important to realize that when you spend between a quarter of a million dollars and a million dollars, that you must hire and train a technician who is going to be dedicated to maintaining this system. We did so in our case.

I must tell you that in the last three or four years the program has been modified every year. It is critically important to train people. These units have to be calibrated, sometimes daily, and it is not an easy thing. All the units are very intricate.

Figure 3 is an emergency light that we have in the reaction area. This light goes on if the VCM concentration in the area is above a certain level in parts per million. In our particular case, we chose five parts per million to activate this light. For the training of

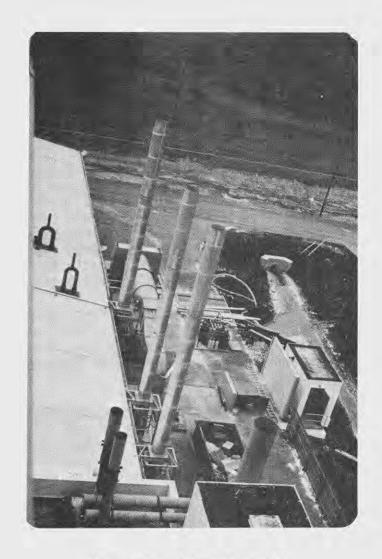


Figure 2. Exhaust stacks.



Figure 3. Emergency light.

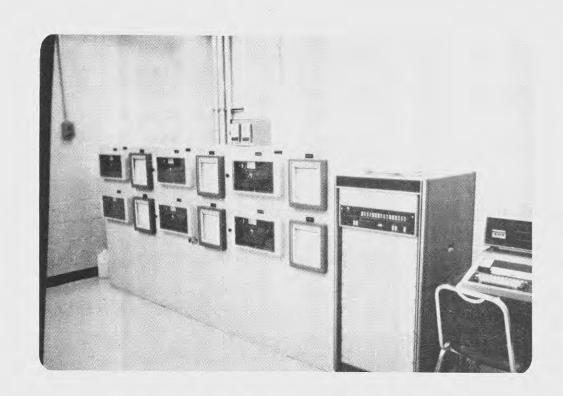


Figure 4. Chromatography system.

employees, it is also important that they recognize the significance of this light and know how to react to it. When you put a warning light in the reaction area, each light should represent a problem in that area, and only in that area. It is important of course to know where to locate these lights, because sometimes an employee will walk into the area and say, "I can't see the light".

Figure 4 is our chromatography system. Throughout the system, we know what the VCM levels in the plant are. We have 60 points monitoring continuously. Recorders indicate the high levels for the day, the low level, average, and mean and where the high points are. We can easily determine where we are at any particular time. When the regulations first went into effect in 1974, I guess, we had levels of VCM that would average in the plant at 1-2 parts per million. On implementing controls, VCM levels in our plant averaged under one part per million. We have also used the system in the auxilliary plants, which use PVC and might come under the regulations.

It is also important that the data stored can be easily retrieved. We have a point monitored every minute and a half. Multiply that by 24 hours a day, seven days a week, 365 days a year. You have to keep all that data. You can't put in a data system without an acquisition system. Some companies have tried, and that's not the way to do it anymore.

Hooker Chemical was willing to spend the money, in the beginning, to put in a system which we believed would work. I am sure that some systems are now available that exceed our capabilities. But, ours is a system that does work. Gas chromatography is a viable way to determining parts per million of vinyl chloride, and it protects the employees, and we're happy with it.

* * *

DISCUSSION:

- MR. R. NICHOLAS WHEELER: Have you been able to use the system to find exposure levels of individual employees, in determining where they go to different parts of the plant, the TWAs and other exposures?
- MR. MARK N. SOBLE: No. We have the capability; we have not done it. We monitor every employee once a month. Considering the number of employees we have working under different job classifications, they would have to be monitored at least every day. That is how we could get TWAs. It is possible to do this; we have hoped not to do that right now.
- MR. WHEELER: Do they use some kind of telemetry on employees to note where they go?

MR. SOBLE: I think Pantasote has a computerized card for each one, and that monitors each one.

MR. WHEELER: How many columns do you have on your chromatograph?

MR. SOBLE: One.

MR. WHEELER: You haven't had any interference, have you?

MR. SOBLE: None at all.

MR. WHEELER: We had. We had to go to three columns because we were picking up solvents.

MR. JOHN L. HENSHAW: You mentioned that you keep the data; for what reason? If you have the TWA data, why do you have to keep the gas chromatograph data?

MR. SOBLE: We keep the data to try to correlate high readings. Sometimes single point data is misleading, and if we have to go back and analyze the situation on a particular day, we would like to have the whole picture.

MR. HENSHAW: This is not required by law?

MR. SOBLE: Not by EPA.

MR. WHEELER: How about OSHA?

MR. SOBLE: I don't think so.

MR. HENSHAW: First, why do you have to have so many changes in your system; secondly, how do you handle the maintenance and calibration?

MR. SOBLE: I think we bought a bummer software system when we put it in three, four years ago. The technology was very new. We were sold the system, and it didn't work exactly to our expectations. I am sure there are programs out right now that will solve these problems. What was the second question?

MR. HENSHAW: How do you handle the maintenance and calibration?

MR. SOBLE: We do the maintenance and calibration daily. We have hired and trained an instrument technician whose responsibility includes the chromatograph and all environmental equipment like portable monitor dosimeters.

DR. JULIUS H. BOCHINSKI: If you have additional questions, would you save them for the end of the panel discussion? The next speaker is Dr. Raymond Sawyer. This talk was prepared by Dr. Raymond R. Sawyer and Mr. Joseph Cappola for Pantasote Company. Dr. Sawyer has his Ph.D. in Physics from the University of Iowa. He is the Director of Marketing and System Application of EOCOM Corporation. He is involved in directing systems engineering concepts of new product involvements. He has more than 25 years experience in program management.

AUTOMATIC MONITORING SYSTEMS FOR DETERMINING TIME WEIGHTED AVERAGE WORKPLACE LEVELS:

FOURIER INFRARED INTEREFEROMETERS

Raymond R. Sawyer EOCOM Corporation Irvine, California

and

Joseph Coppola Pantasote Company

Presented by Dr. Sawyer

ABSTRACT

A description of a unique approach to area monitoring for vinyl chloride, incorporating high resolution, high sensitivity Fourier Transform Infrared technology. The toxic gas monitoring system is specifically designed with the high resolution, sensitivity and speed capability to provide full compliance with OSHA regulations concerning requirements for monitoring vinyl chloride as well as other toxic gases. The system features unique sampling algorithms providing for multi-level sampling sequences based on adaptive techniques, provides for alarm annuciation and provides the statistical processing for required record keeping.

The basic gas analyzer consists of a rapid scanning Michelson interferometer modulator with beamsplitter, and infrared source, infrared detector, Wilks 40 meter sample cell and the required optics in its own free-standing optical bench and electronics console housing the system controller, data acquisition unit, minicomputer and recorder, audio alarm and I/O terminal for programming, systems diagnostics and printing the eight hour averages and alarm excursions.

Applications of the monitoring system will be discussed in detail for VCM as well as for other toxic compounds.

SUMMARY

I Requirements

The monitoring system must be viewed in light of the following major requirements:

- Speed
- Sensitivity
- Specificity
- Multi-compound adaptability
- Multi-sample station adaptability
- Output adaptability for comprehensive display and recording

The requirement for speed is obvious if one considers the aspect of multiple sampling points and the ability to detect toxic excursions that are of a transcient nature which must be considered in time weighted averages. The sensitivity requirement is also obvious as is the specificity. The better the specificity, the higher the integrity of the monitoring system. The ability to monitor more than one compound from a sample point is both a cost and performance advantage but further than that, the system should be capable of changing the compound to be monitored if required. The last two requirements are self-explanatory, and the specific details of sample point location, alarm annunciation, data recording (T.W.A.'s, alarm excursions, etc.) are a function of the individual monitoring installation.

II Technique

The study and analysis of compounds by observing their spectra in the infrared radiation region has long been performed. With the advent and implementation of Fourier Transform Infrared analytical equipment (FT/IR), the technology is well established in the laboratory. Second generation FT/IR equipment is now available which has been designed to bring the laboratory measuring the analytical capability to bear on industrial monitoring problems. The FT/IR technology satisfies all of the requirements of the prime sensor for a comprehensive area monitor yet is rugged enough and reliable enough to perform in the industrial environment. The result is a highly sensitive, fast, extremely specific sensor which requires no consumables, does not lose calibration, and is direct reading for most toxic compounds.

III System

The basic monitoring system consists of three major elements:

- Measurement Bench
- Controller and Data System
- Output and Display Interface

The measurement bench consists of the prime interferometer modulator, infrared source, infrared detector and pre-amp electronics, transfer optics and measurement (sample) cell.

The controller and data system consists of the signal conditioning electronics, analog-to-digital conversion, minicomputer, and digital interfaces to the computer and for output display. The function of this element is for data acquisition, measurement (concentration) calculation, parameter monitor and control and measurement bench control.

The output and display interface incorporates a printer and keyboard for operator control as well as a "dry contact" relay interface for alarm annunciators and mimic panel displays. This section annunciates the eight TWA data, excursion alarm messages, parameter diagnostics and measurement statistics.

IV Adaptive Control

Because the basic system incorporates a minicomputer, the system is easily adapted to what normally would be difficult and sophisticated monitoring techniques. For example, consider multi-level sample point control. Plants and plant processes for VCM can be characterized by virtue of where the potential VCM leaks can occur. By incorporating this data and considering the current concentration levels being measured, the system can automatically adapt the sampling point sequence to optimize the measurement function. Another obvious extension is the automatic calculation of worker TWA's based on his movements within the work area.

INTRODUCTION

The FMSR Monitoring Concept

The EOCOM FMS 7200 Gas Monitoring and Analysis system consists of a high performance prime sensor based on Fourier Multiplex technology, with an integrated data acquisition, analysis and display system. EOCOM Corporation has conducted extensive development efforts and field application studies relating to industrial instrumentation systems for comprehensive real-time, multi-gas monitoring and analysis.

The EOCOM FMS 7200 Gas Monitoring System is a versatile and general gas monitor, capable of monitoring several gases simultaneously from as many as several hundred locations. The monitor is highly selective, thus reducing the chance of interference from other gases (false alarms); and highly sensitive, allowing part per billion measurement of most of the different gaseous substances currently listed by OSHA.

The EOCOM Toxic Gas Monitoring System has demonstrated its reputation for high reliability (better than 90 percent up-time) and extemely stable measurement performance combined with high sensitivity. It can be programmed to monitor one or more of most any of the gaseous substances listed by OSHA in the regulations outlined in the Federal Register 1910.70, Volume 39, Number 125, dated June 27, 1974.

The system has the capability to automatically monitor the concentration of the selected gases at multiple sample points, control alarms and keep detailed records of station TWA (time weighted average) and, optionally, employee TWA. The sampling sequence is tailored to the plant site.

Options can be included such that stations will be sampled on demand from the central control or remotely. The automatic sampling and concentration measurements as well as all calculations, alarms and reports are program-controlled by the system minicomputer.

The block diagrams in Figures 1 and 1a show the major functions of the FMS^R 7200 with all options. At the center is the system minicomputer which controls all functions. Sample gas is selected by the transfer manifold. The prime sensor determines the gas concentration. The employee TWA is determined from the employee data and/or badge reader inputs, The plant mimic panel, remote panels, alarms and controls, printer and CRT display terminal indicate the state of the system; alarm conditions, TWA reports and action taken to eliminate the alarm, if any.

The device in the FMS 7200 which actually determines the concentration (the prime sensor) is a fully-automated high-performance infrared spectrometer. Infrared spectroscopic techniques have been utilized for many applications through the years, ranging from atmospheric studies to chemical analysis. The infrared analytic technique is well founded with literally tens of thousands of infrared spectra on file for ready reference. The technique has proved to be a most useful method for identifying the chemical makeup of a substance as well as determining the concentration of each constituent.

The power of the Fourier method lies in the tremendous information capacity of the "interferogram" signal. This signal is processed by the computer to obtain highly selective information about a particular gas (s). The selectivity is extremely important because it means few, if any, interferences. In fact, and here is a major advantage, interferences can be eliminated by a software change only. This unique advantage is available because of the large information content in the Fourier signal. The fact that all this information is available allows the 7200 monitor the concentrations of several gases simultaneously.

An optional feature of the sampling algorithm is called "adaptive sampling". This means several stations can be sampled simultaneously and randomly, according to probable leakage of the contaminants. In other words, stations which are least likely to leak are sampled less often. Adaptive sampling reduces considerably the net time to detect a leak of the toxic agent and to isolate its source.

Another advantage of any infrared technique is that it uses no consumables other than standard utilities. There is little operating cost to the FMSR 7200. In Table 1, the major features and advantages are outlined.

TECHNICAL DISCUSSION

Interferometer Spectrometer Theory

A scanning Michelson interferometer is shown schematically in Figure 2. It consists of two perpendicular plane mirrors (A and B) and a semi-reflecting film, or beamsplitter mounted at 45° to mirrors A and B. Mirror B is stationary, while mirror A is scanned at a constant velocity v(cm/sec). The infrared beam under investigation is brought to the interferometer on an optical axis perpendicular to mirror A. The partially reflecting beamsplitter divides the incident beam into two separate beams, one passing to mirror B and the other to mirror A. The two beams then recombine at the

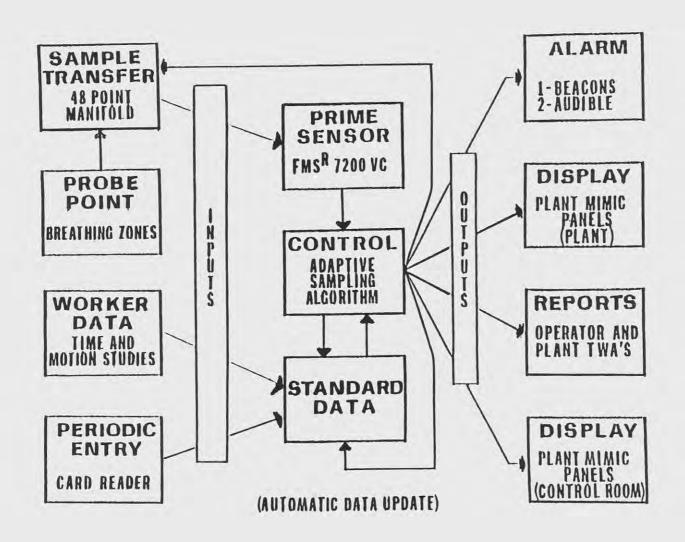


Figure 1. VCM monitoring system.

Figure 1a.

Table 1. Advantages of FMS^R gas monitor.

- High specificity and sensitivities
- Fast measurement time
- Eliminate interference with software change
- Accepted by OSHA equivalent personal monitoring
- Multi-gas capability, monitor several gases simultaneously
- Adaptive sampling, find leaks faster
- TWA records, as required by Federal Regulations
- Alarms and controls, for fast corrective action
- Reliable, only one moving part
- Unattended operation
- Low operating cost, consumes only water, air and electricity
- Automatic "zero" calibration
- · No span drift
- Wide dynamic range (won't clog)
- Field proven 99 percent up-time

beamsplitter. The beam traveling to mirror A passes through a pathlength different from that traveled by the beam going to mirror B. Therefore, when the two beams are recombined, they interfere, either constructively or destructively. The intensity of the exit beam of the interometer I (δ,λ) is a function of the optical path difference (OPD) and between the beams reflected from mirrors A and B. The functional dependence of δ is measured in units of wavelength of the indicent infrared beam (λ) . The actual expression for I (δ,λ) is:

$$I(\delta, \lambda) = 0.5 H(\lambda) B(\lambda)[1 + M(\lambda) \cos \frac{2\pi\delta}{\lambda} + \theta\lambda]$$

where B (λ) is the intensity of the energy of the incident bean, H(λ) less than unity, represent the departures from the actual spectral intensity B (λ) due to instrument characteristics, $\theta\lambda$ is a phase shift instrument function (unavoidable phase shifts from beamsplitter, detector and electronics), and M(λ) (less than unity) is the modulation efficiency that represents the departure from theoretical performance of the beamsplitter and optical system.

(Retardation) B HeNe Laser = $.6328\mu$ Beamsplitter vm = .4 cm/S

Schematic Diagram Scanning Michelson Interferometer

 $f = \frac{2 \text{vm}}{\lambda} = \frac{2 \text{ X .4 cm/s X } 10^4 \text{ µ/cm}}{.6328 \text{µ}} = 12,642.2 \text{ Hz}$

For vm - 0.4 cm/s

λ	f		
.6328µ	12,642.2	Hz.	
1.0µ	8,000	Hz	
2.0µ	4,000	Hz	A continuum of these contained
4.0µ	2,000	Hz	in interferogram as cosine waves
10.0µ	800	Hz	with amplitude directly related
100.0μ	80	Hz	to IR intensity.

Figure 2. Frequency to wavelength conversion - one mirror velocity.

The Interferogram

In a scanning Michelson interferometer the OPD (δ) is varied continuously by moving mirror A at a constant velocity. The effect of this sweeping is to modulate the output intensity $I(\delta,\lambda)$ in a sinusoidal fashion with a frequency $f(\lambda,v)$ that depends on wavelength λ and mirror velocity v,

$$f(\lambda, v) = \frac{2v}{\lambda}$$

The factor of two arises from the fact that a displacement of the moving mirror changes the OPD, or retardation, by twice that amount. The incident beam is a broad band source with a continuum of energy with respect to wavelength. Yet each frequency is modulated independently (each cosine function is linearly independent of all other cosine functions of different frequency) and can be sorted from the continuum by a Fourier Transform. Because of this independence, the modulated exit beam may be focused directly on an infrared detector without monochromatic filtering for a specific wavelength. The entire incident spectrum is recorded in a multiplexed form by the detector during a scan of the moving mirror.

The multiplex function is referred to as the interferogram $i(\delta)$,

$$i(\delta) = \int_0^\infty I(v) \cos (2\pi v \delta + \theta v) \cdot dv$$

whereas is in units of cm $^{-1}$ or Kyser's and is defined as the number of wavelengths per cm, i.e., proportional to the frequency of the IR energy and this is proportional to $1/\lambda$. From the equations given above,

$$I(v) = .5 H(v) B(v) M(v)$$

The interferogram is a function of δ . This parameter δ varies with a constant velocity and therefore $i(\delta)$ has a definite bandwidth of frequencies that is determined by the bandwidth of $I(\nu)$ and the moving mirror velocity ν . For typical mirror velocities and IR spectra the frequency bandwidth f max is on the order of 10KHz. A typical interferogram is shown in Figure 3.

The interferogram $i(\delta)$ is sampled at equally spaced intervals with an analog to digital converter system. These intervals must be spaced close enough so that the complete interferogram is accurately represented by the sampled points. This sample spacing is controlled by an HeNe laser fringe reference system which assures correct sample accuracy as well as wavelength accuracy in the resultant spectra (see Figure 4). The fact that the interferogram has a finite bandwidth allows us to use the sampling theorem to specify a minimum necessary sample spacing (maximum necessary sample frequency). If bw is the bandwidth of the IR incident beam, then the sampling theorem states that the sampling frequency $v_{\rm Sp}$ must be at least twice that, $v_{\rm Sp} = 2v_{\rm bw}$ (Nyquist Criteria).

Or in terms of OPD the sample spacing $\delta_{\mbox{\footnotesize{\rm SP}}}$ must satisfy

$$\frac{1}{\delta_{\rm sp}} \geq 2v_{\rm bw}$$

Once the interferogram is digitized and stored in a manner accessible by a computing system, the digitized equivalent of a complex Fourier Transform can be performed on the interferogram to decode the multiplexed information to obtain a complex spectrum

$$I_{R}(v) + j I_{I}(v) = \int_{0}^{\infty} i(\delta) e^{-2 \pi j \delta v} d\delta$$

The integration of i (δ) provides the identity.

$$I_R(v) = I(v) \cos \theta_v$$

$$I_{I}(v) = I(v) \sin \theta_{v}$$

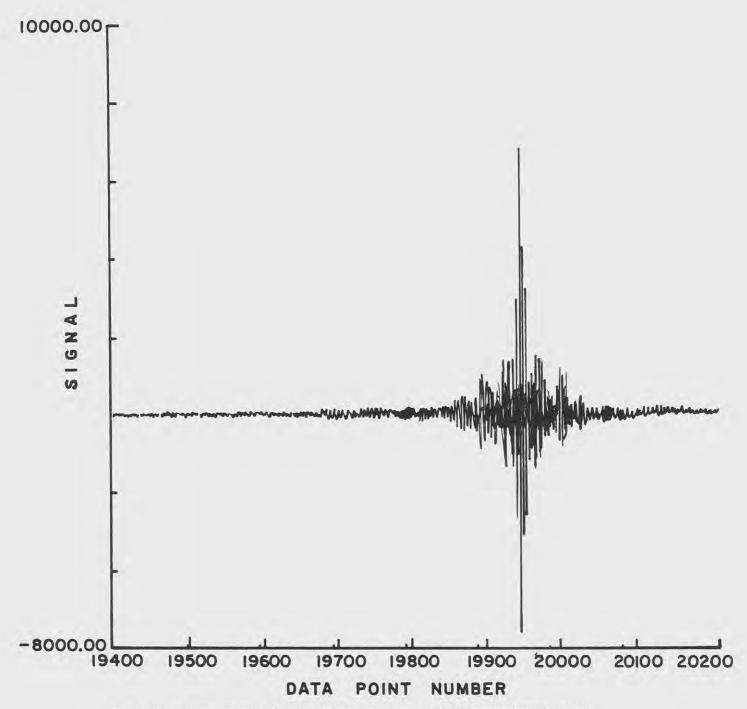
To eliminate the instrumental effects that introduced the phase angle one has to perform the process of phase correction. In this process is measured as a property of the instrument and then one can calculate I(υ) via a linear transformation using the identity equations (Multiply the first equation by cos $\theta \upsilon$ and the second by $\sin \theta \upsilon$ then add the two equations.)

$$I(v) = I_R(v) \cos \theta_v + I_T(v) \sin \theta v$$

In this way $I(\nu)$ can be calculated from the measured interferogram $i(\xi)$. Figure 5 is a typical spectral result of this calculation.

In the above derivations the interferogram has been assumed infinite in extent. However, in reality the moving mirror can only sweep out a finite optical path difference (X). The effect of finite mirror travel can be understood intuitively by considering a spectrum consisting of two closely separated spectral lines v_1 and v_2 . The interferogram consists of the sum of two cosines of nearly equal frequency. As the retardation is increased ultimately the two cosines get out of phase and "beat" is observed. The observation of this beat is sufficient and necessary to distinguish between the two frequencies and therefore resolve the two spectral lines. The beat frequency is the difference of the two frequencies $(v_2-v_1)^1$. Therefore the resolution of a Michelson interferometer Δv is given by

$$X = \Delta v^{-1}$$
 or $\Delta v = \frac{1}{X}$



This is an average of interferograms 2 and 3 from input tape labeled spectra

Figure 3. Typical interferogram.

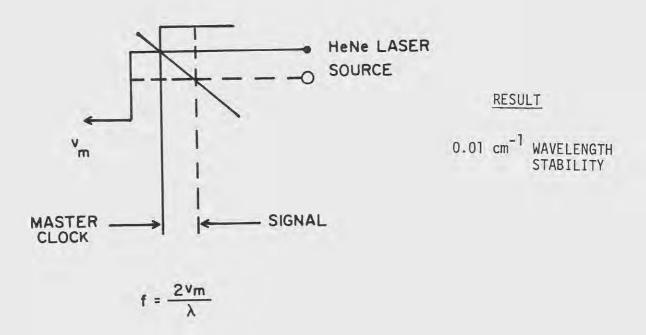


Figure 4. Wavelength accuracy.

Wavelength Calibration

- Knowledge HeNe wavelength
- Mirror velocity
- Angle through interferometer

If mirror velocity changes

- Master clock tells computer
- Thus, at all times, the frequencies calculated by system are referenced to HeNe laser, which is simultaneously measured with each spectrum

Figure 5. CO Spectra.

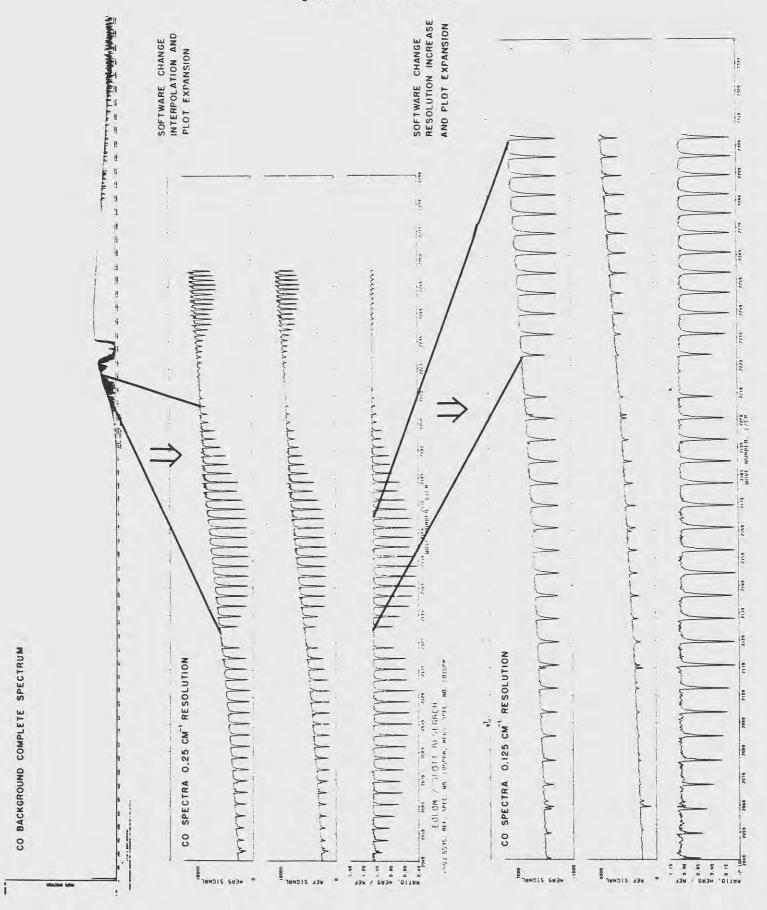


Figure 6 gives the equation for the resolution as defined at the half-power points.

Resolution of an interferometer spectrometer is also a function of the uniqueness of the OPD across the moving mirror. If a significant portion of the extended IR beam traverses a different OPD from that of another portion of the IR beam, then the resolution will be degraded. If this error distance δ_e is of the order 1/2 of a wavelength, then the interferometer will not produce a useable interferogram for that wavelength. This criteria places upper bounds on the flatness of all the optical components of an interferometer and also on the properties of the scanning system (i.e., allowable tilt). This also places a restriction on the divergence half angle, 4 of the incident optical radiation, δ_e for the extreme ray will reach $\frac{1}{2}\lambda_{min}$ at an OPD of $1/\Delta\nu$. Therefore, the maximum divergence half angle that can be allowed for a resolution at a frequency ν_{max} is given by:

$$a = \sqrt{\frac{\Delta v}{v_{max}}}$$

FMS^R 7200 Analytical Method

The FMS 7200 analytical technique used in the Monitoring Mode (gaseous compound concentration measurements) is based on the attenuation of IR radiation at the characteristic absorption frequencies of the particular toxic gas of interest. The basis of the technique is illustrated in Figure 7. As shown, the toxic gas has characteristic absorption at several frequencies (cm⁻¹). There are also regions in the spectrum where the gas does not absorb. The amount of absorption is given by the following relationship:

$$I_{\nu}/I_{\nu_0} = e^{-\alpha_{\nu}} cl \qquad (1)$$

where

αν absorption coefficient

c = concentration

L ≈ absorption path length

 $I_{V} \simeq$ Intensity at the absorption frequency

 $I_{\nu_0} \approx avg.$ of reference Intensities

The reference frequency intensities allow determination of $I_0\nu$ which is the intensity value at the absorption frequency if no gas were present. I_ν and $I_{\nu 0}$ are constantly measured values for each individual

SPECTRAL RESOLUTION: LINE WIDTH AT HALF MAXIMUM OF INTENSITY

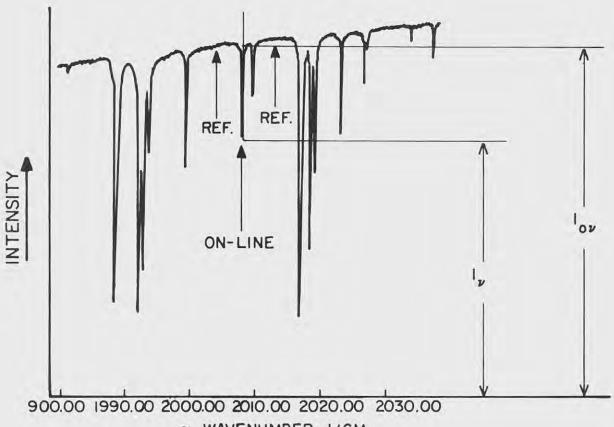
RELATIONSHIP FOR INTERFEROMETER: $\Delta v_{\frac{1}{2}} = \frac{1.22}{2 L}$

L = Optical path difference in the two arms of the interferometer

ATMOSPHERIC LINE WIDTHS: ~ 0.1 - 0.5 CM⁻¹

Figure 6. Resolution Criteria for Fourier transform spectrometers.

INFRARED ABSORPTION APPROACH



V WAVENUMBER I/CM

$$a_{\nu} = e^{-\alpha_{\nu} \text{ pcL}}$$

$$a_{\nu} = \text{absorption co-efficient}$$

$$c = \frac{1}{\alpha_{\nu} \text{ pL}} \ln \left(\frac{1}{\nu} \right)$$

$$c = \text{concentration}$$

$$c = \frac{1}{\alpha_{\nu} pL} \ln \left(\frac{o\nu}{I_{\nu}} \right)$$
 $c = concentration$

lov Avg: $(l_{ref.})$ L = path length

Figure 7.

sample measurement.

The absorption coefficient $(\alpha \nu)$ is a characteristic constant of the toxic gas to be measured and L the pathlength is fixed for any given measurement. Therefore, everything is known in Equation (1) and therefore can be rearranged to yield concentration which is given in Equation (2).

$$C = \frac{1}{\alpha v L} In \left(\frac{I v}{I_{\alpha v}} \right) = (2)$$

The process of the FMS 7200 analytical method is to measure l_{ν} and $l_{0\nu}$ which requires a three frequency measurement per gas and from these determine concentration. This measurement is then repeated in sequence for the required number of sampled points. Similar type calculations are performed for other gases either simultaneously or in sequence depending on the sensitivity and time requirements. This technique has many inherent advantages derived from the interferometer Fournier Multiplexed Instrument. The system provides a multitude of spectral frequencies for performing the analysis in addition to the sensitivity and specificity advantage of an interferometer type system.

This analytical technique provides internal spectral intensity stability. As shown in Figure 8. The signals S1 and S2, the reference line signals from which S3 is determined, have a lever arm effect which reduces the effect of small changes in S1 and S2. Therefore, any of the sources of drift such as electronics, source temperature, detector or wavelength are self-compensating.

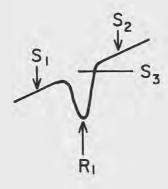
System Specificity

By selecting lines properly there are several ways to avoid interferences. The first is with the spectral resolution capability of the system; a region is selected for the spectral line measurements which is clear of any interferences. This is generally the case because of the large number of spectral elements provided by the interferometer system (high resolution capability).

Another approach is to use line selection and redundancy in the "subtract interference" mode, as shown in Figure 9. This technique is measuring both the interfering gas and the gas of interest and subtracting out the effect of the interferent. There are, in general, two types of situations for interfering gases. The first, which is illustrated in Figure 9a, in which the gas of interest is partially overlapped by the interfering gas. In this case, only a fourth measurement frequency need be included in order to determine the concentations of the two (2) different gas species.

The second case is illustrated in Figure 9b, where the interfering gas completely overlaps the gas of interest. In this case, two additional measurement frequencies from which to measure the concentration of the toxic

NOTE: Lever arm effect reduces effect of small changes in S₁, or S₂ on S₃.



o \mathbf{S}_1 and \mathbf{S}_2 used to determine \mathbf{S}_3

- o System drifts
 - o Electronic Effect S_1 , S_2 , and R_1
 - o Source temperature Can change by 300°C with less than a 10% effect on the calibration at the sensitivity of the system

 - o Wavelength

 Does not drift within accuracy of measurement

Figure 8. Internal stability.

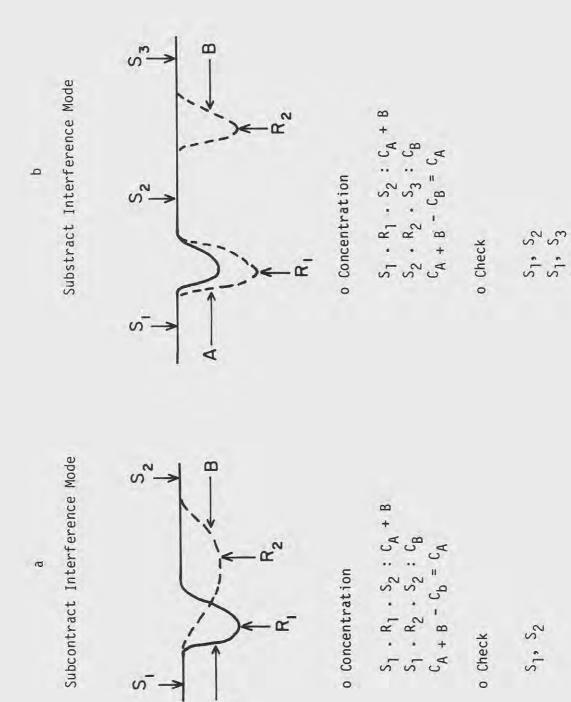


Figure 9. Line selection and redundancy.

gas. In both cases the reference lines are used as internal reference checks for insuring proper and stable operation of the analytical method.

A third method to avoid interference problems utilizes spectral features. In this case, the spectral feature of the gas of interest must be sharper than the interfering gas. As indicated, the reference lines are set at equal absorption coefficient values of the interfering gas and the concentration determined in the normal fashion.

These same techniques may be applied to liquid and solid samples for analytical determination of concentration of known samples. The only difference will be that the spectral features of these type samples are much broader in nature and therefore can be determined with lower spectral resolution than is required for gas phase work. Also, the sample handling and transmission cells will be different based upon the particular measurement requirements.

The analytical technique described above requires a prior knowledge of the spectral characteristics of the sample and interferences for any given measurement requirement. Therefore a spectra must be generated of the sample and interferences in order to properly select the spectral frequencies to apply the analytical technique. The user may acquire this data or EOCOM Corporation will provide this analytical service.

EOCOM's analytical laboratories in Irvine provide this full spectral capability. The broad spectral variations may be obtained on the samples of pure gas, of suspected interferences and samples of the work atmosphere. This spectra are stored on disk and readily available for analysis. The capabilities of EOCOM's full spectral data system with the advanced software and scope display allow rapid data acquisition, rapid Fourier transformation, and easy spectral analysis to arrive very rapidly at the proper set of conditions to apply the analytical method.

Determining the Plant Environment and Employee Exposures

During an eighteen (18) month period, EOCOM Corporation, in conjunction with the Pantasote Company of New York, has very carefully studied the concept of area monitors in conjunction with the following objectives:

- Fast Excursion Detection
- Accurate Employee TWA's
- Eliminate Requirements for Personal Sampling
- Management Information System to Aid in Achieving OSHA "Performance" Standards

After a thorough study, it was decided to embark on a measurement program to find out the in-plant variables involved in trying to achieve the objectives. In order to do this we then proceeded to:

- Quantify the Nature of Gases in the Work Environment
- Determine Appropriate Sampling Sequence for an Area Monitoring System
- Relate the Employees to the Results of the Area Monitor and Determine Their Exposure

Nature of Gas in the Work Environment

In order to understand the work environment and how this relates to employee exposure, we have taken literally millions of sample point data from our various field installations and analyzed the data for the statistical nature of the gases in the breathing zone. The purpose of this effort was to establish the distribution of the gas concentration levels. This obviously is affected by the air flow, molecular weight of the gas, reactivity of the gas in the atmosphere, type of source of the gas, etc. However, from these studies we have sufficient data to say that a "log Normal" distribution is sufficient to represent the distribution of the gases studied in the various plants studied. To our knowledge this is the first in-plant data to confirm the NIOSH report of April, 1975, entitled "Statistical Methods for the Determination of Non-compliance with Occupational Health Standards", by Nelson A. Leidel and Kenneth H. Busch, HEW Publication No. (NIOSH) 75-159 (Reference 1). In this report they use air pollution data to support their "log normal" distribution methods. Now with our confirmation of this data (to be published in the latter half of 1975) (Reference 2), it is possible to use many of their analytical techniques and statistics. These can be used to analyze data from an area monitor to determine compliance (at various confidence levels), to predict plant performance based on the "log normal" statistical model and to easily analyze current plant performance against past plant performance for detection of significant trends.

More specifically the attached Figure 10 shows the difference between the "log normal" distribution and the more commonly used normal distribution. To define the "log normal" distribution it is necessary to determine the Geometric Mean (GM) and the Geometric Standard Deviation (GSD) (similar to the Arithmetic Mean (ω) and Standard Deviation (ε) for the normal distribution).

$$GM = \mu \sqrt{\frac{h \sigma}{\epsilon | n \mu} + 1}$$

$$GSD = \varepsilon - \sqrt{\ln \left[\frac{\ln \sigma}{\epsilon \ln \mu} + 1 \right]}$$

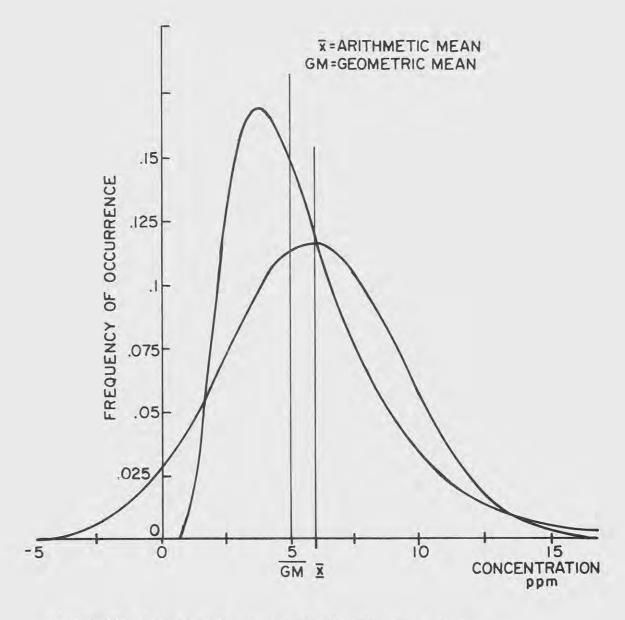


Figure 10 - Log normal and normal distributions with the same arithmetic mean and standard deviations.

FROM: HEW Document No. (NIOSH) 75-159

"Statistical Methods for the Determination of Noncompliance Occupational Health Standards"

The GM and GSD (for any time period long with respect to plant variations), completely defines, from a statistical viewpoint, the "log normal" curve for the frequency of concentration of various levels of the gas being monitored.

That is to say that you now have a definition of your plant environment that allows projection of the probabilities of various ocurrences in the plant as well as to determine compliance with various OSHA "Performance" Standards. Thus, the EOCOM data system, as appropriate, calculated these parameters as well as TWA's.

Sampling Algorithm

Given that the EOCOM data system keeps track of the GM and GSD of each breathing zone sensor probe* (of the area monitor), it is then possible to evolve a sampling algorithm that will have:

- Higher Probability of Excursion Detection
- Turn Warning Systems Off in the Shortest Time to Minimize the Use of Masks
- Isolate the Actual Probe Nearest the Cause for the Excursion

A. Probe Data

First using just the sample probe data (employee time/motion studies will be considered later), management selects a parameter(s) (P [M]) of the gas that is key to their plant operation under the OSHA Standard. For instance in the case of the VCM Standard, management might select individual probe readings of greater than 25ppm until April 1,1976, and 5ppm after that time with the objective of having the correct mask on at all the required times. On the other hand, depending on the general levels of VCM in the plant, management might select eight (8) hour averages of the probes that are higher than 0.5ppm and 1.0ppm as two (2) parameters to determine the sampling algorithm. Another parameter that could be selected is the GSD of a probe. In any case, the selection of the desired parameter (one or more) is made by management as a function of plant conditions relative to the standard as well as any other requirements they may have.

*NOTE: For this discussion, no consideration is given to the number of samples from a probe that yield a useful GM and GSD. Also the effect of high instrument noise (not "log normal" distributed) relative to the variations in plant levels is not considered in this discussion. Both these parameters are a function of the area monitor used with the data system and should be evaluated on an individual case basis and could affect the distribution or time intervals used with the statistics.

For instance, let's take the case of selecting the probability of the sample probe having a reading of 5ppm or greater PI \Rightarrow 5ppm/reading]. Using the GM and GSD for each probe, the axis plural for the "log normal" distribution of Figure 10 is determined and a set of probabilities, one for each probe, is determined.

$$P[M], P_2[M], \dots, P_n[M]$$

These probabilities of probe readings at or above 5ppm are then used to determine those probes that should be sampled more often (i.e. higher P M) and from these probabilities is developed the sampling pattern where the sample probe selection is under the control of the EOCOM System, the result being that those points with most likelihood of a 5ppm excursion are monitored more often.

B. Employee Data

A second level of effort is to also include as part of the sampling probability model, the probability of any employee being at any one breathing zone probe. This data is derived from time/motion studies of the involved employees (or job categories).

From the time/motion study, one obtains the probability of each employee (category) with respect to probes.

$$P[T_{A_1}], P[T_{A_2}]....P[T_{A_n}]$$

$$P[T_{Z_1}], P[T_{Z_2}], \dots, P[T_{Z_n}]$$

By combining the probabilites of all the employees (catagories) with the P M for each point, you then have the probability for that probe that any employee may be exposed at that probe.

$$P[E_1], P[E_2] \dots P[E_n]$$

These probabilities are then used to generate a sampling distribution that is used in the sampling algorithm of the EOCOM System.

C. Search Sampling

In addition to the above statistically controlled sampling, the EOCOM System also goes into a search routine when an initial alarm or excursion occurs. This search is performed to be sure that the highest point of concentration is located so that

effective corrective action can be taken as soon as possible. This search routine takes into account the wind direction (normally known because of forced ventilation) as well as the probabilities of the points around the initial excursion. After establishing all the alarm conditions in the area, EOCOM System then proceeds to monitor the rest of the system while establishing a higher priority for reading the alarmed area more often until the condition is corrected. Again all of the TWA (p)'s are calculated correctly by the trapezoidal integration.

D. Multi-Level Sampling

The EOCOM System also has the capability of multi-level sampling. The multi-level sampling concept is to monitor the mixture of several points simultaneously. That is to take for instance, 3 points and mix them in the gas manifold. Thus the measurement of the three (3) points would provide the average of the three (3) points (1, 2 and 3). In order to make a decision on a 5ppm alarm, the EOCOM System analyzed the data as shown in Figure

Multi-level sampling has the advantage of "sweeping" the plant at up to three (3) times faster than single point sampling. It has certain requirements to be effective and still not deteriorate the TWA and other calculations being performed by the EOCOM System.

- 1. In order to almost achieve the factor of 3 speed improvement the average levels in the plant (for the case of Figure 11) would have to be below 5/3 or $1.66 \mathrm{ppm}$. In no case is the approach slower than single station sampling. The worst case is when all levels in the plant are $5 \mathrm{ppm}$, then the system will measure R, R_1 and R_2 , or three (3) such measurements. Most cases we have observed are such that almost the full factor of three (3) can be achieved.
- One has to take care in selecting the points that are to be averaged so as not to affect the other calculations. We have shown that this is accomplished by selecting points with roughly equal P [E] and/or P [M].
- Although the EOCOM System has the multi-level sampling capability, it may require different gas manifolding than presently in use.

In summary, the multi-level sampling capability does improve:

- Probability of Measuring Excursions
- Average Time To Survey the Plant

SITUATION

1. P[m] 5 ppm.

 Simplified version of program.
 NOTE: Real program takes into account recent measurements of points and probability of most likely point of excursion.

Reading = R (Average of Points 1, 2, and 3)

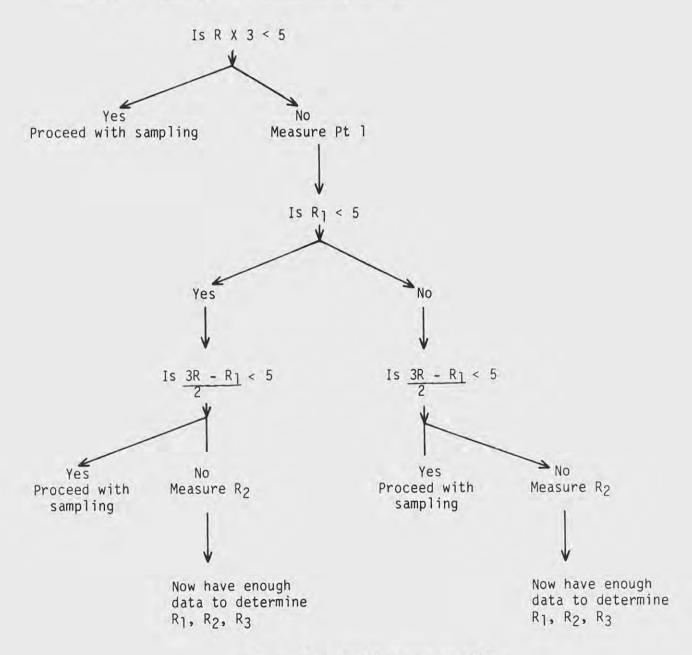


Figure 11. Multi-layer sampling.

Summary of Sampling

In summary, the sampling algorithm of the EOCOM System allows the user to:

- Have a system that responds to its environment. Each day the GM and GSD are updated and the sampling algorithm corrected for plant trends and variations.
- Sample the area monitor in an intelligent fashion based on the "living" statistical trends of the plant environment.
- Select the sampling decision parameters that are deemed important to management.
- Enter new or changed time/motion studies.
- Get to excursions significantly faster than a sequential sample system.
- Correct excursions fast.

Basic Reporting of the EOCOM System on the Plant Environment

In order to provide management with significant information concerning the plant environment, its changes and the degree of complicance with a standard, the EOCOM System reports several parameters regarding the plant data measured by the probes. First, individual probe readings are available through the printer or by optional mass storage device. However, except for investigating specific events, it is felt that the following summary parameters are sufficient to fully define the environment for each probe.*

- TWA (P)
- Trend TWA: TWA (TP)
- GM (P)
- Trend GM: GM (TP)
- GSD (P)
- Trend GSD: GSD (TP)

The total plant (floor or area) environment is defined by the sum of the probe data for the plant (floor or area).

A) TWA (P): TWA (P) is calculated from the basic data points measured by the sensor probes. It is important to note that the non-uniform sampling (with time caused by the sampling algorithm in section above) requires careful attention to the means of calculating the TWA. The EOCOM System calculates the TWA with a trapezoidal integration of the individual readings, yielding the correct value for the area under the curve, which then for any

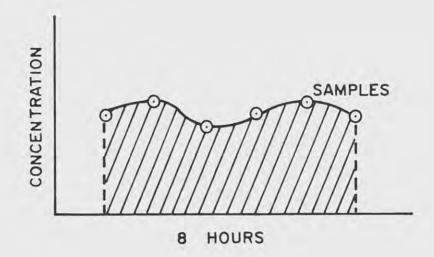
*NOTE: The EOCOM System calculates many other parameters as noted in its specific specification sheet. The parameters discussed here are those used to describe the plant environment and employee exposure.

given time period (15 minutes, 1 hour, 4 hours, 8 hours, etc.) provides the correct TWA (P).

The area under the curve is shown in Figure 12. It is this true area divided by the time that yields TWA values. It is interesting to note that most management selection criteria for P[M] will lead to an optimum sampling of the eight hour period. That is to say that most of the selection criteria used by management will lead the sampling algorithm to sample active exposure areas more often than less active exposure areas. This is shown by the following condition:

- A) Small number of samples per 8 hours:
 - · Low P (M)
 - Low P (E)
 - Low GSD (EP)





- B) Many samples per 8 hours
 - High P (M)
 - High P (E)
 - · High GSD (TP)



Figure 12

In both cases the system samples the data correctly to provide the correct time weight average (P).

C) Trend Responsive TWA (TP): In order to compare today's performance with past performance, the EOCOM System outputs an exponential TWA which is:

TWA
$$(P)_0 = 0.X$$
 TWA $(P)_0 + (1 - 0.X)$ TWA $(TP)_Y$

Where the subscript 0 indicates today's data and the subscript Y indicates yesterday's data, the factor X determines the number of days that are used to determine the trend (TWA (TP). The factor X is selectable by the user and can be varied to give very long term trends or shorter term (such as a week) trends. The effect of setting X to a time constant of seven to ten days is to smooth out any abnormalities of a given day, while at the same time giving data on the most recent performance of the plant. This is depicted in the following figure:

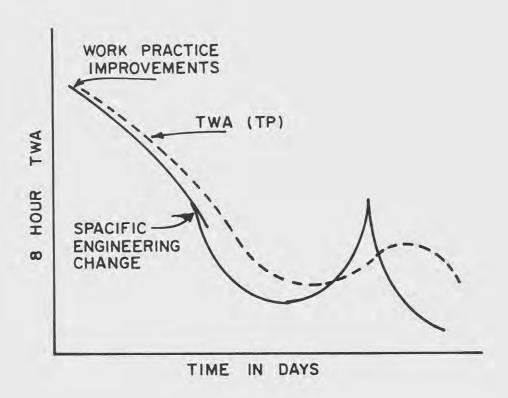


Figure 13

By this method you can readily compare today's performance TWA (TP) with the average of a previous (selectable) set of days and decide if today's performance is significantly different. An alternate path is to simply calculate the TWA for extended periods of time (rather than exponentially). This is possible with the system; however, it is our opinion that the most recent data contains more management significance. However, either is available from the EOCOM System.

D) GM and GSD:

The significance of GM and GSD is that they allow one to completely describe the plant in terms of statistical numbers. This uniquely defines the log normal curve in Figure 1 from HEW Document No. (NIOSH) 75-159, (Reference 1). Again it is significant to compare the present to the most recent plant data. By using this data, you can easily assess the plant performance for the day both in actual levels and in variations. Since it has been shown that the data is log-normal distributed, it is also possible to use the GSD and GM from a series of days to project the plant environment into the next shift or day with a confidence level attached to projected performance on a future shift or day. Again, the continuing GSD and GM are reported as trends also. Thus the system reports: GM(P), GM(TP), GSD(P) and GSD(TP) in the same fashion as the TWA(P) and TWA(TP) values.

Further, using the GM and GSD allows one to assess whether any given shift or period is within the previous experience and whether, a combination of shifts represents a new trend. Depending on the process and results from the system, it may be more appropriate to keep separate records on the shifts in each day rather than running the average from shift to shift through the day into the next. In certain industrial cases, we have noted a substantial difference in the value of GM and GSD from shift to shift. In one case, the night shift runs significantly higher than the other two shifts.

It is worthwhile to comment on the effect of the sampling algorithm on the calculation of GM and GSD for the eight (8) hour periods. The actual log normal distributions are based on random samples. The samples taken (at least for a short period) cannot be considered random. However, our data to date does show a substantially log normal distribution for periods as short as one hour.

Employee or Job Category TWA

The EOCOM System calculates employee (or job category) exposure by using the measured TWA (P) for the time period of interest for each point and the time/motion study data (P $[T_A]$P $[T_A]$.)

This approach leads to extremely good long term TWA of employees. Certainly it is based on more information than a 1 or 2 time/month personal sample. The time that the EOCOM System takes to converge on accurate TWA (when compared to charcoal tubes) is a function of many variables, such as:

- Conditional exposures
- Validity of time/motion study and its variability
- Placing of the sensors in the breathing zone
- Number of samples per measurement period provided by the area monitor
- Cyclic (or non-cyclic) nature of the process etc.

It has been our experience to date with an installed VCM monitor system that with the inclusion of the conditional exposure (man in reactor) that calculated TWA values converge to the measured TWA values in less than eight (8) hours.

For those situations where the employee may perform several job categories within a shift or from shift to shift, the job category concept should be used and the employee should log in on a per shift basis the time spent in each job category that is a regulated job category.

EPA Requirements

With the present proposed standards for EPA monitoring in plant effluents for substances such as VCM (EPA 40 CFR Part 61: National Emission Standards for Hazardous Air Pollutants Proposed Standard for Vinyl Chloride) EOCOM intends to offer an optional accessory to EOCOM System to perform either a mass calculation of VCM in the air in the plant and that VCM that escapes the plant into the environment or to accept data from an exhaust sensor (one or more) and provide the appropriate data analysis, such as 10ppm per hour limit. In view of the status of this proposed EPA VCM standard we have not chosen the final approach.

Effect on Employees

A true interactive intelligent monitor, as installed in a VCM monitoring situation has been observed to have the following effects:

- 1. Excursions due to work practice have significantly decreased due to the speed of the monitor and its ability to capture 94% of the excursions. This has, without intervention of management, brought a force to bear on the employees which had the effect of dramatically reducing excursions due to work practices.
- 2. A previous monitor system was circumvented by the employees knowing the sequential nature of the sampling device. Knowing this they were able to perform critical operations that might cause excursions while the monitor was not sampling in the area. With installation of the new system and its sampling algorithm, this was no longer possible, and a significant change in work practices occurred which also improved productivity.

REFERENCES

- HEW Publication No. (NIOSH) 75-159. Statistical Methods for the Determination of Noncompliance with Occupational Health Standards.
- 2. Coppola, J., D. Mattson, K. Lindelin and S. T. Dunn. The Use of Area Monitors for Determination of Compliance with OSHA Performance Standards. (To be published).

Nomenclature

GM : Geometric Mean

GSD : Geometric Standard Deviation

P [M] : Management Selected parameter for determining sampling algorithm

(one or more can be selected)

P [TA1] : Probability of man A being at point 1, etc.

P [E] : Probability of exposing any employee at a sensor probe

TWA : Time weighted average as defined in 29 CFR 1910.93 (d) (1)

TWA (C) : Measured eight (8) hour time weighted average of an employee

or job category

TWA (P) : Eight (8) hour time weighted average of a sensor probe

TWA (TP) : Exponential average of eight (8) hour time weighted average

of a sensor probe

GM (P) : Eight (8) hour geometric mean of a sensor probe

GM (TP) : Exponential average of eight (8) hour geometric mean of a

of a sensor probe

GSD (P) : Eight (8) hour GSD of a sensor probe

GSD (TP) : Exponential average of an eight (8) hour GSD of a sensor probe

Subscripts

1, 2, 3, n...: Probe numbers

A, B, C....: Employee or Job Category

GLOSSARY OF TERMS

ADAPTIVE SAMPLING

Adaptive sampling is the process by which those areas where a worker together with an excursion are more likely measured more often than those areas less likely. It is a combination of the probability of man, probability of excursion, data from ancillary inputs, data about transient workers and conditional exposure to determine in which order probe points are to be measured.

ANCILLARY INPUTS

The auxiliary data that record employee movement, wind direction, process conditions etc., used as parameters in the adaptive sampling algorithms.

BREATHING ZONE

Area containing the air being inhaled by a worker.

CONDITIONAL EXPOSURE

Those times during a normal cycle of production where a worker will automatically become exposed to an excursion based upon his deliberate action of performing a required task.

DATA CURRENT

Data that is \leq 10 days old and \geq 1 minute old.

DATA HISTORICAL

Data which is available for review from other analytical methods. i.e., Charcoal Tubes, Gas Chromatographs, Grab Bag, Hand Held Monitors etc., and is more than 10 days old.

DATA REAL TIME

Data that is < 1 minute old.

EMPLOYEE EXPOSURE

The amount of subject gas that comes within an employee's breathing zone. Usually expressed as a function of time such as a time weighed average (TWA).

FMS 7200/GC UP-GRADE

A technique where an EOCOM FMS 7200 system is integrated with an existing gas chromatography system.

EXCURSION

An increase in contaminant level that is greater than or equal to a predetermined standard.

GAS FUTURE

Those gases which may require monitoring by either the government or management at a later data.

GAS CHROMATOGRAPH DRIVER

An interface in a FMS 7200/GC Monitoring System which directs the sequence of the multi-streamer GC system.

GAS-SUBJECT/INTEREST

Gas that is being monitored.

INTERFERENCE PROTECTION

Monitoring the gas of interest in such a manner to determine the existence of interferences to the gas measurement.

INTERPOSING RELAYS

Electrical contacts that drive the sample collection system, field alarms, mimic panels and audio-visual enunciators.

MULTI COMPOUNDS

Measuring more than one gas of interest and comparing each to specific standards.

MULTI-PROBE SAMPLING

A measurement technique where more than one probe/point is sampled.

MIMIC PANEL

A collection of lights mounted on a panel within the outline of the regulated area that represents the sample probe or point locations, and is used to communicate the location of excursions.

PROBE/POINT

A stationary point where air samples are drawn.

PRIME SENSOR

The equipment that analyzes the sample for the subject gas.

PRINTER-ALARM

Dedicated to recording the sequential alarms in excess of the standard.

PRINTER-REPORT

Produces hard copy for management, EPA, OSHA and other special reports.

PROBABILITY OF EXCURSION

Probability of Excursion is the probability of an excursion greater than or equal to a predetermined level at any point or area.

PROBABILITY OF MAN

Probability of man is probability of a man or employee of a specified job classification will be found at a point or area.

PROBABILITY OF MAN MEETING AN EXCURSION

The probability of man or an employee of a specific job classification will be at a point or area when an excursion occurs.

REAL TIME

Data that is less than 1 minute old.

REAL WORLD MEASUREMENTS

The actual levels of subject gas at all points within a defined area at a specific time.

REGULATED AREA

That space that is controlled and monitored for excursions of a subject gas.

SAMPLE COLLECTION SYSTEM

The required equipment, vacuum pumps, manifolding, traps, lines and valves, etc., required to move the sample from the probe point to the prime sensor.

SPECIAL REPORTS

That which may be required by management but not necessarily OSHA or EPA.

VALIDATION PROGRAM

A plan of action to insure employee exposures are being computed accurately.

WORKER MOVEMENTS

The cyclic pattern of worker as he performs his daily job requirement. This is usually a job classification, and is used to predict the probability of a man being within a defined area.

WORKER-TRANSIENT

Those workers who do not normally perform in a cyclic manner within the regulated area, i.e., Maintenance people, Management Supervision, Outside Contractors, etc.

WORKER-TWA

The time weighed average of a workers' exposure defined by OSHA.

* * *

DR. BOCHINSKI: The next speaker is Paul A. Wilks, Jr. Mr. Wilks has been associated with the area of infrared spectroscopy and gas chromatography since joining the Perkin-Elmer Corporation. Upon finishing Harvard University in 1944, he participated in many phases of that company's instrument development program practically from its inception, and was Director of Marketing when he left Perkin-Elmer in 1958, to become a co-founder of Connecticut Instrument Corporation.

While with C.I.C., Mr. Wilks was responsible for the commercial introduction of several new infrared sampling techniques. Most notable of these was the development of equipment for attenuated total reflection (ATR) measurements. When C.I.C. merged with Barnes Engineering Company in 1961, he became General Manager of Barnes Commercial Instrument Division.

In 1963, Mr. Wilks left Barnes to form Wilks Scientific Corporation, which has become an innovator in infrared analytical instrumentation and accessories. Wilks Scientific was acquired by the Foxboro Company in 1977. Mr. Wilks has recently formed General Analysis Corporation with headquarters in Darien, Connecticut. The new company will provide ambient air analysis on a nationwide basis through a network of locally owned analytical laboratories.

Mr. Wilks has published a number of papers on infrared instrumentation and applications, and has been the editor of several company publications. He has had seven patents issued and several more are pending in the instrumentation field.

AUTOMATIC MONITORING SYSTEMS FOR DETERMINING TIME WEIGHTED AVERAGE WORKPLACE LEVELS:

INFRARED MONITORS

Paul A. Wilks, Jr.
Foxboro Analytical
Wilks Scientific Corporation
South Norfolk, Connecticut

I would feel much more comfortable if one of you gentlemen were giving a talk on the instrument I am going to talk about. Unfortunately, the first MIRAN-801 multi-station, multi-component, stationary ambient air monitor left our shipping platform only last Friday. However, judging from the backlog that we are building up, I think we will have a number of people who could give some indication of its performance in a short time. This is an evolutionary instrument. It has been developed as a result of five years of effort on the part of Wilks Scientific, (now Foxboro Analytical, Wilks Infrared Center) in the field of area

monitoring. It is aimed at providing the kind of information that NIOSH and OSHA are looking for in terms of time weighted averages and exposure for individuals to many different toxic materials in workplace areas.

I would like to take just a minute or so to review infrared analysis and show why it is a very useful and viable method in the field of toxic vapor analysis. Every organic molecule has a characteristic infrared spectrum, and this information can be used for both identification purposes and for quantifying the amount of material present. Approximately two-thirds of the toxic materials that are listed in the OSHA listing have sufficiently strong infrared spectra that they can be detected by means of infrared at their action levels. The initial use of infrared has been in the form of portable instruments to take to various locations and monitor the concentrations of toxic materials in work space areas and map variations in levels throughout the area. Typical portable infrared instruments are shown in Figure 1.

The infrared method has a couple of very significant advantages in this application. The most important is that it is a continuous measuring system. It gives practically instantaneous indication of concentrations which makes it an excellent tool for the detection of active leaks or alarming when levels exceed safe conditions. Another advantage of infrared is that it doesn't require any services other than power. Some of the portable models are battery operated, others operate from local power sources.

The disadvantage of infrared is its sensitivity, which is not quite as sensitive as GC, for example. In most cases, the minimum detectable range is around one part per million. In some cases, where strongly absorbing materials are being measured, fractional parts per million can be detected. The one part per million range is the reasonable limit in most cases. Another disadvantage is that while it is quite true that each material has a characteristic infrared spectrum, if you have many materials present in an atmosphere, there may be interference or overlapping in the spectra. These interferences are always positive, however, an infrared analyzer cannot indicate less than actual concentration. The new micro-processing systems used in the MIRAN-801, to be talked about later, sort out these interferences and permit accurate indication of each component present.

Infrared calibration curves (Figure 2) are usually quite linear, although some compounds, such as carbon monoxide, do have a non-linear calibration curve. In any event, once a calibration curve is prepared for a given compound, accurate concentrations can be obtained by measuring absorbance at the analytical wavelength and reading the concentration from the curve.

The portable instruments have evolved into area monitoring type systems (MIRAN-II) and Figure 3 shows a single component, multi-station monitor. It is designed to look at one component at many different locations. We have built systems having 15 sample points, located up to

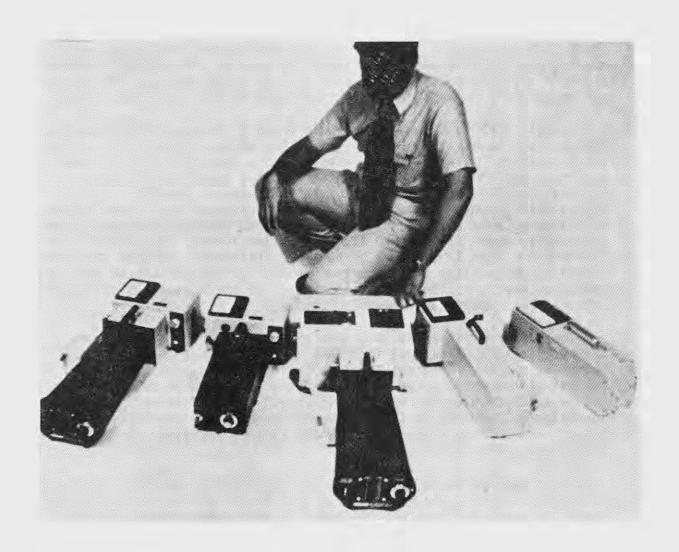


Figure 1. Typical portable infrared instruments.

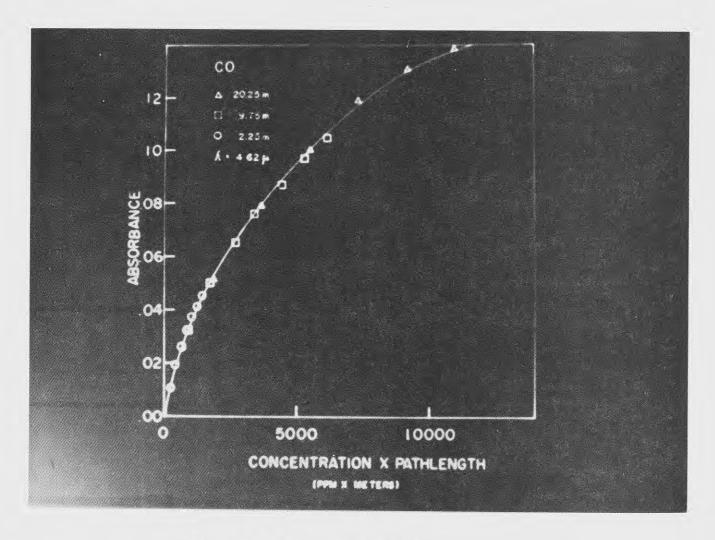


Figure 2. Infrared calibration curves.



Figure 3. Single component, multi-station monitor.

1500 feet from the analyzer. Figure 4 shows the MIRAN-201, a more automatic system with alarm set points and digital printout. This is still a single component multi-station system.

When several components are present, the absorption bands may overlap so that absorbance readings at given wavelengths have contributions from more than one component. With the recent development of micro-process techniques, it becomes quite easy now to sort out this overlapping data and compute the concentration of each individual component. Figure 5 is a typical mixture of solvents that might be present in an atmosphere. The overlapping of the bands is clear, however, the analysis can be made in a few seconds with the micro-processor. We have modified our initial single component instruments to include micro-processors which make multi-component measurements. The basic IR Analyzer is shown in Figure 6; the MIRAN-80 Gas Analyzer is a semi-portable instrument with a micro-processor. The instrument is designed to look at up to ten components and print out concentrations about once every minute, or less frequently, if desired. The only real factor in causing a time delay is the time taken to pump a sample through the cell and then get a new sample into it to get a measurement.

This instrument has evolved into the MIRAN-801 (Figure 7). It is designed to provide all kinds of data handling capacities; time-weighted averages on a shift versus location versus component basis, alarms at present action levels, and almost anything else that is needed in order to meet Government regulations and to provide safety backup.

Figure 8 shows the schematic of the instrument, indicating the pump and sample manifold system. One of the advantages of this type of instrumentation is that calibration for specific components does not change once the instrument has been calibrated. The only thing that changes is the energy through put. If the cell windows or mirrors begin to get dirty, energy levels in the system drop, but this does not change the calibration. We have designed a number of different sample handling systems. Normally we run tubing out to where we want to make the measurement and bring back the sample through a manifold and put the sample from different points into the instrument successively. If higher speeds are desired, or feed from extremely remote stations, a manifolding arrangement can be provided that pumps all line continuously, thus insuring that current samples are always admitted to the sample cell.

The inside of the cabinet is shown in Figure 9. The basic analyzer is at the bottom with the micro-processor in the box toward the right hand side. The upper portion of the instrument contains the sample manifold, case heaters. On the right side are the alarm lights. This portion of the MIRAN-801 is set somewhere out in the plant. It can be remote from the printer by several hundred feet. If a particular station shows a component level above the allowable value, the alarm signal can be sent to that location and also back to the central control room and will show at the instrument itself. We have installed one of the systems

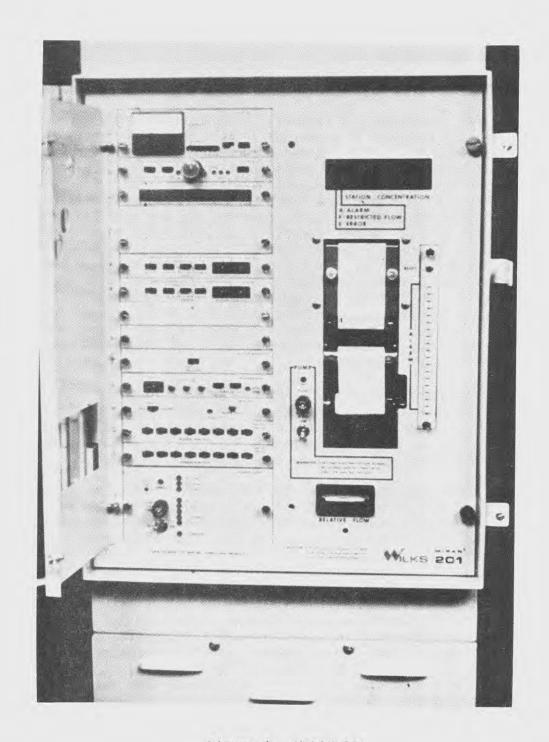


Figure 4. MIRAN-201
Single Component Multi-Station System

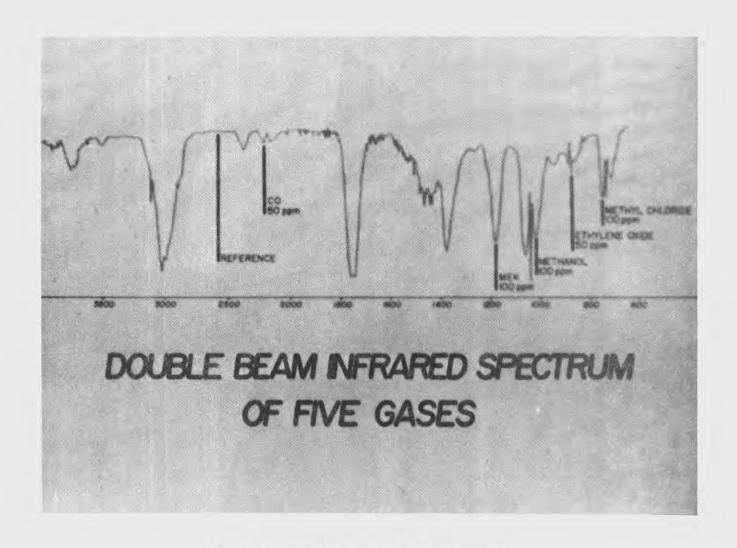


Figure 5. Typical mixture of solvents.

Figure 6. MIRAN-80 gas analyzer.

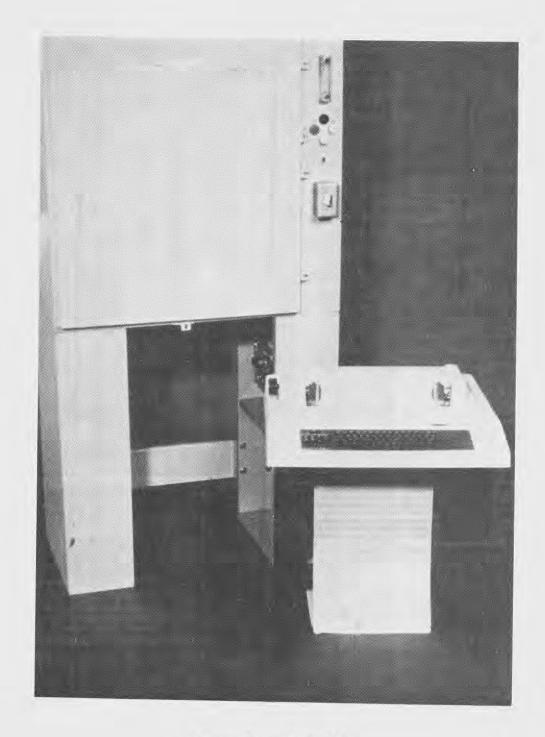


Figure 7. MIRAN-801

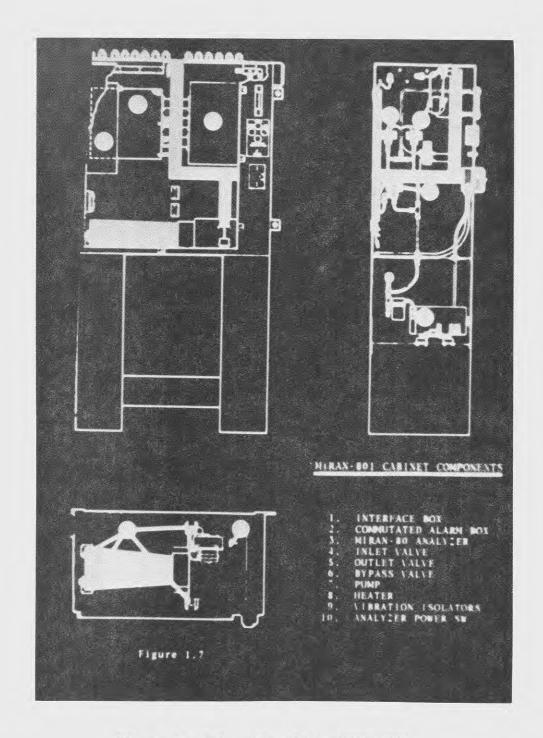


Figure 8. Schematic of the MIRAN-801.

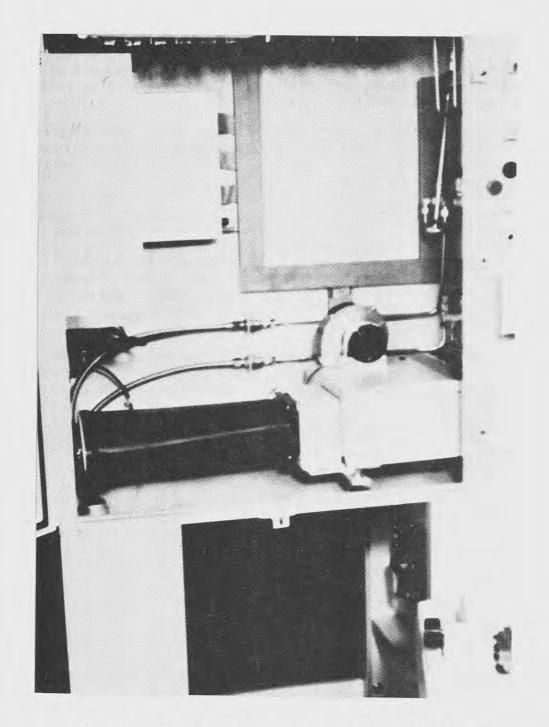


Figure 9. Inside of the cabinet of the MIRAN-801.

L V

in our own optical shop, where we have five or six different solvents in the atmosphere; toluene, isopropyl alcohol and several others, and have been running it for about six months.

The sample probe is simply the end of the tube with a dust filter attached (Figure 10). In Figure 11 is shown the printout and control center. The program is very flexible. There are many different instructions that can be given to the system and the data can be retrieved in a number of different formats. There is enough storage capacity to be able to store data for up to a month of 10 component measurements at 24 stations. Printouts of time weighted averages can be obtained on a shift, weekly or monthly basis. A typical printout is shown in Figure 12. Indicated are the number of readings made during the shift, the time weighted averages and the ppm for each component, together with alarm reading, if any. Another type of printout, which gives the highest concentration for each component at each site is emphasized in Figure 13.

The format in Figure 14 is another arrangement of data that is available from the standard program. Like any other computer system, the software is a changing and evolutionary situation, and as we began to market the instrument, we discovered that there were a lot of different requirements that can be met by suitable software modifications. Some applications involve four components at one site and six different ones at another, and it appears feasible to program the instrument to handle such a situation.

Infrared provides tremendous analyzing capabilities as I mentioned at the beginning of my talk. It is much easier to program in a new analytical wavelength than to install a new GC Column! I am convinced that infrared instruments such as the MIRAN-801 have both the analytical and data handling capacity to meet most of the foreseeable OSHA requirements.

* * *

DISCUSSION:

MR. JOHN T. BARR: I have a couple of questions for Dr. Sawyer. It is my understanding that the OSHA people have accepted your system in lieu of personnel monitoring at one of Pantasote's plants, but not at the other?

DR. RAYMOND R. SAWYER: That is correct.

MR. BARR: Do you know the reason they refused to accept it at the West Virginia plant?

DR. SAWYER: No, I do not.



Figure 10. Sample probe.

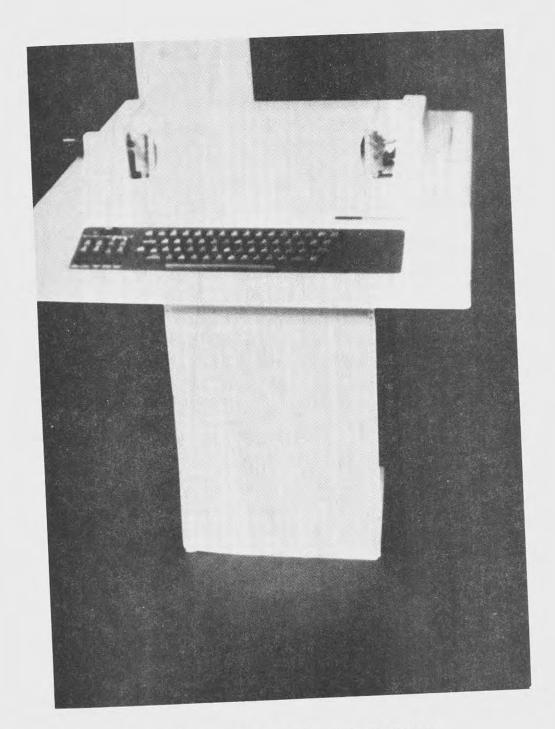


Figure 11. Printout and control center.

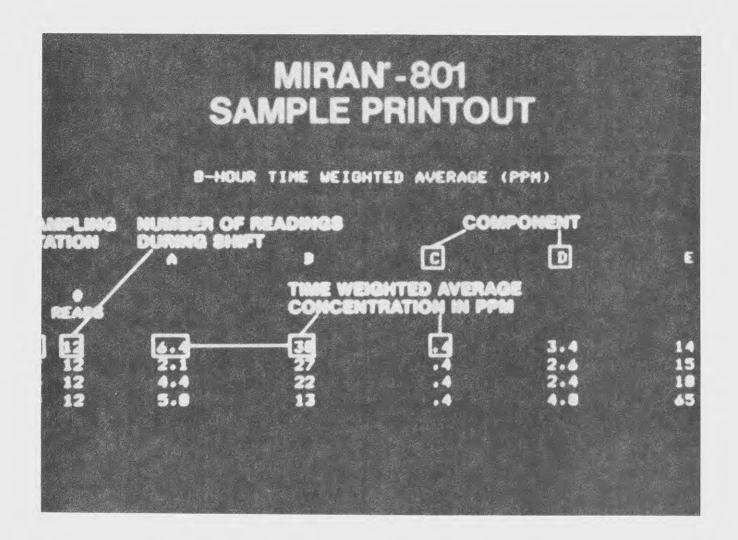


Figure 12. MIARN-801 sample printout.

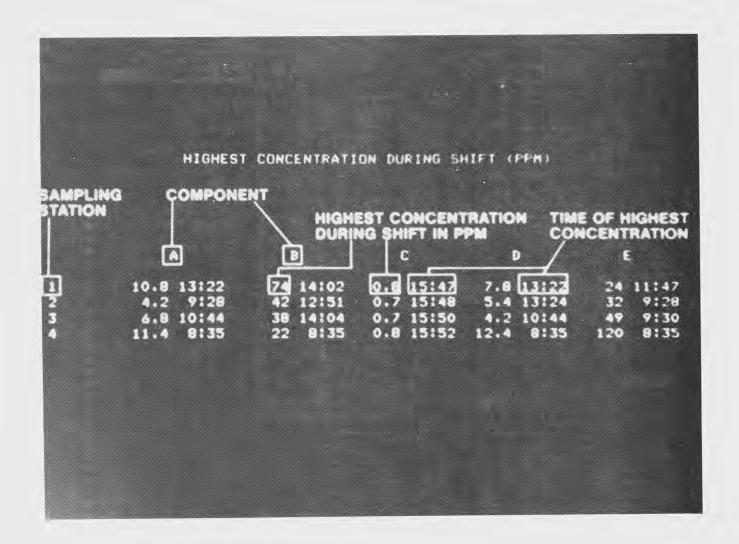


Figure 13.

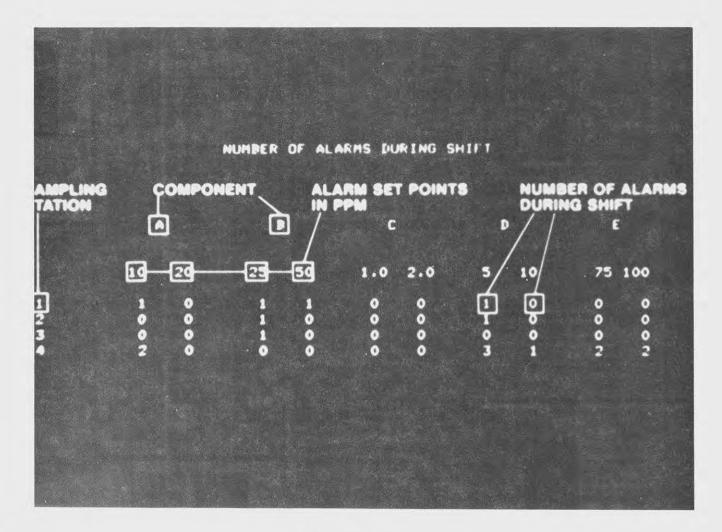


Figure 14.

- MR. BARR: What would be the present day installed cost of your systems in a PVC plant?
- DR. SAWYER: The total system and a software program such as we saw here would be in the neighborhood of \$275,000.
- MR. BARR: It is my understanding these instruments cost approximately \$100,000 a fourier.
- DR. SAWYER: It might be more than that. The basic fourier multiplex unit is \$82,000. Then, it's entirely up to what management needs to add, plus the installation and the sample points bring it up to about a quarter of a million dollars.
 - DR. BOCHINSKI: What is the present installed cost of an 801?
- MR. PAUL A. WILKS: The basic instrument price is about \$30,000 depending on options and that sort of thing.
- MR. JEREMIAH LYNCH: Going back to what Mr. Soble has said about the requirement of essentially a full-time technician to maintain and calibrate the system, is this the case with your equipment?
- DR. SAWYER: No, it is not. Calibration is automatic, built into the basic unit. It has a helium neon laser, which every time a measurement is made, the wavelength is calibrated back to that. There is also a white light zero. A plant engineer or instrument engineer may check the system, probably twice a month. That's entirely up to the plant management. I will give you an example: One of these systems has been in operation for over two years. The first service call that had to be made on it was just recently, when the beam splitter became fogged because the instrument engineer got involved in it. We have a continuing program which they are responsible to improve their system. Therefore, they have an instrumentation engineer there that dillies with the interferometer at times, and does not have that background. If someone gets into that modulator, he has a problem. That modulator is a patented system, and that's the key to why we are able to do what we can do with it.
- MR. ROY DEITCHMAN: Have you any feel as to the maximum length of the tubing?
- DR. SAWYER: We have not addressed that directly. The maximum length of sample tubing I don't know exactly how to put this; there is probably no limit. I don't know if you're going to get up to ten miles, of course, but EPA and OSHA may push us that way.
- MR. JERRY M. SCHROY: In terms of the question relating to absorption, if you have an upset or surge of concentration of the source, is there a time response problem because of absorption, not just delay, is that reading valid?

- DR. SAWYER: If we have a large concentration surge from there, and it is outside of the dynamic ranges that's been established with the system, we should get a fast reading, but we would only get it for that one, because after every one of our samplings, the system is automatically purged.
- MR. SCHROY: The question is, if you're going to have a false reading on that situation, what happens when you come down? How long does it take to get the line in equilibrium?
 - DR. SAWYER: We have no experience in that.
- MR. WILKS: We have been making quite a study lately on different materials with different compounds, and we find that there isn't any material that is good for everybody. Teflon is most generally useful. In some cases we are forced into stainless steel and sometimes polypropylene which seems to have a better set of characteristics than Teflon. You can get a situation where there is a real surge to the line and it will take some time to sweep out the sample, but the flow rate is very high. It shouldn't be more than two or three minutes before you get back to a normal situation. This is assuming that you have stopped dumping material in the tubing.
- MR. SCHROY: You all talked about a cycle time ranging from five minutes to ten or fifteen minutes, depending on the circumstances and in a six to twelve minute cycle time, there is no problem. You talked about the fact that the problem was sweeping the sample from a previous point out of the instrument; the fact that you're measuring 24, 28 or 10 points. This sounds like very much of a problem, not in terms of monitor engineering conditions, but given that you're talking about a delay between one point, how can you come back with only one in the 15 minutes and represent that as an average of that 15 minutes? Is there enough data base in all the work you have done to say that a 15 minute period is not going outside of the point?
- MR. SOBLE: Let me answer that question from our chromatography system. We have our system on a minute and a half cycle per point. If you get a high reading, you can interrupt that sweep and monitor every minute and a half, which means you are taking away from the other points. We have placed the probes in strategic points where they can project what is happening in the plant. It is not an easy answer, you know. We try to do our homework. You are talking about a million readings every month.
- MR. LYNCH: Are there any instances where OSHA has accepted an automatic monitoring system in lieu of personnel sampling?
 - MR. WILKS: Not to my knowledge.
- DR. BOCHINSKI: Have you had a probes located outdoors by some operation?

- MR. SOBLE: Yes
- DR. BOCHINSKI: Some people have problems with the probe lines getting cold and condensing or absorbing the sample. Did you take any special precaution to protect your probe?
- MR. SOBLE: The probe is only activated when a monomer car is unloaded.
 - DR. BOCHINSKI: What if it is in the middle of winter?
 - MR. SOBLE: We haven't seen any problem.
- MR. JAMES A. GIDEON: I am trying to make a little comparison of the systems. Could you reiterate what the detectability limits are on vinyl chloride and acrylonitrile for the three instrument systems.
- MR. SOBLE: Gas chromatography in PVC application goes to parts per billion levels. We have never measured acrylonitrile.
- MR. SAWYER: Vinyl chloride in the fractional parts per million. Acrylonitrile, probably at 10 parts per million.
- MR. WILKS: Our minimum detectable limits in vinyl chrloride would be tenth of a part per million. You wouldn't get a very accurate reading at that level, but you can detect activity as far as acrylo is concerned.
- DR. BOCHINSKI: This part of Session III is concerned with work practices. Our first speaker is Nick Wheeler, Coordinator with the Union Carbide Corporation on environmental protection, health problems and regulations. He represents Union Carbide Corporation to OSHA, EPA and NIOSH on such problems. He is a graduate chemical engineer from Virginia Polytechnic Institute in 1943. He was employed by Union Carbide Corporation in various capacities for 35 years. He is experienced in the manufacture of polyvinyl chloride, polyvinyl acetate, polyvinyl butyral, polyvinyl alkyl ethers and related monomers.

TRAINING AND WORK PRACTICES

R. Nicholas Wheeler Union Carbide Corporation S. Charleston, West Virginia

Thank you. I get the chance to talk about my favorite subject; training is one of my favorite things. My subject today is training and work practices, which I think has tended to be overlooked.

Work practices are the keys to an effective safety program and to an effective program for the safe operation of all chemical plants, not just those that happen to be handling hazardous materials. Work practices are not limited to workers; they also involve owner-operators and supervisors. A program of good manufacturing practice should be soundly based on process technology, on the personal commitment of all involved personnel, and on the optimum mix for that particular plant of work practices, engineering controls, and administrative controls.

At Union Carbide Corporation commitment can be summarized in three simple policy statements:

- 1. UCC expects to provide all necessary technical and financial resources to achieve the objective.
- 2. UCC expects each supervisor and employee to make a personal commitment to achieve the objective.
- 3. UCC expects to aid and to cooperate with the various governmental regulatory bodies.

These statements are not in order of priority but must be considered as a whole. Since Union Carbide Corporation must pay its taxes and its stock-holders it should be obvious that balances must be struck in terms of cost and benefit, and that full usage of resources must be obtained.

The most expensive, the most flexible, and the most under utilized resource any organization has is its people. The most effective way to fully utilize people is to organize them, i.e., direct their efforts through various programs, through guidelines and through manuals, and to train them in the knowledge and skills that are essential in their jobs.

To introduce the subject of training let's focus on the person to be trained. This is a chemical operator. He has two feet and legs permitting an infinite variety of lateral and vertical movements. He has two hands which can act as sensory organs (touch) and which can turn knobs, turn valve wheels, push buttons, and use a variety of tools such as pencils, wrenches, and the like. He has two eyes, two ears, and a nose which act as sensors to evaluate the environment and to receive a variety of communications. Between the ears and back of the eyes he has a brain which is capable of memory, deductive and inductive reasoning and which controls all his actions. Depending on the time available, the quality of instruction and his desire to learn, the operator

can be programmed to perform as a computer in certain areas and as a reasoning creature in many other areas.

This operator is not cheap. He costs about \$30,000 per year to maintain after a cost of possibly \$10,000 in his training. This man, at some point in his training, is placed in charge of \$5,000,000 worth of equipment to operate in a safe profitable manner.

Personnel training today can no longer consist of brief lectures on company policies, job organization and personal safety, followed by assigning the new hire to old experienced workers for two to four weeks of on-the-job hands on instruction. Process technology is changing rapidly, the cost of doing business requires increased performance, and safety and environmental regulations make little or no allowance for learning errors. Today's training program must be structured and well-based on the following:

- 1. Job analysis
- 2. Systematic development of training
- 3. Competence requirements identified
- 4. Performance orientation
- 5. Objective evaluation of progress

As regards the man being trained:

- 1. Weaknesses must be recognized
- 2. Improvement must be desired
- 3. Learning climate is permissive
- 4. Trainers must be available and knowledgeable
- 5. Opportunity to practice must be provided

All this is summarized on-the-job trainee needs as follows:

- 1. A systematic training outline
- 2. Daily bite-sized assignments
- 3. Specific tasks assigned
- 4. Hands-on training
- 5. Frequent testing to gauge progress

The program for the training of chemical operators within UCC's chemicals and plastics varies from one plant to another depending on the needs and the facilities available for such training. Despite such variation, each training program has much in common with another.

The program consists of two basic parts. Part one consists of general training. Instruction that is generally applicable throughout the plant. These are general safety rules such as no smoking, no horseplay, and the wearing of hard hats and goggles. Safety procedures such as wearing respirators and ladder usage. The longest and most useful portion of this part is the familiarization with plant equipment and its operation.

Part two of the training program is the on-the-site job instruction. The new operator must have knowledge of the properties of the materials he

is to be working with on the job. He is assigned a detailed operating manual for the department. The specific departmental safety rules are reviewed with him. Finally he is assigned to a trained operator-trainer for individualized on-the-job training.

At the South Charleston, West Virginia plant during his first two days work, the new hire receives safety orientation. This consists of a combination of films, lectures, slide presentations and training exercises, including operation of some safety equipment. The first two days instruction is as follows:

- 1. Introduction-Safety Department organization
- 2. Basic plant safety rules
- 3. Safety procedures manual
- 4. Lifting procedures
- 5. Personal protective equipment
- 6. Fire extinguisher training
- 7. Eye safety
- 8. Ladder safety
- 9. Equipment lock-out/tag-out procedures
- 10. Hazardous work permits
- 11. Safe handling of chemicals
- 12. Vapor cloud procedure

The new chemical operator, after his safety orientation, starts one week of classroom work known as Intro I.

Intro I covers seventeen (17) general safety related subjects. Instruction is carried out via training modules for each subject. The module consists of a formal instruction on the subject by a knowledgeable instructor followed by a general group discussion of the subject and sometimes training exercises. The trainee's understanding of what he has learned is then evaluated by a review questionnaire. On completion of this training module, the class then moves on to the next subject. Subjects covered in this initial formal training class are:

- 1. Introduction to the training course
- 2. Plant history and layout
- 3. Pay practices and timekeeping
- 4. Operations improvement program
- 5. Safety rules and regulations
- 6. Protective clothing and safety equipment
- 7. Safety-related reporting procedures
- 8. Emergency procedures and squad organization
- 9. Master tag/lock-out
- 10. First minute first aid
- 11. Self-contained and supplied air breathing respirators
- 12. Portable fire extinguisher
- 13. Static electricity
- 14. Filter-type gas and dust respirators
- 15. Vessel entry
- 16. Principles of accident control
- 17. Safe lifting

There is presently some overlap between the safety orientation and Intro classes. Plans are to reduce this to a minimum but not to completely eliminate repetition of critical subjects. Intro subjects are limited to general use items, i.e., useful in over half the plant's operations. Specialized training is given in the operating units.

On successful completion of Intro I, the new operator is assigned a training project and reports to his assigned manufacturing operation. Here he is assigned to an experienced operator for hands-on training. He is given any OSHA required training such as the acrylonitrile standard. He is introduced to the hazardous and reactive chemicals manuals which he must study and he is given an operating manual for that unit. This introductory period covers one week after which he resumes his classroom work for three more weeks.

The second part of the classroom work, Intro II, is more work-related and consists of the following modules:

- 1. Introduction to chemical operations
- 2. Sprinkler system and hydrants
- 3. Plant hose standards
- 4. Sampling procedures
- 5. Cardio-pulmonary resuscitation
- 6. Job hazard analysis
- 7. Reactive and hazardous chemicals (Attachment I)
- 8. OSHA
- 9. Basic hand safety
- 10. Plant piping and pipelines
- 11. Valves
- 12. Safety valves and vents
- 13. Steam traps and strainers
- 14. Pumps
- 15. Bearings
- 16. Gaskets, packings, and mechanical scale
- 17. Steam turbines
- 18. Reciprocating compressors
- 19. Lubrication
- 20. Heat exchangers
- 21. Steam jets
- 22. Electric motor operation
- 23. Condensers
- 24. Transfer procedures
- 25. Loss prevention/loss reporting
- 26. Instruments
- 27. Distillation

After having successfully completed his classroom training, the new operator is assigned to his operating unit and to his initial job in-company with his operator/trainer.

Under the direction of his foreman who has received trainer-training himself, the new man receives training in specialized operations and equipment for that unit, completes his reactive chemicals training. After demonstra-

ting his knowledge and job proficiency to his foreman in 120 days, he is no longer considered a probationary operator. At this time he receives a raise in pay and begins to handle a single job.

When the new man has gained experience in the job and is performing it well, he will be assigned to a second job again with an operator trainer. Having mastered the second job he will be assigned to a third job. This later job rotation and training is not rigidly specified, but depends to a great extent on the man's proficiency and the availability of training operators. The only limit is that an operator must master at least three separate operating jobs in four years before he is considered for maximum pay as a skilled craftsman.

Training materials can be homemade or obtained from a variety of sources. The American Petroleum Institute has a very good series of training manuals. DuPont also markets training and safety manuals. Training materials can be obtained through the various trade organizations such as the Manufacturing Chemists Association or the National Safety Council. Many companies will make training materials available for very nominal fees. EPA, OSHA, and NIOSH are very good sources of training materials.

Training procedures must be varied depending on the subject, the number of trainees and the facilities available.

Attachment II on vinyl chloride is an example of training material for technical and supervisory employees. Attachment III on acrylonitrile is oriented toward hourly personnel and can be used for training one man or 100 men.

The most difficult part of any training program is maintaining commitment and continuing the training of each man indefinitely through refresher courses and through good supervisors. Technology changes and people tend to forget little used but important parts of their training such as emergency shutdowns. There is also a very human factor to be considered, that is, a worker is constantly testing the limits of acceptable performance. A lack of continuity or a poor supervisor can negate the best initial training program very quickly. Training should not be limited to new men but should be made available on a demonstrated need basis to all.

A safe workplace results from a good training program in rules, procedures and operations. The best and most effective control device for the chemical and plastics industry is a well-trained and motivated work force supplemented by other controls where needed.

* * *

DR. BOCHINSKI: Our next speaker will be Mr. Nathan W. Clauss. He is a graduate in chemical engineering from the University of Michigan. He has recently retired from the Union Carbide Corporation. He is a member of the American Institute of Chemical Engineers, Fellow of the American Institute of Chemical Society. He has over 29 years' experience in the operation, control and development of facilities producing sulfuric acid production and concentrations; synthetic ethanol; air oxidation of aldehydes; organic acids; glycol ethers; esters; plasticizers; agricultural chemicals; food products, and ethylene oxide.

He has seven years as a Process and Equipment Safety Administrator. He is going to discuss the requirements of maintenance of new and old processing facilities; management commitment to these programs; audit review of new facility programs and updating old facilities.

CHEMICAL PROCESS AND EQUIPMENT SAFETY OR LOSS PREVENTION IN THE WORKPLACE

Nathan W. Clauss Consultant S. Charleston, West Virginia

All of us are concerned and hope to control technology in a manner which will provide a safe workplace at a reasonable cost to the consumer.

New equipment or technology is not the whole answer. Programs must be used and audited, which provide education, training and motivation on a permanent basis.

Process and equipment safety and loss prevention specialists can help in the reduction of worker exposure and equipment and malfunctions, accidents and major disasters. I am not talking about TLV's or TWA's but about exposures from large or massive material losses.

An analysis of loss data in one chemical company indicates that about six of the seven million dollar loss in 1976 could be attributed to the lack of knowledge.

The Need

A newly commissioned unit in a chemical plant usually has the benefit of the latest research, development, engineering and construction technology. It is at this point in time that operating and emergency manuals are up to date and the operators and supervisors are best trained and the most knowledgeable. The same chemical plant will also operate older, and frequently even old, units which have suffered through time by metal loss, non-compliance with the newest standards, loss of knowledge and experience, or changes in the process or equipment used.

What Does It Take?

What does it take to maintain the integrity of new facilities and to upgrade old facilities to comply with changing standards and regulations? Or put another way, what is required to achieve a goal of total loss prevention?

It takes commitment, knowledge, training and motivation!

Commitment to Programs

The basic starting point for supplying this need is a total commitment by management to implement, fund and control programs on a long-range basis.

These programs include:

- 1. Education, training, motivation and the auditing of knowledge retention.
- 2. Scheduled updating and audits of operating and emergency manuals.
- Review of process, engineering design and equipment changes for compliance with current standards and regulations.
- 4. Scheduled preventative maintenance to ensure integrity and reliability of:
- a) Equipment, valves, piping, etc.
- b) Control systems
- c) Pressure relief devices
- d) Insulation
- e) Electrical systems
- f) Fire protection systems
- 5. Test and Inspection programs which include schedules, record keeping and equipment evaluation.
- 6. Timely correction of all deficiencies.
- 7. Audit programs, schedules and follow-up Insurance carriers, team audits by Company specialists, unit self audits.

How Good Is New?

An indepth review of a new and complex unit, designed and constructed according to the latest technology, revealed such deficiencies as: the lack of protection against freezing, weakening of a column base section when used for pipe support, excessive material loss and personnel

exposure during cleanup for maintenance, lack of drainage for relief device collection headers, inadequate emergency shutdown systems, incomplete operating procedures and no emergency operating procedures.

All management was, in my opinion, totally committed to compliance with the latest standards and regulations. So I can only conclude that such deficiencies in a newly constructed unit emphasize the need for better education, training, and experience.

Can You Upgrade Old Facilities?

The need to meet changing environment and occupational health requirements coupled with two major still system fires, created a "Major Equipment Safety Review Project" to upgrade over 300 systems ranging in age from one to fifty years.

The Objective

The objectives were defined and are stated as follows:

- 1. An indepth study of each major system will be made to determine the action required to conform to ASME Pressure Vessel Code Standards and to ensure the adequacy of
- a) pressure relief capacity
- b) inerting systemsc) control systems
- d) emergency shutdown systems
- 2. All deficiencies including non-compliance with good engineering practice, regulatory agency standards and other applicable Code Standards are corrected.

How It Was Done

A team of specalists in test and inspection, operation, pressure vessel design, materials engineering, project and process engineering reviewed each system to determine the present status and the need for inspection and thickness measurements required for updated pressure vessel rating. Process and operating data requirements were defined.

About forty per cent of the equipment required inspection and thickness measurements and one-third required evaluation by process vessel designers to determine the necessary alterations or repairs, or to downrate the maximum allowable working pressure (MAWP).

Using the new information and a process diagram showing flows, operating conditions, relief devices and control systems, the project and process engineers made an indepth review and reported all deficiencies along with the recommended corrective action. The line organization prepared work orders and scheduled the outrages required to complete the required work.

The Results

Ninety-six (96) per cent of the 201 systems reviewed as of September 1, 1978 required some corrective action. The major deficiencies included:

333 changes in, or new, pressure relief devices required

173 vessels required replacement, alteration or repair

142 hydrostatic pressure test not made

91 relief devices with improper set pressure

79 emergency shutdown systems

Such a major upgrading effort requires total commitment on the part of management and is justified by the reduction in loss of material, equipment and people as well as reducing environmental and occupational health exposure.

We cannot continue to emphasize employee procedural protection efforts and ignore the potential for fatalities and material losses resulting from inadequate process, design or operating knowledge.

All chemical facilities are, because of balanced consideration of cost, loss prevention and safety, constructed with some element of risk in operation. We must provide enough technology to create a critical and analytical approach to process and equipment changes and the hazards they create. We must also generate a feeling a personal responsibility for safety and loss prevention in all phases of development, design, construction and operation.

A Base For Training

To provide this technology and motivation I prepared a "Process and Equipment Operating Safety Manual" with some help from other Chemicals and Plastics Division specialists. This manual deals with all disciplines involved in design, maintenance and operation of chemical processing units and is now being used as a training base for plant design engineers, operating engineers, supervisors and operators.

The purpose of the manual is to provide the technology needed to deal with the hazards of chemical plant design, operation and loss prevention.

Let's take a look at some situations that could have been avoided if sufficient knowledge had been provided and utilized.

Example Cases

Case 1 - Bottom dropped out of a 2 liter flask filled with mercury. - 10 yr PhD. - Density

Case 2 - Density, temperature, thermal expansion and vapor pressure.

21,000 gallon tank - 9 ft. diameter x 46 ft. high Calibration curve for TEA, temperature not specified.

Density - 0.7320 at 60°F. (Usual plant std.)

124,000 lbs. max. oper. level at 390" diff. pressure. (Completely full at 128,800 lbs. - TEA)

Service changed at TMA - Vapor pressure~1500 mm. Density - 0.6114 at 100°F, 0.638468 at 60°F. Completely full at 107,500 lbs and 337" diff.

10" R. D. blew at 9 psi - Set for 21 psi. Lost 36,000 lbs of TMA by vaporization.

Case 3 - Temperature, concentration, physical properties.

Concentrated alkaline catalyst and exceeded exotherm temperature of 175°C when stripping glycol ethers from residues. Property damage, three injuries, loss of material and production. Common knowledge not known - new personnel.

- Case 4 Concentration, controller leakage. Butadiene column put on total reflux during a unit maintenance outrage. Overhead make value leaked concentrating vinyl acetylene in the base. Blew up when concentration reached the detonation level.
- Case 5 Process and equipment change. The piping was changed in a common catalyst supply system for several vinyl resin autoclaves to facilitate washing and cleanup. The new piping also provided a bypass around the control valves when a valve was left open. Loss of life, extensive property damage and lost capacity.
- Case 6 Operating Error.

New operator set gas valves wrong during the purge period prior to lighting up a boiler. The deflagration upon ignition destroyed the precipitator.

Case 7 - Inerting, physical properties. Acetone (10%) and water (90%) mixture to be stored in an atmosphere pressure 300,000 gallon tank. Should the vapor space be inerted?

The flammability limits for acetone in air are 2.6 (LEL) and 12.8 (U.E.L.). A process engineer, using ideal gas laws, calculated the acetone concentration to be 1.26% or

48% of LEL and said inerting was not required. The solution is not ideal and the correction for non-ideality was 5.8 and the acetone concentration would be 7.3% - In the flammable range.

Wet hydrocarbons are very prone to static electrical discharge.

- Case 8 Metal temperature, relief discharge. Vapors from a relief device on a still column ignited and impinged on the surface of a pentane storage sphere. Sphere ruptured, 500,000 gallon fire ball, 19 firefighters injured.
- Case 9 Raw material and product change. A physical property factor relating temperature, pressure, latent heat of vaporization and molecular weight can be used to compare processes and determine the need for relief capacity change. Relief capacity is designed for the largest PPF.

$$PPF = \frac{1}{\Delta^{H_{V}(sp)}} \times \sqrt{\frac{T(sp)^{O}R}{M}}$$

Case 10 - Hydrostatic Testing

Must correct test pressure for stress/temperature ratios of the material of construction. Example: Everdur SB96 at 177°C.

Test Pressure = 1.5 x $\frac{12,000}{5,000}$ x MAWP

Test Pressure = 3.6 x MAWP

Test Pressure = 4.8 x MAWP (01d Vessel)

Case 11 - Insulation and relief capacity.

Four monomer storage tanks corroded under insulation. Proposed permanent removal.

Relief capacity based on fire exposure heat transfer rate of 6000 Btu per hour per sq. foot. Rate without insulation 20,000 Btu/hr/sq.ft.

Relief capacity inadequate by a factor of 3.3.

Conclusion

In conclusion, total management commitment to programs for upgrading and maintaining well designed and well operated facilities is needed to ensure a safe workplace with a minimum of personnel exposure and loss of material.

The goal of total loss prevention cannot be achieved without good educational and training programs, and requires enthusiastic commitment on the part of the work force to participate in these programs and share in the responsibility for providing a safe workplace.

* * *

DISCUSSION:

MR. RALPH C. BARLEY: I would like to ask either of the gentlemen in connection with the review I assume that the review is required as part of the formal procedure, and if I am on the right track, is it an overall procedure that triggers the beginning of this review, how is it implemented?

MR. NATHAN W. CLAUSS: The major equipment safety review project, as I said, was really kicked off by having two major industrial fires. The project was actually one of upgrading an old plant to meet current standards, so I guess you cannot call that a continuing review project. It is now set up to be maintained on an evergreen basis. My part in managing that project was to survey the entire plant, find any deficiencies and get them corrected.

MR. JEREMIAH LYNCH: Mr. Wheeler, aside from the training of operators that you discussed initially, or assistant operators, maintenance mechanics and other people, do you provide peridoic training, and if so, would you say it was better to do it in terms of frequent sort of interval training or less frequent, longer interval training, and who is the training done by; done by the foreman or professional trainers?

MR. R. NICHOLAS WHEELER: Short interval training is really the most effective, because your interest time span spread is somewhat limited. You determine a particular man or group of men have a deficiency in one of the modular subjects, then you take them and set up a class, and they are handled by trained trainers. Part of their job is to determine deficiencies and schedule people to be trained or retrained. This retraining is also quite important, like I said before, the guy tends to forget a fair amount of things. As soon as you get the feeling that he doesn't really know what he's doing, you retrain him again.

MR. JOHN HENSHAW: You mentioned the lower level operator and assistant maintenance people. How about contractors? What does Union Carbide do about contractors?

MR WHEELER: That is a little difficult. In the case of contractors, we usually made sure they know the basic safety rules and know their responsibilities, and if they're into an area where there is a hazardous chemical, they do receive training on that particular subject. Like I say, that one is a little difficult because you're caught between the idea that the contractor doesn't want to waste too much of his time having you train his men in safety. We simply must say, you've got to do this, and put that in as part of the contract.

MR. HENSHAW: You stipulate in the contract that you have the responsibility of training the individuals and what the liabilities are as well?

MR. WHEELER: Yes.

MR. HENSHAW: What type of medium do you use in your training sessions?

MR. WHEELER: We use television tapes, slide presentations and several written materials, it simply depends on the subject. Now, pay practices, everybody is very interested in pay practices. He is going to read that very thoroughly. He may not be so interested in the tag-out or lock-up procedures in the training module.

MR. EDWARD YANNE: How do you handle short-term employees like vacation replacements, if they're going to work on the site for six, eight, ten weeks?

MR. WHEELER: These so-called co-op students are actually assigned and mainly the responsibility of a particular technical man. It is up to him to see they are properly trained. They do receive their initial training, but they are as a whole, assigned to a "father" who is responsbile for their well being. We don't do too good a job of training temporary people and co-op students, as such.

DR. KEN BRIDBORD: What role, if any, do the labor unions play, either in the actual training or the review of the training material along with management?

MR. WHEELER: They most assuredly approve it, but basically it is still management's perogative on the training level. Like I say, our labor unions enthusiastically endorsed the making of the manual, making us fully aware of their problems. They like to have it all spelled out in black and white that you go from step one to step two to step three. I think we have seen an enthusiastic response for this program, and as I say, the atmosphere is quite permissive. If he doesn't get it the first time around, he can take it again, which is where the testing comes up. We have had several people go through this course several times before they were at minimum training level, and you determine this by testing and evaluation of his training at the end of the course.

DR. BRIDBORD: Are there professional people in unions involved with working with management to help decide what material is worthwhile and important?

MR. WHEELER: No.

- MR. DOUGLAS FOWLER: Who is responsible for initiating a design review, and at what level is the review approval given? Is this planned at the corporate level?
- MR. CLAUSS: There are several check points in the review of all design process changes. They have an in-depth safety review and halfway through the design, it is attempted to correct it. The report is turned over to the operator for their use, or for the plant engineer who works on smaller projects; they have a specialist whose job it is to review energy considerations, pipe control valves to try and find all the hazards that he can locate. Hopefully, this catches most of them. I might also mention that as far as manufacturing facilities are concerned, they will not start any facility until they have picked a team of talented people to go through the facility just before it's ready to go on the line and make a final survey.
- DR. JULIUS H. BOCHINSKI: Any other questions? As indicated earlier, Mr. Beliczsky and his panel were not able to participate. Instead, we will have a slide presentation by Mr. Nick Wheeler. He was faced with the problem of training people in seven different locations at the same time. He advised me that Union Carbide had made this training film available to the public at a minimal cost.

SESSION IV

IMPLEMENTATION OF CONTROL AND CONCLUSIONS

Moderator

John T. Talty National Institute for Occupational Safety and Health Cincinnati, Ohio MR. JOHN TALTY: This is the final session of this symposium called Implementation of Controls and Conclusions. I am John Talty with NIOSH, Branch Chief of Control Technology Research, located in Cincinnati, Ohio. One of the things I am responsible for is the implementation of the control technology assessment studies, one of which is being discussed at this symposium. In that capacity, I feel motivated to respond to a few of the comments that were made yesterday, without being overly defensive. I want to say thank you to the companies that did participate in the plastics and resins study. Their cooperation was very instrumental in providing our contractor and NIOSH with the opportunity of documenting exemplary programs.

Our contract with Enviro Control was for approximately \$90,000, close to two man-years of effort. We feel that the contractor did a top notch job for us, given the amount of money received, and the difficulties encountered.

Personally, I think this is one of the best investments I have seen in over 18 years with the Public Health Service. We got a very good piece of work on this particular contract. It was implied yesterday that the results of our control technology study may become requirements. That is not the intention at all. We do plan to develop a technical guide for control technology, using the Enviro Control study and the symposium, later this fiscal year. It is not our intent to translate these findings into mandatory requirements.

Moving onto Session 4, Implementation of Controls; I recently had an experience and the privilege of participating in a ceremony for my son who became an Eagle Scout which emphasized the motto of the Boy Scout movement, "Be Prepared". I think that is the theme of the session we are having this afternoon.

As new or improved plastics and resin plants are designed and constructed, the engineering designer must be prepared to prevent occupational hazards in the design process. This calls for an awareness of the need, and obviously the ability to do so. The papers this afternoon are intended to address this specific topic. Looking at some of the trade journals in the plastics field, I noticed in January of 1978 there was a very interesting editoral in the Plastics Engineering magazine on plant obsolescence, and a discussion of the newly licensed Union Carbide process for making low density polyethylene. Some of the comments made in that editoral are very pertinent to what we're going to be talking about today. New variables need to be considered in the planning of absolescence, including the all prevading consideration that must be given to the effect of plant operations on plant workers and the environment. Forward looking thinking is what we're really trying to stimulate in this symposium.

I think that leads right into the first speaker today, Mr. Jerry Schroy.

He graduated from the University of Cincinnati as a chemical engineer. He joined Monsanto directly out of school, and has worked for them in a variety of assignments during the past 15 years. He is presently assigned to the Engineering Department in St. Louis, involving the control of wastewater effluents. He is a registered professional engineer and considers his function to be that of a process engineer with primary concern for control of dilute effluents and low-level emissions. His most recent assignments involved testimony on the OSHA acrylonitrile standard for both Monsanto and the Society of the Plastics Industries. His talk today will outline a method of dealing with emissions to the workplace during project design.

PREDICTION OF WORKPLACE CONTAMINANT LEVELS

Jerry M. Schroy Monsanto Company St. Louis, Missouri

The prediction of concentration of specific chemicals in the work-place based on engineering design data is a major concern for the designer. A workplace procedure which utilizes emission rate data and gaussian dispersion models has been developed for the process design engineer.

The information presented provides vapor emission rate data for estimating losses from equipment, piping and open pools of pure components when actual data are unavailable.

Case studies related to vinyl chloride and acrylonitrile will be discussed in terms of present OSHA regulations for these materials.

Introduction

The papers presented during the past two days have principally addressed situations related to existing facilities. The questions of controlling personnel exposure have involved field testing actual exposure conditions, revising work practices and retrofitting engineering controls. While this approach is effective for existing facilities it does not meet the needs of revised or new technology. And with the increasing number of chemicals considered to be hazardous at low concentrations, field correction of design errors is becoming even more impractical. In fact, the drain on technical resources at the plant level is also limiting production innovation and product development activities.

It is important to note that the problem is in effect created by good engineering practices. The designer selects the most economical equipment which fits the process requirements. And present chemical processing technology involves use of equipment and/or operating and maintenance techniques with a wide range of loss or leakage characteristics. (1, 2, 3, 9).

While the design engineer can attempt to economically optimize a process, by maximizing conversion, yield and/or recovery; the process economics do not preclude loss of small quantities of raw materials, products and/or by-products to the workspace. Unfortunately, present research and development practices provide little or no data on the loss of leakage rates of specific chemicals from key process equipment. For these reasons, the problems of controlling emissions have been left unanswered during the design phase of project. While this practice has been satisfactory for materials with low volatility or high allowable

exposure limits (i.e. 100 ppm(v)), this practice has proved to be costly for volatile materials such as vinyl chloride. The costs are not just capital they also involve overcommitment of human resources.

When exposure concerns arise in an operating unit the corrections must be handled by the plant hygienist and operating personnel as a retrofitting project. While most hygienist are capable of identifying exposure control concerns they frequently have little engineering background. Therefore, design changes which would have involved simple layout revisions during design, often become expensive local ventilation systems.

Until recently, stipulations to correct exposure concerns during design have led to installation of engineering controls which may unnecessarily increase the cost of the facilities.

To avoid committing our human technical resources to retrofitting work and/or overcommitment of capital resources to unnecessary controls, a design procedure is needed to predict the impact of design decisions prior to completion of project definition. One method which has been developed based on literature data, and which shows merit if properly applied, is described below.

Discussion

To meet the need described above a method was developed to define the impact of a chemical's physical properties on its behavior as a workplace contaminant. When the importance of physical property differences was described it became obvious the methodology was a valuable design tool.

The design procedure is based on a gaussian dispersion model.(1) At present gaussian models represented the most practical method of analyzing the downwind impact of an emission to the workplace. The dispersion correlation has been developed for use when the source and receiver are relatively close.(5) The relationship is designed to predict maximum downwind concentrations as a function of distance from the source, where the dispersed plume does not reflect from a solid surface (i.e. an unconfined plume, see Figure 1 in the appendix). Utilizing vapor emission rate data, the design engineer can calculate the expected workplace concentration from either one source of a number of sources which would impact the same point.

The air dispersion equation for maximum downwind concentration, assuming that there is some air movement, at a given downwind distance from the unconfined vapor leak is given by Equation 1:

 $C'_{max} = 1337.786 \cdot Q/[M \times \overline{U}'] \cdot [1/(2\pi\sigma_y\sigma_z)]$ (Eng. 1)

Where

- Q = is the quantity of the chemical of concern being released from the source in grams per hours.
- T' = is the velocity of the workplace ambient air passing the point of release in feet per minute.
- σ_{y} & σ_{z} = are diffusion coefficients in meters which are functions of the distance, d, from the leak source which is being considered gives values of the function $1/(2\pi\sigma_{y}\sigma_{z})$ as a function of distance, d. (See table 1 in Appendix, also a graphical representation is given in Figure 2.)
- M = molecular weight of the chemical of concern.

Graphical presentations of Equation 1 are given in the Appendix for Acrylonitrile and Vinyl Chloride (i.e. Figures 3 and 4 respectively). The graphs allow rapid determination of the maximum workplace concentrations for a set of normal ambient conditions. For ambient conditions not covered by the graphs, Table 1 (Diffusion Functions) is given to allow calculation of the workplace concentrations.

The correlation can also be used to provide conservative results for large surface sources (eg. pools or open tanks). However, if the results of the emissions from an open surface are critical to the design, a more detailed correlation, which recognizes the importance of pool length and width, should be considered. 96) Predictive methods are available for calculation of emission rates from quiescent pools (7) and surface aerated pools. (8)

Emission rate data is tabulated in the Appendix (Table 3) for quiescent pools of pure vinyl chloride (VCM) or pure acrylonitrile (AN) and water-VCM or Water-AN mixtures.

As can be seen from the relationship (Equation 1) or the graphical presentations (Figure 3 and 4) valid emission rate data is the key to determining the maximum workplace contaminant concentration. Whenever

possible this data should be determined experimentally during the research and development phase of a project. When emission rate data are not available, from material balances or R&D results; estimates of emissions should be used. The data presented in Table 2 (Vapor Emission Rates) represents the best literature values for Acrylonitrile or vinyl chloride emissions from specific process loss points. It is critical to note that emission points are not unit operations but seal points, either dynamic or static seals.

Recommendation

Utilizing the correlations and data described above the designer should determine the impact of proposed design alternatives. The following methodology should be applied to quantify the workplace risks for alternate methods to control workplace contaminant levels.

- 1. Summarize all key emission points and tabulate either actual or estimated emission rate data, for each design case being considered.
- 2. Define the ambient conditions, including prevailing wind directions, and identify key operations areas which will be impacted by know vapor emissions. For a process which is subject to frequent maintenance access, periodic emissions should also be defined.
- 3. Workplace concentrations should be calculated for each "hot spot" by summing the concentrations due to individual sources.

$$(C'_{max})_{total} \equiv \sum_{i=1}^{n} (C'_{max})_{1}$$
 (Egn. 2)

4. The risk associated with each engineering control or operations change should be summarized and reviewed to identify the actions which provide the maximum benefit in terms of its cost.

APPENDIX

Table 1 Limit of Correlation Validity

Diffusion Function

Figure 2 Diffusion Function

Figure 3 Dispersion of AN Emissions

Figure 4 Dispersion of VCM Emissions

Table 2 Compliation of Emission Rates

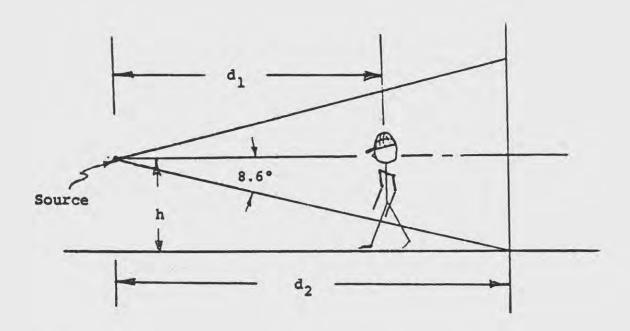
Table 3 Emissions from Unconfined Surfaces

Example Calculations

Figure 5 Example Layout

Table 4 Emission Analysis

Bibiliography



d₂ = limit of correlation validity

 d_1 = distance from source of interest

h = source height above confining surface

 $h_{max} = d_2 \times tan 8.60$

Figure 1. Limit of correlation validity.

VALUES OF (1/(2 m $_{\rm Y}$ $_{\rm Z}$)) FOR EQUATION 1, m $^{-2}$

Meters (1/(2m ⁰ y ⁰ a ₂)) Feet Meters (1/(2m ⁰ y ⁰ a ₂)) Feet Meters (1/(2m ⁰ y ⁰ a ₂)) Feet Meters (1/(2m ⁰ y ⁰ a ₂)) Feet Meters (1/(2m ⁰ y ⁰ a ₂)) Feet Meters (1.2.0 0.1458 12.0 0.01447 13.12 4.0 0.07074 98.4 3.0 0.1347 16.0 0.06844 131.0 4.0 0.01326 16.0 0.06844 131.0 4.0 0.01326 16.0 0.06873 229.7 70 0.1259 18.0 0.05873 229.7 70 0.1059 20.0 0.05873 229.7 70 0.00929 25.0 0.0 0.05451 295.3 90 0.009288 29.53 9.0 0.04912 328.1 100 0.09853 30.0 0.04131 3.0 0.08853 30.0 0.04131 3.0 0.08853 35.0 0.03521	DIST	DISTANCE, d	VALUE OF	DISTA	DISTANCE, d	VALUE OF	DISTANCE,	NCE, d	VALUE OF
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0.09288 29.53 9.0 0.08653 30.0 4 3.0 0.08120 32.80 10.0 0.08069 35.0	7.0		0.09929	26.25	8.0	0.04528			
0.08653 30.0 3.0 0.08120 32.80 0.08069 35.0	8.0		0.09288	29.53	0.6	0.04188			
4 3.0 0.08120 32.80 10.0 0.08069 35.0	0.6		0.08653	30.0		0.04131			
0.08069 35.0	9.84	3.0	0.08120	32.80	10.0	0.03789			
	10.0		0.08069	35.0		0.03521			

Table 1. Diffusion function.

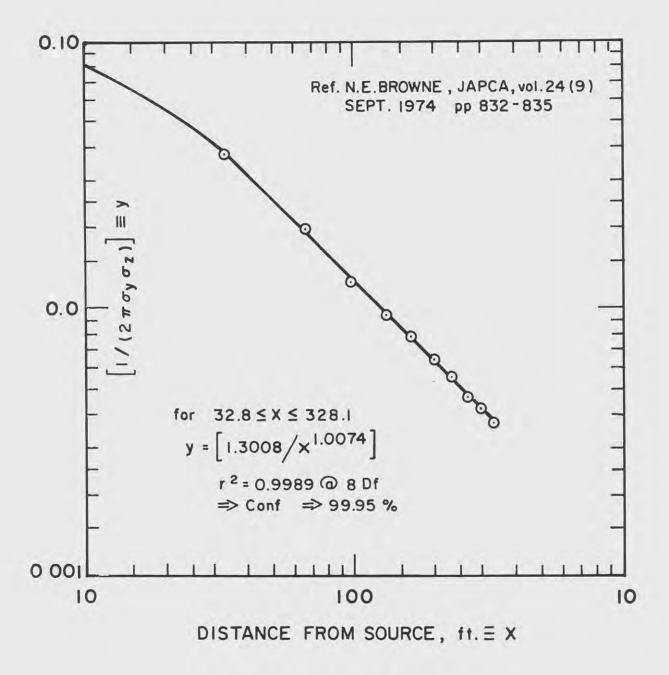


Figure 2. Diffusion function.

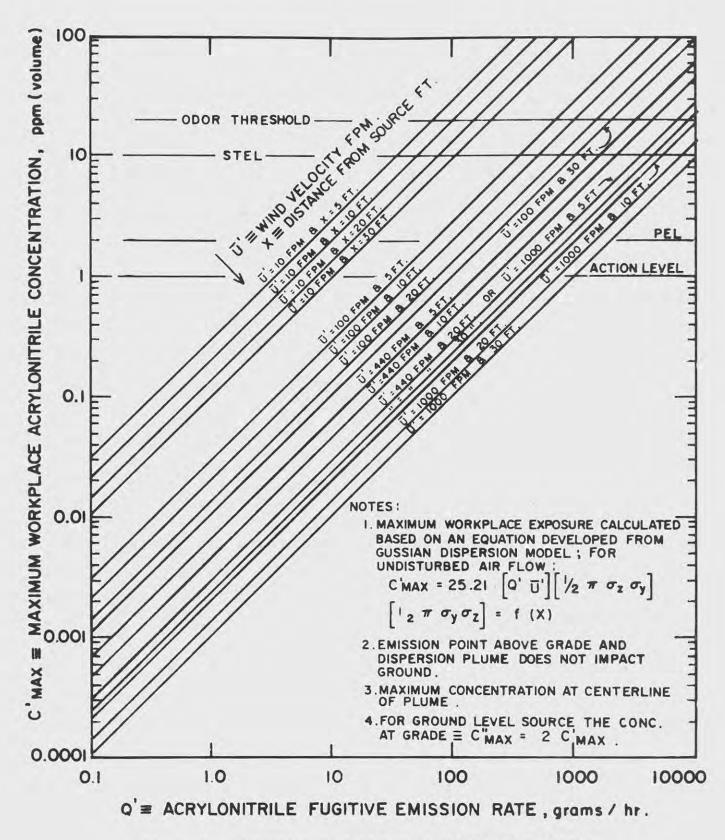


Figure 3. Dispersion of fugitive acrylonitrile emission.

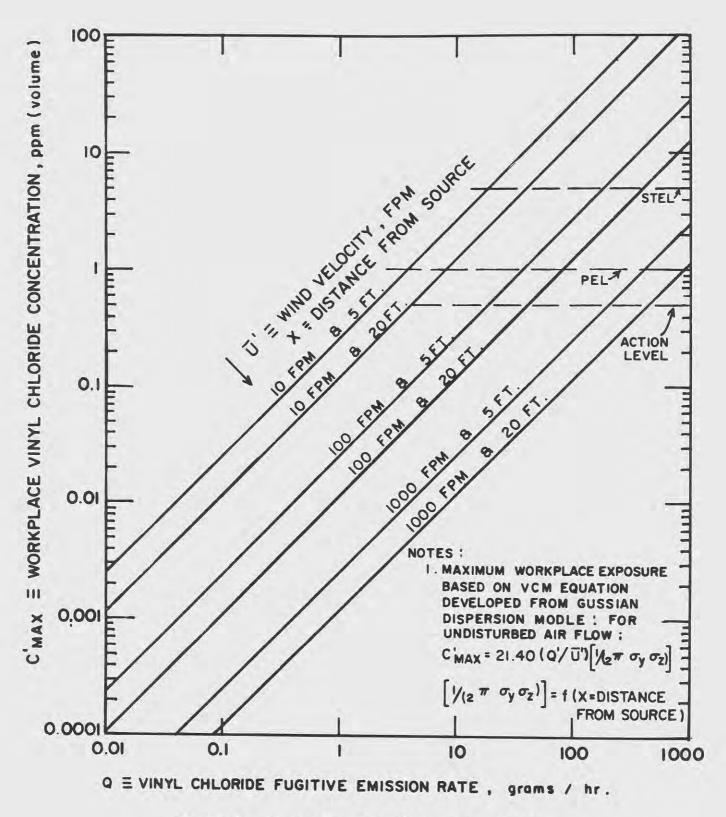


Figure 4. Dispersion of fugitive VCM emission.

TABLE 2

COMPILATION EMISSION RATES FROM PIPING SYSTEMS AND PROCESS EQUIPMENT

|LEAKAGE RATE, GRAMS PER HOUR (Except as Noted)

_		Good Preventive Average to Poor				
	ITEM	Good Preventive Maintenance	Average to Poor Prev. Maintenance	Remarks		
1)	FLANGES					
	a) 150-300 lb:					
	·Gas Service ·Liq.Service	0.0061 (1) 0.0610 (1)	0.061 (1) 0.610 (1)			
	b) 600-1200 lb:					
	'Unspecified	0.0031 (1)	0.061 (1)			
2)	<u>VALVES</u> (Stem Seals)					
	a) Gate & Control:					
	·150-300 lb ·600-1200 lb	6 0.1	30 2.8			
	b) Ball (1/4 Turn)	0.015	2.8			
	c) Press Relief to ATM	2.8	5.5			
	d) Press Relief w/ rupt. disk	NIL	55 (2)	Poor Maint. No Rupt.Disk Replacement		
3)	PUMPS or COMPRESSORS (3)			Nepracement		
	a) Rotary Seals:					
	Packed Single Mechanical	80	473	Estimate of Face Velocity on Seal is 375 fpm		
	-Proc. Fluid Flush -Water Flush(2)	6 0.02	60 60	Estimate Poor Maint. Seal Fluid Failure		
	· Double Mechanical	NIL	6+ (2)	+Flush Fluid Problem or Interna Seal Problem		
4)	COMPRESSORS			5641 1165164		
	a) Reciprocating Seals:					
	Rod packing (2) Single Double	16 13	509 104			
5)	AGITATORS	or Double Mechan	using data on Pack nical Rotary Seals gitator=Pump Seal			
6)	TANKS (D)		/elocity,fpm ÷ 375 f	Lmd		
	a) Floating Roof	Use 60% of API Bul. 2517 Calcs				

Refs: (A) A. Bierd, A. Stoekel, R. Sinn & H. Kremer, Chem-Ing Tech, 49 (1977) 589 (2/77)

⁽B) F.D. Snell, <u>Benzene Survey</u>, Memo to MC (from J.A. Mullens with Shell Oil Proposal, September 20, 1977.

⁽C) D.D. Rosebrook "Fugitive Hydrocarbon Emissions" Chemical Engineering Deskbook, October 17, 1977, pp 147, McGraw Hill.

Compilation of Air Pollutant Emission Factors, 3rd Edition (with Supplements 1 to 7), U.S. Environmental Protection Agency, Apr 77, PB 270281, (AP42).

⁽¹⁾ Grams per Hour per Pt. of Outer Flange Circumference. Approximate flange circumferences given in Table 4.

⁽²⁾ Estimated value also valid for use of a high molecular weight oil as a flush fluid (3) Values for Pumps would be estimates for Compressors

TABLE 2 COMPILATION EMISSION RATES FROM PIPING SYSTEMS AND PROCESS EQUIPMENT

LEAKAGE RATE, GRAMS PER HOUR (Except as Noted)

		DEARAGE RATE, GRAMS FER HOUR (Except as Noted)		
	ITEM	Good Preventive Maintenance	Average to Poor Prev. Maintenance	Remarks
1)	FLANGES			
	a) 150-300 lb:			
	Gas Service	0.0061 (1) 0.0610 (1)	0.061 (1) 0.610 (1)	
	b) 600-1200 lb:			
	*Unspecified	0.0031 (1)	0.061 (1)	R
2)	VALVES (Stem Seals)			
	a) Gate & Control:			
	-150-300 lb -600-1200 lb	6 0.1	30 2,8	
	b) Ball (1/4 Turn)	0.015	2.8	
	c) Press Relief to ATM	2.8	55	
	d) Press Relief w/ rupt. disk	NIL	55 (2)	Poor Maint. No Rupt.Disk
3)	PUMPS or COMPRESSORS (3)			Replacement
	a) Rotary Seals:			
	·Packed ·Single Mechanical	80	473	Estimate of Face Velocity on Seal is 375 fpm
	-Proc. Fluid Flush -Water Flush(2)	6 0.02	60 60	Estimate Poor Maint. Seal
	· Double Mechanical	NIL	6+ (2)	Fluid Failure +Flush Fluid Problem or Interna
4)	COMPRESSORS			Seal Problem
	a) Reciprocating Seals:			
	Rod packing(2)			
	SingleDouble	16 13	509 104	
	AGITATORS	or Double Mechan Pumps. Losses Ad	! using data on Pack nical Rotary Seals gitator=Pump Seal	for
6)	TANKS (D)	Losses x (race)	/elocity,fpm +375 f	Pm.)
	a) Floating Roof	Use 60% of API Bul. 2517 Calcs		

Refs: (A) A. Bierd, A. Stoekel, R. Sinn & H. Kremer, Chem-Ing Tech, 49 (1977) 589 (2/77)

(3) Values for Pumps would be estimates for Compressors

⁽B) F.D. Snell, Benzene Survey, Memo to MC (from J.A. Mullens with Shell Oil Proposal, September 20, 1977.

⁽C) D.D. Rosebrook "Fugitive Hydrocarbon Emissions" <u>Chemical Engineering Deskbook</u>, October 17, 1977, pp 147, McGraw Hill.

[,] Compilation of Air Pollutant Emission Factors, 3rd Edition (with Supplements 1 to 7), U.S. Environmental Protection Agency, Apr 77, PB 270281, (AP42).

⁽¹⁾ Grams per Hour per Ft. of Outer Flange Circumference. Approximate flange circumferences given in Table 4.
(2) Estimated value also valid for use of a high molecular weight oil as a flush fluid

Table 3 - Emissions from Unconfined Surfaces Chemical Emission Rate, grams/(hr x ft²)

Chemical Emission Rate, grams/hr/ft² Solar* Radiation, BTU/hr/ft² Wind Speed, fpm (mph) 114) 100(1.14) System 10(0.114) 440(5) Pure Components (Pool depth 1/2") Acrylonitrile 0 24.2 111.6 255.9 250 437.3 65.4 234.9 Vinyl Chloride 0 764.9 2392.6 5052 250 1243.6 2280.4 6304 $\frac{\text{Water Mixtures}}{\leq 4} \quad \text{(At concentrations at or above saturation, water depth } \\ \leq 4 \quad \text{feet, for Solar Radiation of 0 or 250 BTU/(hr ft^2))}$ Acrylonitrile ≥ 7.0 wt% Vinyl Chloride ≥ 0.27 wt % 24.2 111.6 255.9 764.9 2392.6 5052

	Concentration wt %			
Acrylonitrile	0.2 *	0.70	2.62	4.17
	0.2 **	0.55	1.29	1.58
	7.0 *	20.14	81.75	140.12
	7.0 **	16.54	43.46	55.83
Vinyl Chloride	0.135*	3.96	4.07	4.09
	0.135**	1.25	1.26	1.26
	0.27*	7.89	8.13	8.16
	0.27**	2.49	2.51	2.52

Notes: Solar radiation = 0 ≡ Dark or indoors, and 250 ≡ Daylight

The rate is highly dependent on liquid phase diffusion. Therefore maximum rates (i.e. initial) are given for each condition noted. To correct the data for pool depth divide the emission rate by pool depth (feet) to the 0.85 power. For correction of the rate for concentration multiply the value noted by the factor of the desired concentration divided by the reference concentration (note: do not exceed the solubility limit noted).

Example Calculations

The example presented below is intended to clarify use of the tables and graphs. The designer should note that the intent of the guideline is to define conditions which will protect people. For this reason assumptions should be made which will give conservative answers, or the assumptions should be clearly identified as operating criteria. A few examples are as follows:

- 1. When emission sources are at different elevations, such that the maximum plume concentration will not coincide, the designer should assume that the maximum concentrations will be additive.
- When a large surface source, such as an open manhole, is evaluated the designer should consider the center of the surface as a point source.
- 3. When using estimated vapor emission rate data, values for good preventive maintenance practices may be used. However, operations must commit to this type of a maintenance program.

An acrylonitrile (AN) mix tank and transfer pump are to be installed in an existing unit. The objective is to install the tank the pump such that the AN concentration in the workplace will not exceed the action level (i.e. $1\ ppm\ (v)$) at a nearby work station.

The unit is an indoors installation with once through building ventilation. The average air velocity is 10 feet per minute. The tank is to be installed as shown in Figure 5. The AN is at ambient temperature, 75° F.

The design questions to be answered are as follows:

- What type of agitator seal should be used: Packed or double mechanical seal?
- What type of pump seal should be used? Packed, single or double mechanical seals? (An oil flush fluid would be compatible with use in either a single or double mechanical seal).
- Is a ventilation system needed to collect emissions during additive additions?

As indicated in the procedure outlined on Page 4, the process emission points are summarized in Table 4. Using Table 2 the emission rates are tabulated for various scenarios with Table 3 used to determine the emission rate from the open manhole.

The scenarios considered are as follows:

- I. Packing glands are used on both the pump and agitator and no control is used to limit emissions from the hand hole.
- II. A single mechanical seal with flush fluid is used for the pump and a double mechanical seal is used for the agitator. A fume control system is used to limit emissions from the hand hole.
- III. Double mechanical seals are used for both the pump and agitator. A fume control system is used to limit emissions from the hand hole.

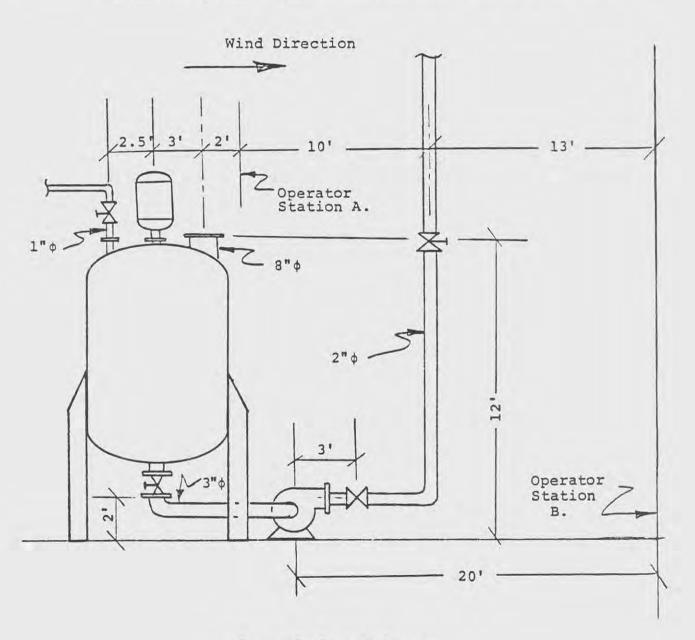


Figure 5. Example layout.

Table 4. Emission analysis.

	point of emission receptor	t of sion to otor ft	Emission Rate (grams/hour) for Scenarios	hour)	**	Conc Once 1	entrat A hru Ai	Concentration at Work Station, (ppm (v)) A B B Once Thru Air, 10 fpm Once Thru Air, 10 f	ĕ	Station, (ppm (v)) B Once Thru Air, 10 fpm	10 fpm
Emission Points/(Number)	A	Д	I	II	III	I	II	III	_	II	III
1" \$ Ball Valve Stem/(1)	7.5	30.5	0.015	0.015	0.015	₹0.01	40.01	₹0.01	₹0.003	₹0.003	K 0.003
Flanges on 1" valve/(2)	7.5	30.5	0.156	0.156	0.156	0.038	0.038 0.038	0.038	0.011	0.011	0.011
Agitator Seal Packed/(1) Double mechanical/(1)	N IA	28	8 1	1 0	1 0	23.5	0	0	60	٥	•
8" 4 Hand Hole/(1)	7	25	0	0	0	3,22	0	0	1.11		0
2" & Ball Valve Stem/(1)	10	13	0.015	0.015	0.015	< 0.01 <0.01		< 0.01	\$ 0.00e	< 0.006 < 0.006	<0.006
Flanges on 2" valve/(2)	10	13	0.208	0.208	0.208	0.042	-	0.042	0.037	0.037	0.037
Subtotal @ EL = 12			89.394	0.394	0.394	<26.8	<0.10	≤0.10	210.0	≥0.06	20.06
3" \$ Ball valve stem/(1)	'n	28	0.015	0.015	0.015	\$00.0	<0.004	<0.004 ≤0.004	≤0.002	<0.002 <0.002	<0.002
Flanges on 3" valves/(2)	10	28	0.264	0.264	0.264	0.08	0.08	0.08	0.03	0.03	0.03
Pump Seal Packed/(1)		20	80			27.16			11.0		
Single Mechanical*/(1) Double Mechanical?(1)	mm	20		0.02	0		₹0.007	0		₹0.003	0
2" \$ Ball Valve Stem/(1)	9	17	0.015	0.015	K0.015 0.004	10.004	0.004	0.004 <0.004	≤0.002	\$0.002 \$0.002	\$0.002
Flanges on 2" Valve/(2)	9	17	0.208	0.208	0.208	0.056	0.056	0.056	0.032	0.032	0.032
Flanges on Pump 2" 4/(1) 3" 4/(1)	₹ m	19	0.104	0.104	0.104	0.033	0.033	0.033	0.015	0.015	0.015
Subtotal @ EL = 2'			80.738	0.758	0.738	≤27.4	0.023	≤0.22	511.1	≤0.1	50.1
Total All sources	-		170.132 1.152	1.152	1.132	1.132 <54.2 <0.33		<0,32	<21.1	50.16 <0.16	<0.16

* with flush " with seal fluid

As can be seen from Table 4 Scenario II offers the desired emission control for a building with once through air flow.

The data compiled in Table 4 can also be used to determine the impact of a ventilation system which recirculates air. Considering the workspace volume shown in Figure 5 as representative of the building, the equilibrium concentration can be calculated using the chemical emission rate and air exhaust rate from the workspace. The workplace volume is 9000 cubic feet (15'x20'x30') and for a ventilation rate of 15 air changes per hour the exhaust air is 2250 CFM. The concentration in the exhaust air is assumed to be equal to the room air and can be claculated as follows.

Conc., ppm =
$$\frac{\text{(Emission rate gm/hr / (454 gm/lb x mol wt.)}}{\text{[Exhaust volume CFMx60 min/hr.]}}$$

$$= \frac{\text{Emission Rate gm/hr}}{\text{Exhaust Volume, CFM}} \begin{cases} \frac{390 \times 10^6}{454 \times 60 \times 53.1} \end{cases}$$
Conc., ppm =
$$\frac{\text{Emission Rate, gm/hr}}{\text{Exhaust Volume, CFM}} \begin{cases} 270.05 \end{cases}$$

For the conditions cited for Scenario I, II and III a recirculation air system with 15 air changes per hour would have the following workplace contaminant levels.

Scenario	Workplace Acrylonitrile Concentration, ppm (v)
Í	20.4
II	0.14
III	0.14

To achieve a level of 1 ppm (v) for conditions given in Scenario I, air recirculation would require 306.3 air changes per hour or a once through wind velocity of 153.2 fpm (1.74 mph).

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- 5. Brown, N. E., "Diffusion Rates," <u>Journal of the Air Pollution Control Association</u>, 24 (9), Sept. 1974, pp 832-835.
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- 9. Tierney, D. R., Khan, Z. S., Hughes, T. W., "Measurement of Fugitive Hydrocarbon Emissions from Petrochemical Plants," <u>Third Symposium on Fugitive Emissions: Measure and Control</u>, San Francisco, California, Oct. 23-25, 1978.

* * *

MR. JOHN T. TALTY: Thank you, Jerry. If there are any questions later you can bring them up.

The next speaker is Louis C. Knox. He's the Vice President and Chief Engineer of Catalytic Incorporated. He is a chemical engineer with 35 years experience in the refining and engineering/construction industry. The title of his presentation is Design of High-Containment Polymerization Process.

DESIGN OF A HIGH-CONTAINMENT POLYMERIZATION PROCESS

Lewis C. Knox Catalytic, Inc. Philadelphia, Pennsylvania

INTRODUCTION

A recently designed plant for the production of suspension type polyvinyl chloride and vinyl acetate vinyl chloride copolymer incorporates several systems to reduce exposure of employees by limiting the release of vinyl chloride into the atmosphere to acceptable values. The plant, represented in simplified fashion in Fig. 1 is an adaptation of the classic batch polymerization process. The parallel recovery of vinyl acetate is not shown.

The reactors discharge slurry to a blowdown tank which is vented through a water scrubber to a large gas holder acting primarily as a surge tank in the suction of the liquid ring compressor feeding the monomer recovery condensers. The cold condenser vent is disposed of in an incenerator fitted with a tail gas scrubber. The gas holder and the incinerator are two departures from the old norm. These and some other departures are the subject of the paper. The reader will note that the paper discusses the containment of vinyl chloride without regard to whether a given regulation stems from OSHA or EPA rules; these rules in any case often overlap in their effect even if they differ in intent.

The protective measures taken in this design divide themselves, at least for purposes of discussion, into three classes. They are:

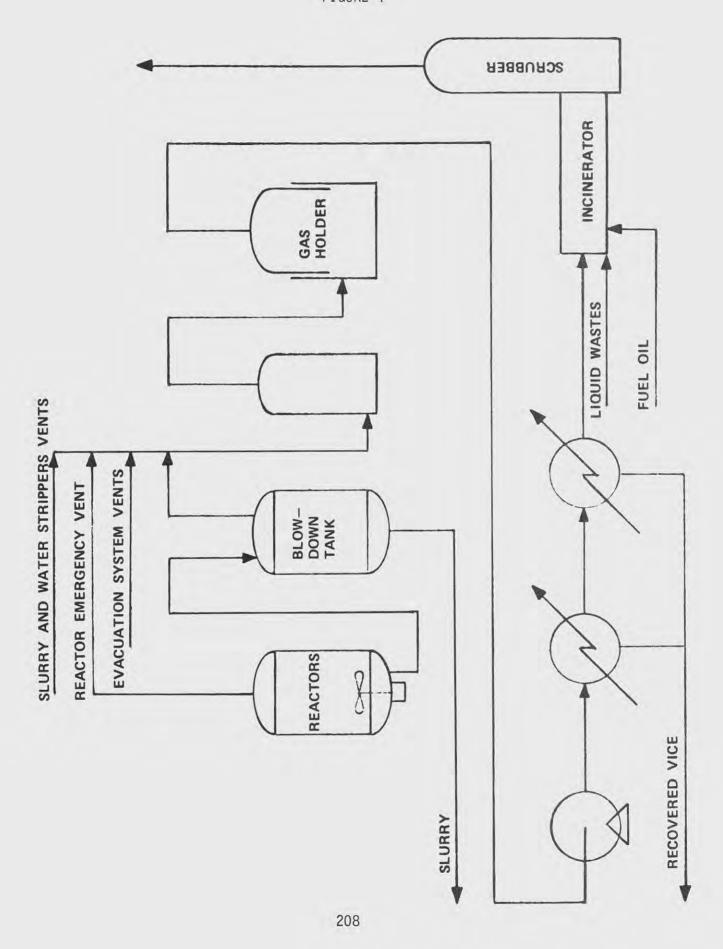
Systems permanently installed to protect personnel from vinyl chloride concentrations exceeding the standards:

- Breathing air network
- Gas chromatograph monitors
- Lower explosive limit (LEL) detector and alarm system

Systems to contain or reduce emissions connected with mechanical devices or maintenance operations.

- Gas holder in recovery system
- Fugitive emissions capture system
- Reactor safing procedure and the water displacement system
- Double mechanical seals

FIGURE 1



• Reciprocating shaft seals

Systems dealing with irreducible process vents.

- Steam stripping of slurry (and water)
- Incineration of the cold condenser vent

BREATHING AIR NETWORK

This system is by now standard in every installation handling vinyl chlorides. Air is taken in high, preferably well to windward (and not to leeward of some other plant's discharge) compressed in oil-free, spared machines, filtered, passed through active carbon adsorbers, and distributed at 70-100 psig to a number of quick-connect outlets. The outlets in this installation, provided with sintered bronze final filters, are located near vessels which must be periodically opened (reactors, filters) or where a serious leak may unexpectedly develop (large pumps). Hose lengths stored near the outlets are connected by the use of a reducer and half-face mask. In this installation the air reservoir is continuously monitored by a gas chromatograph set to alarm at ½ ppm. The carbon is changed periodically and safely disposed of.

GAS CHROMATOGRAPHS

Four gas chromatographic analyzers are installed to continuously monitor some 35 sample points throughout the installation. They indicate locally on a strip chart and store each reading in a computer for daily print-out. Alarms in the control room and lights near each sample point indicate excursions from the norm.

About half the sample points are in the polymerization and monomer recovery units, the rest are near likely sources of leaks. Two are in each incinerator stack and three are in the air intakes of the two control rooms.

COMBUSTIBLE GAS DETECTOR

Some 30 sample points throughout the plant are connected to catalytic oxidation type combustibles detectors, sometimes referred to as LEL or lower explosive limit detectors. Their distribution is similar to the chromatograph sample points. All are set to indicate a warning at 10% of the LEL and to sound a general alarm at 60% of the LEL. Those at the polymerization and the monomer recovery areas will also trip off the local deluge system, if in a five second grace period the operator does not defeat the action with a manual selector switch. The same switch can be used to start the deluge system if the automatic system malfunctions. In any case, when the polymer area deluge valve is tripped open, the ventilating fans are simultaneously shut down.

The detector at the control room air intake shuts off the air at a level of 60% of the LEL.

Besides all this, there is a detector at each (indoor) motor control center that close the ventilating louvers at a level of 60% of the LEL.

GAS HOLDER IN RECOVERY SYSTEM

Most of the unreacted monomer remaining in the PVC reaction mass (suspension process) is released in the blowdown tank when the slurry is tranferred from the reactor (at high pressure) to the blowdown tank (at low pressure, essentially atmospheric). The VCM vapor release from the blowdown tank is a batch operation and relatively large volumes of vapor are released in a short time, say $\frac{1}{2}$ to 1 hour.

A vapor recovery system (since the vapor cannot be discharged into the atmosphere), sized to handle the instanteneous discharge would be too large and uneconomical. A gas holder, to act as a surge tank is, therefore, installed to collect these vapors and feed the recovery train at an average rate. The recovery train can thus be operated continuously. The recovery train typically consists of a compressor, followed by multistage condensation, followed by carbon adsorption or incineration.

A water scrubbed is provided upstream of the gas holder to minimize carryover of foam (solids) into the gas holder.

In addition to collecting reacted monomer discharge from blowdown tanks, the gas holder collects various VCM-containing vapor streams for recovery, thus avoiding atmospheric discharge of those streams. Other vapor streams are as follows:

- 1. Reactor Vent: EPA permits manual discharge of reactor contents to reduce the discharge to the extent possible of the vapor to atmosphere via a relief valve. This will be vented to the gas holder.
- Slurry Stripper and Waste Stripper Vents:
 These strippers reduce the VCM content of the slurry or waste water to limits acceptable by EPA.
- 3. Displacement Water Tank Vent: This tank holds water which is used to purge reactors or any other equipment of VCM Vapors. The tank is maintained at gas holder pressure, slightly above atmospheric.
- 4. Fugitive System Vent:

 The fugitive vent collection and evacuation system discharges all vapors to the gas holder for recovery.

5. Monomer Charge Tank & Recovered Monomer Tank Vents:
The pressure regulating vent valve(s) discharged from these tanks are piped to gas holder to avoid atmospheric discharge.

Figure 2 is a sketch of the scrubber and gas holder

FUGITIVE EMISSIONS CAPTURE SYSTEM

The term "fugitive emission sources" as discussed in EPA guidelines, pertains to VCM discharges at loading or unloading operations; leakage from pumps, compressor and agitator seals, leakage from relief valves; manual venting of gases; opening of equipment for maintenance; leakage at sampling points; leak detection and elimination procedures; and emissions from in-process waste water.

Here, Fugitive Emissions System means essentially that system provided to minimize VCM discharges due to opening of equipment and/or piping for maintenance purposes.

According to EPA regulations, before opening any equipment for any reason, the quantity of VCM is to be reduced so that the equipment contains no more than 2% by volume VCM or 25 gallons of VCM vapor, whichever is smaller at standard temperature and pressure.

An evacuation and collection piping system is provided throughout the plant in all areas which process VCM. This system has a capability of reducing the pressure in the equipment or piping to 2 psia an thereby limits the applicability of this system to pieces of equipment or piping that have a maximum enclosed volume of approximately 170 gallons, calculated as follows:

$$25 \times \frac{(460 + 60)}{(460 + 60)} \times \frac{14.7}{2} = 172 \text{ gallons}$$

All equipment or piping which contains enclosed volume of 170 gallons or more will be evacuated by using a water displacement procedure similar to the one practiced during reactor "safeing" procedure. All vapors being vented to a gas holder for recovery. See Fig. 3 for a simplified arrangement.

Procedure for use of the Fugitive Emission Containment System is as follows: (up to 170 gallons)

1. All equipment and/or piping containing VCM is provided with blind flanged vent connections and necessary valves to connect it with the fugitive emissions evacuation system. When such equipment and/or piping is taken out of service for maintenance, it is first vented to gas holder, which brings the pressure in the equipment to near atmospheric.

GASHOLDER

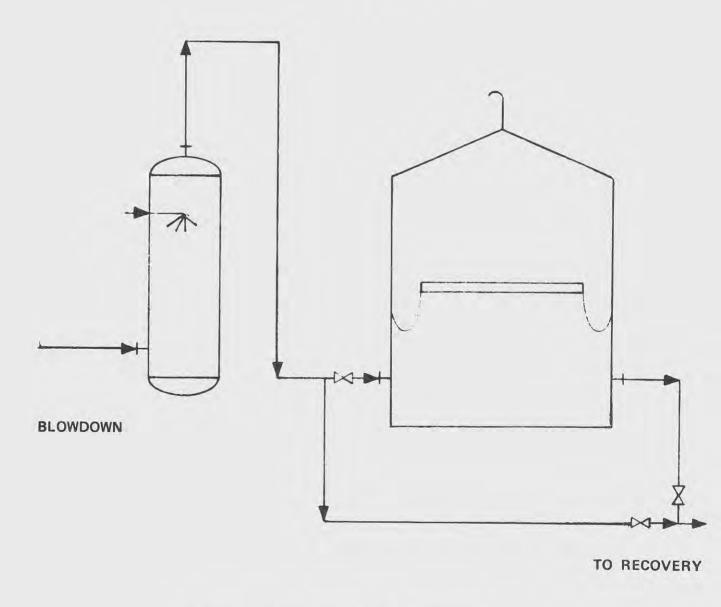


Figure 2. Scrubber and gas holder.

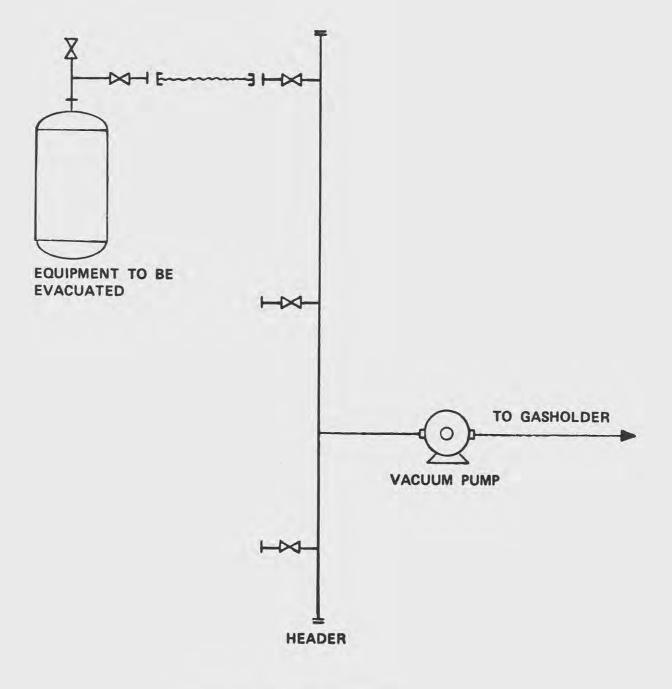


Figure 3. Capture system.

- 2. The equipment and/or piping is then connected to the evacuation system and evacuated to a pressure of 2 psia. The vapors are sent to gas holder for recovery.
- 3. The equipment and/or piping is then vented to atmosphere.

SUMMARY

O to 25 Gallons System Volume at Standard Conditions

- a) Vent to gas holder directly.
- b) Vent to atmosphere directly.

25 to 170 Gallons System Volume

- a) Vent to gas holder directly.
- b) Vent to gas holder via vacuum pump.
- c) Open to atmosphere.

Above 170 Gallons System Volume

- a) Vent to gas holder directly.
- b) Vent to gas holder using water displacement
- c) Open to atmosphere and pump out the displacement water to the water stripping system.

REACTOR SAFING PROCEDURE AND THE WATER DISPLACEMENT SYSTEM

The reactor is rinsed, purged with water, and chemically cleaned with solvent to remove all monomer vapors and PVC resin sticking on reactor walls before personnel entry. The sequence of operation is as follows:

- 1. After the polymer slurry has been transferred to the blowdown tank, isolate the reactor from the blowdown tank.
- 2. Make sure that adequate amounts of displacement water and the solvent are available in storage tanks.
- 3. Fill reactor with displacement water while venting all vapors in the reactor to a gas holder.
- 4. Pump displacement water back to the water storage tank. This water is to be steam stripped for removal and recovery of VCM. Allow the reactor to be filled with N2 or other oxygen-free inert gas. The inert blanket is required to minimize the explosion hazard due to the use of a chemical solvent in other steps of the operation.
- 5. Spray rinse the reactor with high pressure water using spraying valves such as Fetterolf valves. These valves use high pressure water at 200 psig or above to wash down loose PVC resin from the walls. Drain the rinse water.

- 6. Fill the reactor with heated solvent. Circulate the solvent for 8 to 9 hours with agitation.
 - 7. Pump the solvent out under a nitrogen blanket and spray rinse the reactor with high pressure water jets.
 - 8. Evacuate nitrogen to atmosphere by using steam jet ejectors or any other vacuum pumps, till the pressure in the reactor is reduced to about 2 psia.
 - 9. Open the reactor to atmosphere. At this point the reactor should be safe for "personnel entry." A portable VCM monitor must be used to determine that VCM in the reactor is below OSHA quidelines.

DOUBLE MECHANICAL SEALS

Vinyl chloride emissions from seals on all rotating pumps in vinyl chloride service are to be minimized by installing seal-less pumps, pumps with double mechanical seals, or equivalent as provided in the vinyl chloride standards.

If double mechanical seals are used, vinyl chloride emissions from the seals are to be minimized by maintaining the pressure between the two seals so that any leak that occurs is into the pump or by ducting any vinyl chloride between the two seals through a control system from which the concentration of vinyl chloride in the exhaust gases does not exceed 10 ppm. Similar requirements apply to rotating compressors and rotating agitators.

Water or non-freezing sealing fluids compatible with the process, and as 50/50 ethylene glycol/water mixture may be used. When water is used as the sealing fluid, freeze protection is required when the equipment is placed outdoors.

In mechanism under discussion, 50/50 ethylene glycol/water mixture was selected as the most suitable fluid. Small leaks of the mixture into the process were not considered detrimental.

For rotating pumps, double mechanical seals were provided with the seal fluid circulation system as shown in Fig. 4.

For rotating compressors double mechanical seals were provided with a centralized seal fluid system, because all compressors were located in one area. (Fig. 5)

Similar systems may quite obviously be applied to ganged pumps or, for that matter, to single pumps.

For agitators the seal system was similar to the system provided for pumps. However, the finned tube exchanger was not required since the

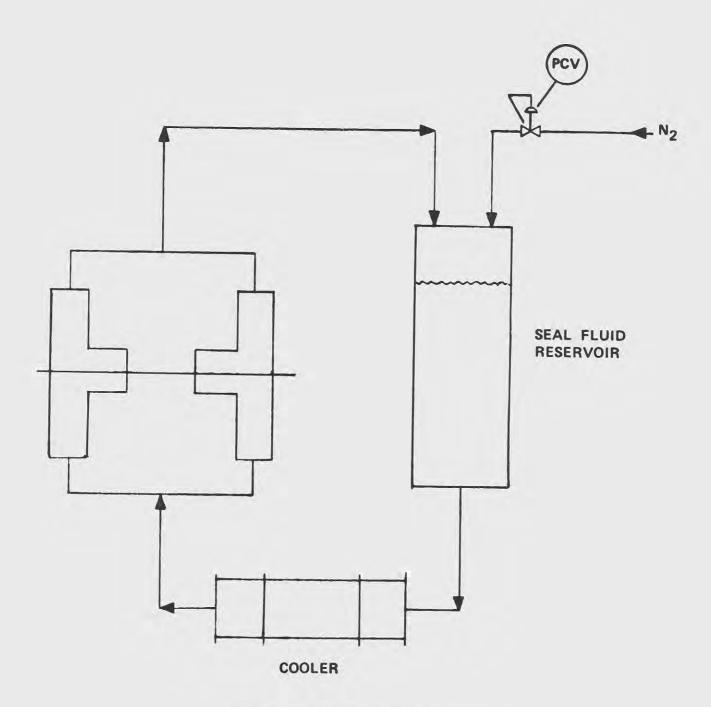


Figure 4. "Non-pumped" seal.

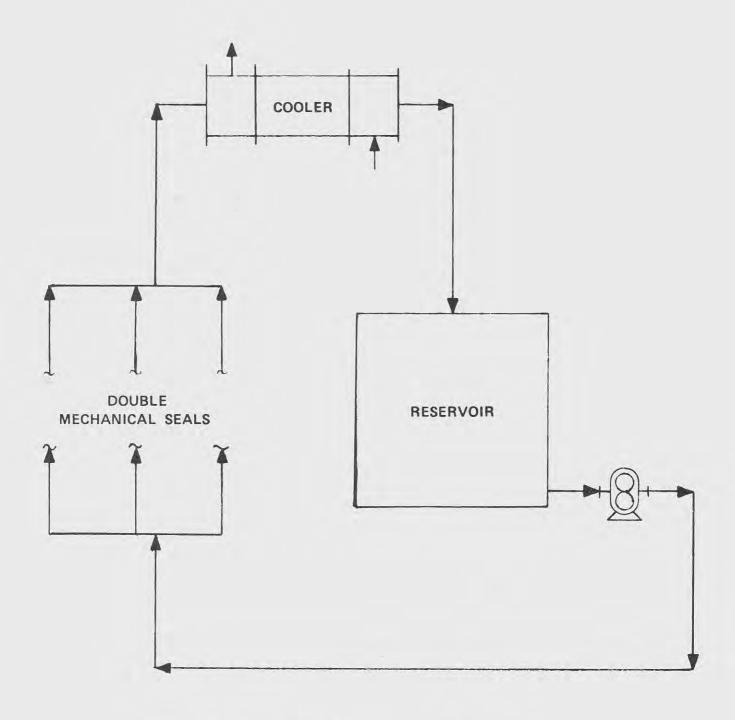


Figure 5. Ganged double seals - pumped system.

agitators did not operate continuously and the seal housings were provided with water cooled jackets.

RECIPROCATING SHIFT SEALS

Where reciprocating compressors are employed, the preferred method of sealing with leakage is the purged double distance piece.

Where a reciprocating shaft emerges from a cylinder three packed glands in tandem are employed. The spaces between are purged with inlet gas and vented to the gas holder. (Fig. 6)

STREAM STRIPPING OF SLURRY AND WATER

This design makes use of one of the several available proprietary processes for stripping the PVC slurry. These are adequately described in the literature and will not be enlarged on here.

A second stripper is employed to remove vinyl chloride from water blown down from various points in the plant. Chief of these are excess water from the displacement water tank and the excess scrubbing water ahead of the gas holder.

Condenser vents from both these strippers are fed to the gas holder.

INCINERATION

In PVC production, unreacted vinyl chloride monomer (VCM) is vented from the reactor to a VCM recovery system. A typical VCM recovery system consists of vapor collection, compression, condensation (often refrigerated), storage, and recycle. Non-condensibles, which are eventually vented to the atmosphere, are saturated with VCM at the final condensation temperature. These saturation levels of VCM generally exceed the environmental regulations. Therefore, to meet the regulatory criteria, a pollution control system is required.

Three systems presently in use in PVC production facilities to control VCM emissions are:

Three systems presently in use in PVC production facilities to control VCM emissions are:

- Activated carbon adsorption and recovery
- Destruction via thermal oxidation (incineration)
- Solvent scrubbing of vent gas

We chose inceneration because:

It can consistently meet the EPA emission criteria of 10 ppm VCM.

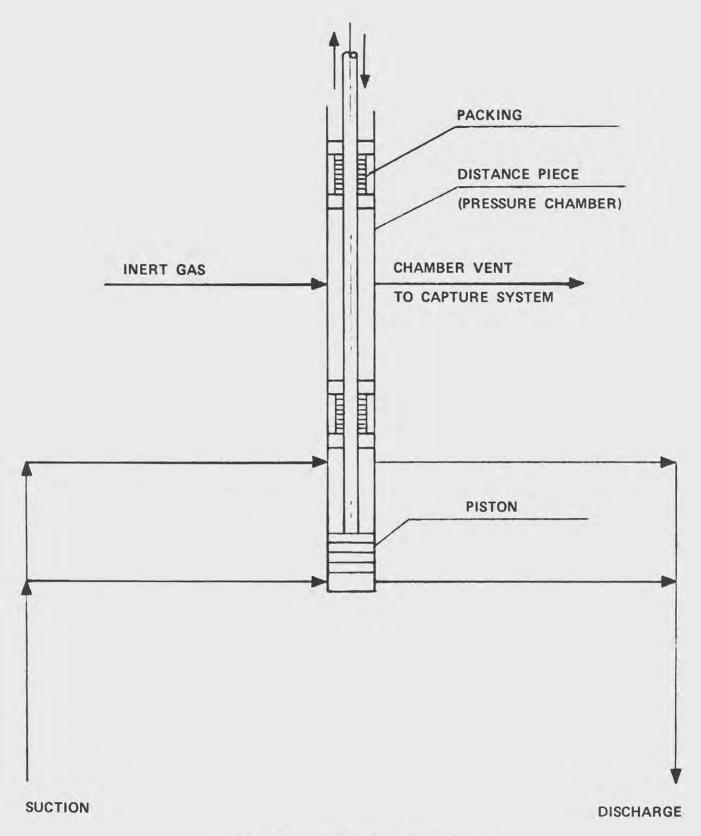


Figure 6. Reciprocating seal.

- 2. It can accept both gaseous and organic liquid wastes either simultaneously or alternately.
- 3. It helps to minimize build-up or non-reactive VCM containments (methyl chloride) which can occur when operating with a high degree of VCM recovery and recycle. Methyl chloride in the waste gases is destroyed along with VCM in the incineration process, whereas it is recovered and recycled in the activated carbon adsorption process.
- 4. It conserves energy; VCM is flammable and has a sufficiently high heating value, and the incinerator can be (a) made nearly energy self-sufficient when designed to oxidize both gaseous and liquid organic wastes or (b) designed to recover energy via a waste heat boiler if a separate fuel source is required to oxidize the waste gases.

There are, however, two limitations to the use of incineration as a pollution control method for VCM emissions from a PVC production facility, namely:

- 1. Reliability: Incinerators generally do not enjoy as high an on-stream time as the process facility they serve, thus necessitating a shut-down of the production unit during an incinerator outrage. This problem can be solved by installing two full size incinerators (one spare). Where one unit is operational, the other can be maintained in a "standby" condition, i.e., the unit is hot and ready to immediately accept wastes.
- 2. When incinerating chlorinated hydrocarbons, the combustion (oxidation) process generates the following objectionable by-products which cannot be discharged directly to the atmosphere:
 - a) Hydrogen Chloride (HC1)
 - b) Chlorine (Cl₂)
 - c) Particulates
 - d) Nitrogen Oxides (NO_x)

These noxious emissions can be reduced by the following techniques:

a) HC1, C12, and Particulates - Scrubbing the incinerator stack gases with an alkaline solution or water is effective and is the usual control method. If water is used for scrubbing, the resulting acidic solution must be properly neutralized prior to discharge to the environment.

Particulates and NO_{X} - Proper design and control of the incineration process variables and parameters such as combustion temperature, present excess air and residence time of the wastes within the oxidation zone are effective in reducing formation of these constituents, and are the most commonly used control techniques.

Further reduction of emissions in the stack discharges, if necessary, can be achieved by additional equipment depending on the requirements of the particular vapor stream.

Finally, incineration is an effective and viable method of meeting present and anticipated future environmental regulations with regard to controlling VCM emissions from PVC production facilities.

In summary, the design described here provides:

A breathing air network,

Chromatographic and explosive limit monitoring,

and

a gas holder connected to

a fugitive emissions capture system,

a water displacement system,

double rotating mechanical seals, and

double seals on reciprocating shafts,

and finally,

slurry and water stripping and

 incineration to dispose of otherwise irreducible process vents.

We expect these design measures, coupled with strict attention to proper operation and maintenance, to result in a safe and environmentally acceptable installation.

* * *

DISCUSSION:

MR. JOHN T. TALTY: Any questions of Mr. Knox or Mr. Schroy?

MR. ARTHUR SPIEGELMAN: Mr. Knox, you indicated on one of those charts that in order to check the lower explosive limit, you had a sniffer that was picking it up at 60 percent, and that would activate the deluge system at that time and also mechanical fans.

- MR. LEWIS C. KNOX: It shuts down the fans at that point.
- MR. SPIEGELMAN: I have seen one where they operate the fans, too. Our experience with one particular plant, or I have actually seen that operation which failed to operate correctly, is that sniffers -- first of all, we would insist that they be inserted at 25 percent of the lower explosive limit, but even when it did pick it up, it did not function quickly enough. This was a plant up in Rhode Island, very close to a school, and the people in that locality opposed the plant when they put it in. We went up and took a look at it, and we would have agreed with you that would be the best way to handle this problem, was to knock the walls out of the building. They said they would prefer not to do that and they put in sniffers, and in six months, the plant had a major leak, and they had the explosion, and the sniffer did not function quickly enough to actuate the deluge system or the fans.
- MR. KNOX: Let me say that, first of all, we did go to our insurers at length and discussed it; we went to the client's insurers and at length discussed what percentage of the lower explosion limit they thought it should be set at. After a lot of doing and frowing, 60 percent was decided on. The reason for the five seconds -- there is the disadvantage that a man finding himself in the middle of the deluge may have a difficulty finding his way out, and more damage might be done under those circumstances, certainly if it was a false signal. The second thing, if it will help to put your former friend's mind at ease, there has been a system such as this installed at Calvert City, and was shut down. It is still there in some kind of condition if you would like to see it.
- MR. D. G. IRWIN: I am concerned about the amount of polymer that might carry over into the line in the scrubber system as a result of venting a reactor under emergency conditions. To your knowledge has this type of system been tried in industrial practice before?
- MR. KNOX: I don't know that. Perhaps John Barr can answer the question. It was certainly considered, and it was not intended to vent the reactor suddently.
- MR. JEREMIAH LYNCH: Mr. Schroy, where would we go with the methodology now; is it more fruitful to try to perfect the emission rate data; what do you think?
- MR. JERRY M. SCHROY: Validating the model, since it is a gaussian model that has been worked up on a myriad of people, would not be fruitful. I think it would be better to define good emission rate data. That is the reason I mentioned the EPA study and their intent to define emission rate in basic terms, such that the data would apply from location to location and one chemical to another. We are trying to provide a validation of as much as we can and get it into literature. The question of validating the area pools and area sources, we feel has been validated enough. The accuracy of the gaussian model is at best a factor of two.

If you're extremely lucky, you might be able to predict levels which are within a factor of and a half and the worst might be a factor of three. But since you're trying to protect people, there's nothing wrong with using the model even considering potential errors of this magnitude.

MR. BILL THOMAS: I was wondering if any of these predictive design techniques are promulgated in standards?

MR. JERRY M. SCHROY: I think they would be helpful in understanding the impact. The idea of a standard being set from a method like this goes against the use of a method. The idea of being able to understand the impact of a seal in an acrylonitrile design situation versus the same seal in a vinyl chloride plant in valuable. I think it has merit in defining the situation for the person writing the regulation but not as part of the regulation. I agree with Nick Wheeler on the performed standards requirement.

MR. RALPH BARLEY: Relative to Arthur's comments a couple of minutes ago, I would like to offer an opinion. First of all, I don't think the deluge system is intended to relate to any compliance with EPA; another is I don't think it is intended, at least directly, to prevent explosions. The next point is that if it relates to an OSHA requirement, I think it is more or less incidental if it just happens to. I believe the main purpose of the deluge system is to reduce insurance premiums relative to equipment losses. In other words, to prevent fire; to keep the equipment from damage in an ensuing fire.

MR. SPIEGELMAN: First of all, you're wrong in just two counts. First, it is intended to quench the explosion that may take place. I don't think it works too well myself, but you know that certain insurance organizations have been sold on the idea that you can quench an explosion by flooding the area with little drops of water. It sometimes works the other way because the water droplets may turn to steam and add to the explosion force. But there are opinions which honest people can have and still not agree. It does not affect the insurance rates, as far as I know. As far as I know, it wasn't intended to be a means of reducing insurance rates.

MR. SCHROY: A deluge system, as we use it, whether or not it is the system he is talking about, is meant to disperse the material that is generating the vapors; not to quench a fire or quench an explosion.

MR. JOHN T. BARR: I was present at the conversation with the insurance people when the design was established, and to my knowledge no one else in this room was. The reason the insurance company insisted that we have this was to protect the equipment after the inevitable fire occurred. It has nothing to do with stopping explosions. It has to do with keeping the steel cool so the building doesn't fall down.

MR. JOHN T. TALTY: Our next speaker is William Wier, an attorney. He received his bachelor of arts Degree in Philosophy from Colgate University, and his law degree from Yale Law School in 1960.

He has been a member of the Legal Department with DuPont out of Wilmington for two years. He is a member of the American, Delaware State, and Federal Bar Association, and he's presently a member of the firm of Bader, Dorsey & Kresshtool in Wilmington, Delaware, where he has been involved in many cases throughout his career involving anti-trust and patent infringement cases. The topic of his presentation is Methods of Dealing with Proprietary Information in the Transfer of Technology.

METHODS OF DEALING WITH PROPERIETARY INFORMATION IN THE TRANSFER OF TECHNOLOGY

William Wier Bader, Dorsey & Kreshtool Wilmington, Delaware

I gather it is my happy duty to talk to you about a subject none of the other speakers has addressed: proprietary information and the various ways that such information is disseminated. For the purpose of establishing that we know what we're talking about propreitary information, let me tell you what I think it means, then I would like to expand my topic a little bit to a more general question of why are we here, what do you think you are doing here, and what is it that you hope to accomplish by this meeting? It seems to me that those are key, critical questions that have got to be answered and answered quickly.

Now, I am not a scientist; I am simply a layman, but I have spent most of my professional career in translating what went on here for the last two days into English so that a jury with a mean I.Q. of .04 can understand it. Sometimes it is a difficult task, but not always.

First, let me address the question of what is a proprietary right. Now, for the purposes of understanding I will break it down into three subjects. First of all, there are patents. We all know what patents are, and you realize, I am sure, that patents can be assigned, can be licensed exclusively, nonexclusively, and the information disclosed or taught by a patent can be disseminated in that manner. A patent, as opposed to other types of proprietary information, is a guarantee to the patentee to exclusive use of the technology which is the subject of that patent for 17 years. It is what we call a legal monopoly. It is permitted by the Constitution of the United States. However, it has been one of the major types of proprietary information that has funded my profession, because inevitably once the patent is issued you get involved in the infringement litigation which provokes antitrust litigation and unfair competition claim, all of which are interesting cases and highly remunerative for my profession, but from the standpoint of what you are trying to accomplish, they are of little help.

The second type of proprietary information is what is called a trade secret. The third type is what you would call simply confidential information. A trade secret can be a number of different things. It can be a formula, a process, it could be manufacturing know-how, manufacturing show-how, it could involve specific products, plans, designs, patents vital to a particular type of technology, customer data lists, pricing information, et cetera. Trade secrets or confidential information are information which individuals or the company that possesses the information wishes to keep secret. Nevertheless, they can be licensed and frequently are licensed in the form of know-how or show-how licenses.

The major distinction between a patent, on the one hand, and a trade secret or confidential information on the other is that when a person obtains a license to utilize confidential or trade secret information or material, he is really paying for the disclosure of that information. The concept of a trade secret or confidential information does not contain any sense of exclusivity. That is to say, if a company has a particular formula which it regards as a trade secret and maintains it as a trade secret, the law does not hold that he is entitled to utilize that information exclusively absent the confidential or secret status. It is only valuable to him or his licensees so long as the secrecy status of the information is maintained.

Of course, proprietary information may take the form of a patent or patent application, or may take the form of a trade secret or confidential business information, not because of the type of information involved or whether it might be patented, but because it is more important to the holder of such information that the type of information concerned be maintained as a trade secret. Frequently, of course, much information which is maintained on a trade secret basis would not be patentable, would not rais to the standards of novelty of a patent. On the other hand, there are a lot of pieces of technical information, highly important, which might be patentable, but which are not. They are maintained on a trade secret basis. The reason for that he can best utilize that information by maintaining it secrecy and using it in that form or even licensing it in that form. The best example of that type of information that I can think of is perhaps the Coca-Cola formula. Furthermore, there are some types of important information which can't be patented. For example computer software or valuable fermentation bugs. While they may be of a most critical nature to the kind of technology that is involved, such developments (at least in those two areas) are not patentable. At least, not at this time. As far as computer software is concerned, as you probably know, the Congress is working on trying to adopt suitable means for protecting that type of technology. In my judgement, they have not yet done so, and the only way to really protect that type of technology is as a trade secret.

Proprietary information is maintained, patented or not patented because of various business decisions which are involved in how the holder of such information wishes to use the technology in connection with the conduct of his business. These same complicated factors also inform the decision of a given company as to whether or not they shoull license this technology. You can license a patent and since a patent is a disclosure to the world as to what it covers, what it teaches, the licensing of that patent does not diminish its value or the value that one can achieve in the form of income from licensing. Indeed, that's why patents may be licensed, because of the royalty income they bring. However, on the other hand, with respect to technology which is within the domain of trade secrets or confidential business information, the licensing of that type of information does diminish its value, because the more it is licensed the more it becomes known and the higher the probability that its secrecy may be diluted, that such information will become a part of the public domain. Once that happens, the owner or a licensee loses all rights to assert any exclusive or semi-exclusive rights to such information.

Questions on whether or how to license proprietary information interface with another area of the law known as the antitrust laws. A continuing problem, today, which must be addressed by you or your lawyers is how and whether different kinds of proprietary technology can be disseminated by licensing or by some other means of conveyance withou violating the anti-trust laws. Solutions to this question in my judgement, will affect what is one of the most critical questions which must be answered if the type of problems which you have been discussing are to be solved; namely how can members of industry join together to conduct joint research and development activity without intentionally or unintentionally violating the strictures imposed by the antitrust laws. This question, this type of discussion, to my knowledge, first came up in a public session in one of the meetings of the Antitrust Section meeting of the American Bar Association about 1975. To my mind, from a practical standpoint, it is a critical question. Its answer would reduce the overall amount of money, effort and time that is otherwise required to address the problems that you have been experiencing concerning industrial hazards such as worker exposure or consumer exposure to carcinogens in processes, materials or products.

Furthermore I think it is critical that this point be addressed promptly, because of recent developments in the area of product liability law. It is absolutely clear that juries and courts think you have the ability and the technology to correct these problems even if in fact you do not. This fact is evidenced by the increasing size of damage verdicts and by the appearance of court formulated rules establishing new areas of industry exposure which enhances a finding of liability. An example of such a doctrine which is now developing on the fringes of product liability law, is the court formulated doctrine that a worker can circumscribe the shield provided by the Workmen's Compensation Law where an employer knowingly subjects the worker to conditions that are hazardous, -- and it's off to the races against the employer.

Because of these developments in the law, from the standpoint of simple economics, it is my view that we have to come up with some kind of a method to permit joint development of technology which will minimize the type of worker or consumer exposures such as those which heretofore have taken place and have been the subject of litigation. It is critical because of the money that a company may be required to pay for those kind of damages drains a company's profits and constricts the money which otherwise would be available for research and development efforts. This is true whether a given company is self insured or pays premium to obtain product liability insurance. Yet to my knowledge, since that meeting in 1975, this particular issue has never really been squarely faced. Instead, what has taken place, to reduce such hazards is the ever increasing appearance of Government regulation by such organizations as OSHA. Yet the enforcement of such regulations increasingly make private industry and the government organization antagonists -- which results in more litigation. Its a catch 22 situation.

This leads me to address the philosophical questions I raised earlier: namely, what do you hope to accomplish by the type of proceedings such as the one you have attended this week? And is such a proceeding really productive toward meeting the needs of industry in terms of the transfer of proprietary technology to solve the problems involved in worker or consumer exposure to hazardous drugs or compounds? I have indicated that there is a whole range of proprietary information, patents, trade secrets, confidential information, all of which can be licensed, -- which can be disseminated. To meet the problems which have been discussing the key question which must be addressed is how to encourage such dissemination within the framework of our present system of free enterprise -- a question which ultimately is reduced to monetary considerations.

Thus, the real question, with regard to the solution of the problems which have been addressing in these proceedings is, in my mind, where is the money going to come from? Is private industry going to pay royalties to obtain technology to reduce the exposure? Is the Congress going to be forced to expand the concept on mandatory licensing in order to encourage you to do that?

Parenthetically, I heard somebody say we haven't yet reached the state of mandatory licensing. That's not true. The EPA, in the nuclear field, has already promulgated rules for the mandatory licensing of patents and other information in that field. Furthermore, if these problems continue, it would seem that Congress may look further into the utilization of that kind of technique to force industry to come to grips with the problems of reducing hazardous exposure to workers and the consuming public.

It seems to me that the question that you should be addressing there, or that somebody should be addressing, is not what is the state of the art, in a given technology which by definition does not include proprietary information: -- information that you, as the people who are the leaders in the field must already have. Rather, in my view, what you should be discussing is how do we create a method of dissemination of proprietary information which fairly compensates the developer of technical information, and at the same time makes that information available to be utilized by other members of the industry for the purpose of reducing the kind of hazardous exposures and similar types of problems that have existed is the past? At first blush I know, this question may seem to have a socialistic ring. I do not intend it as such. I have raised it because its answer in the long run may hold the only practical solution for getting the problems which are otherwise going to cost you millions of dollars behind you.

Industry, today, in my judgement, is really at a very critical stage of development. I am talking industrywide. It is in a state of development where there is so much regulation that, actually, the degree of experimentation, the degree of attempting to develop new and different products or manufacturing procedures is being seriously hindered. For

example, there is little incentive for drug companies to attempt to patent for a given development, it has to spend another 12 years processing a new drug application, and is therefore left with only a three year lead time under the protection of the patent to develop a market for the drug. From a business standpoint, it makes no sense to do that. Until something is done to change the effects of that kind of regulation, little incentive is provided to people in that industry to make new products and to market new products which are subject to such regualtion.

As you probably know, this is a general concern that has been voiced by many administrations including the present one. They are aware of these problems not only in terms of the limited example that I gave you, but generally. But in this regard the government and industry are both faced with a dilema. On the other hand, the public, or at least the Congress, believes that you should be subjected to regulation to protect the public. On the other hand, you're in business to make money, even though you are confronted with the expenses of complying with governmental regulations which increasingly cost money, in a climate of public awareness which is spawning increased damage awards and novel theories of liability in the area of produce liability litigation. In my judgement, as a layman, as a lawyer, it is a very serious situation. I am not sure I know of a solution. My only point here is that at meetings such as this you should be discussing how these problems can be addressedby using the latest technological developments -- including proprietary information -- and not simply reviewing information which is a part of the state of the art with which you are all already familiar. In this meeting, it is my judgement that you have not been about that task. Thank you very much.

* * *

DISCUSSION:

MR. JOHN T. TALTY: We have time for questions if you have any questions of Mr. Wier.

MR. ROY DEITCHMAN: Could it be possible for the Federal Government, to buy licenses for control technology that can be used by the general public.

MR. WILLIAM WIER: That is possible, or maybe we should go to some joint industrial program of funding this kind of research. What I wanted to convey today is a simple point. There is no problem as far as the legal profession is concerned is developing the kind of instruments or documents that are needed to convey proprietary information. It only involves the particular technical problems of making sure what the agreement is; an looking to the duture, drafting the agreement in such a fashion that the Justice Department won't decide at some future date to

make it a target for an antitrust investigation or suit. Other than these considerations, the techniques for transferring technology really raise only technical legal questions which I am sure your counsel are immenently able to resolve. I personally would be in favor of such kind of an arrangement which would exploit the reservoir of knowledge that industry has through some form of joint research and development. This NIOSH type of endeavor really does not, in my judgement, encourage the utilization of industry information and knowlege developed by private industry to focus on the problems which have to be solved -- at best it is a back door approach. However, in the absence of attempting to create some kind of an alternative research and development arrangement, I am afraid you are going to see more and more situations where the Government is going to undertake the necessary research -- probably not as well or as quickly as you could otherwise do it. Such a system penalized the taxpayers, penalizes you and penalizes the Government. You wind up being regulated by regulations or law which you cannot live with for technical or other reasons and you haven't developed or been given the type of technological input that is needed and that should be given to expeditiously correct the types of problems which we have discussed.

MR. JOHN BARR: Then, you haven't offered any solutions, merely posed the question. How would you propose that you better utilize industries? You visualize some form of lessening antitrust laws so that trade associations could work more closely together on developing these things as opposed to branches of the Government doing it.

MR. WILLIAM WIER: Yes. The answer is yes. That makes a great deal of sense, and of course, the reason trade associations or others, maybe your vinyl chloride committee --

MR. JOHN T. BARR: Safety Association.

MR. WILLIAM WIER: The reason they have not gotton into this more deeply is because they have people like myself as counsel, who say, "hey, wait a minute, if you engage in such joint development work you're going to wind up at the end of some kind of an antitrust action which in these days may result in felony convictions, fines, or astronomical damage awards." So, the answer is, yes. What I ma saying is some thought is going to have to be given by your representatives and you as to how to bring about some method, some means, through trade associations or what not to permit joint research and development to solve these kinds of problems within the preview of the antitrust laws because I think that the answers, the practical answers for industry and for the country lie really within the minds of the people who are involved in the industry I mean private industry, as opposed to Government.

MR. JOHN T. TALTY: Moving on to the last presentation which will be followed by the wrapup, Don Telesca will be speaking to us. His degree is in Chemical Engineering is from M.I.T. and he has a B.S. degree in Business Management from Rutgers. He has over 31 years of experience in all facets of the chemical industry. He has experience in all facets of chemical engineering, R&D, and pilot plant operations and management experience at all levels from shift supervisor to and including general manager and vice president. He is currently a Management Consultant with Enviro Control in Rockville, Maryland. The topic of his speech will be Means of Implementation of Controls. The talk will discuss the general method of implementing control technology in the plastics and resins industry.

MEANS OF IMPLEMENTATION OF CONTROLS

Donato R. Telesca Enviro Control, Inc. Rockville, Maryland

MEANS OF IMPLEMENTATION OF CONTROLS

You have heard a number of talks during the past two days dealing with the technical aspects of control technology. We have dealt with the methods of measuring the effectiveness of the engineering controls, and we have talked about the implementation of controls in new facilities.

The NIOSH technical report of the control technology assessment of the plastics and resins industry consisted of a series of in-depth surveys on the polymerization and compounding processes. The findings were presented as case study summaries. The case study summaries for each of the sites surveyed included:

- Major toxic chemical and harmful physical stresses;
- Engineering controls and work practices;
- Workplace monitoring systems and air sampling program;
- Personal protection equipment;
- Exposure data and conclusions; and
- Planned or ongoing improvements.

The question is: How can all the information that has been collected be used to implement controls that are necessary to protect the workers in any and each of the plants? It is a difficult problem.

Many people feel that the major problem lies with management. I suggest, rather, that the implementation of controls is a three-way effort by management, labor, and regulatory agencies.

This effort can be symbolized by a three-legged stool. Each leg must bear its fair share of the weight, and each leg is important to maintain the balance of the chair to avoid any failures. Thus, this effort to reduce exposure of the workers is somewhat like a three-legged stool.

LABOR

The role of labor in this three-pronged attack on the implementation of controls is to note areas where there are emissions in the operating

equipment in the plant and to bring these problem areas to the attention of supervision so that the proper corrective measures may be taken.

Members of the R & D forces who are making a study to reduce exposure make changes in the process or equipment, etc., will be limited by the time of the study and may not be aware of all the problems which may occur during the operation of a particular process or plant. The members of the operating groups, or the maintenance groups, are the people who are most familiar with the operation of equipment in any and all situations. During their various experiences in the plant, they may find a better solution for a particular problem which is occurring in the plant. This solution can be based on previous experience, on training sessions, or on word-of-mouth from other maintenance people in similar situations. These solutions should be suggested by labor to management so that they can be incorporated in any suitable spot in the plant.

In my past experience, when sent to a plant for trouble-shooting assignments, I would request the "laziest" operator who was available. In questioning this operator, I often found that he had better work practices and knew of better methods of performing his job. Additional questioning would show that the quality of the product was not hurt by these better methods, and often I would point out to the plant management the value of this operator's method and have them introduced into the standard operating procedures of the plant.

It is also the responsibility of labor to adhere to rules established as a result of regulations. Labor must be honest in evaluation of a problem and not "blow a simple problem out of proportion."

Further, more experienced members of the labor force have the responsibility to properly educate new members in the safe methods of operation of the equipment and process. These experienced workers should also emphasize the reasons for the regulations which were established for the safety of the job.

REGULATORY AGENCIES

The role of regulatory agencies in this three-pronged attack on the problem of implementation of controls is primarily to establish rules and regulations which are obtainable, fair and nonpunitive. It is of no value for the regulatory agency to request a standard which can neither be measured (and consequently is not enforceable) nor one which cannot be obtained in a reasonable length of time by the available commercial equipment.

It is also the responsibility of the regulatory agencies to have a reasonable cost associated with the implementation of any regulation. Each plant has the cost data for meeting the regulation. Some of this information is proprietary and cannot be used in discussions with the regulatory agencies. However, it is the responsibility of the regulatory

agency to make an estimate on the best available information at the beginning of the procedures for the institution of the regulation because this estimate will help guide the agency in pursuing the level of controls desired.

Another area that the regulatory agencies should examine is a request for reports, many of which are overlapping, and many of which are unnecessary because the information requested is available from other agencies. It is suggested that an interagency committee be established to monitor and/or develop reports to minimize duplication and to reduce costs to the various plants developing the information required by the report.

There is a recognition of the problems faced by the regulatory agencies, and a partial answer may be found in the draft form of a document titled Making Prevention Pay dated December 14, 1978. This is the final report of the Interagency Task Force on Workplace Safety and Health, and it may be obtained by writing to the Interagency Task Force at 1815 North Lynn Street, Rosslyn, Virginia 22209.

Specifically, the task force was directed to:

- Explore the incentives that might supplement direct workplace safety regulations;
- (2) Evaluate government-wide administration of federal workplace safety and health activities, including duplication, overlaps, and gaps in the Federal agency jurisdiction; and
- (3) Review other ways to improve the safety and health efforts of all Federal agencies, including those programs that affect Federal employees and resources devoted to them.

There are a number of areas that were identified for study. It is a work of some 150 pages and recognized in detail a number of the problems faced by industry.

MANAGEMENT

Management has the responsibility for taking the initiative in the implementation of controls. The major difficulty for people in management is to implement a number of controls and changes which may be required by regulatory agencies and/or suggested by the labor force at a plant. Implementation of these controls and/or changes may be difficult because:

- (1) It may not be cost effective;
- (2) It may be the pet "project" of some group or individual and may not be necessary for the welfare of the general public; and

(3) It may not be possible because of the lack of equipment and/or instrumentation required.

Before the institution of any regulation, a notice is put in the Federal Register requesting comments regarding the regulations. It is management's responsibility to comment on the proposed regulations in response to these requests from the regulatory agencies. Management must analyze the effect of the regulations on the industry as a whole or, where warranted, the effect on a specific sector within the industry. The response from industry should be objective and open in order to have the best possible regulation issued as a control for the industry.

Another responsibility for management is to draw to the attention of the regulatory agencies the cost that would be associated with the implementation of the required control equipment. In discussions with the agencies or their representatives, management should be frank about the problems to be faced. In the past, a requirement from an engineering group often resulted in a high estimate for the implementation of controls because of the speed at which the estimate was made. The end result was that the credibility of the estimate and of the company was questioned.

Further, in many cases management will not make a change in the equipment unless there is a payout period for the change. Often, this payout period is unreasonable because of the length of time that is required for payout. It is recognized that money is valuable and that the established payout period is based on the competition with the income that this money can generate if invested in other locations. Unfortunately, this attitude regarding payout often leads to arbitrary decisions by regulatory agencies and/or higher members of management. The result can be ineffective installation of equipment that is inadequate for the required regulation.

There are a number of ways for management to implement the controls in the plants or industries. First, there should be an industry group whose function is to review the proposed regulations which are issued in the Federal Register. This group should also be empowered to submit to the federal agency their objections to any of the sections of the regulation and to suggest a better or more efficient control method.

Second, the plants can establish incentives for the work force to encourage the suggestions by members of the labor force which will lead to better controls. Again drawing on past experience, in one location we instituted a safety suggestion box which made cash awards for suggestions that were accepted. This was a number of years ago, so the amounts will appear to be small. But, as an illustration, for a suggestion that could be used at one specific location, the award was \$5.00. For a suggestion that could be used within one plant, the award was \$10.00. For a suggestion that could be used in a number of plants within a company, the suggestion was awarded \$25.00. While the amount of money can be changed to

reflect the present times, the important thing is that the suggestion box can be used to encourage the participation of the workers within the plant in an effort to make a better working place.

The areas that management should consider for the institution of controls are as follows:

- Category I: Elimination by substitution of unit process or hazardous materials (this will be the most expensive way);
- Category II: Application of current technology to specific equipment designed to contain emissions within process equipment;
- Category III: Devices to control hazardous emissions once they enter the work environment;
- Category IV: Controls used to isolate workers or prevent contact with the toxic agents; and
- Category V: Monitoring system which warn workers of hazards and initiate corrective measures.

CONCLUSION

In summary, the implementation of controls is dependent upon a cooperative, three-pronged attack of the problem, with the "attacking" force composed of members of management, labor, and regulatory agencies. Each of these team members has a definite function to perform in the implementation of these controls, and with a cooperative, objective method of operation their efforts will result in a plant which will be a better and safer place in which to work.

WRAP-UP COMMENTS

Walter Haag
National Institute for Occupational
Safety and Health
Cincinnati, Ohio

As the symposium draws to a close, it is interesting to reflect back over the past two days. One overall impression is the variety of topics that have been addressed. We have heard a number of broad policy-type presentations pertaining to the effectiveness of government regulations. We have heard a presentation of the NIOSH control technology assessment, and then a reaction to this study by a representative of industry. Other presentations were directed toward particular areas of technology such as automatic workplace monitoring and process stream sampling. The people-factor was covered by topics dealing with work practices, loss prevention and additional incentives through the insurance industry. The issue of designing new plants as contrasted to retro-fitting older plants was discussed. We were reminded that business considerations and laws such as the antitrust legislation can have decisive effects on the transfer and implementation of control technology.

I think the degree of variety that we have seen here reflects the complexity of social, political, and technical problems that are wrapped up in meeting our mutual goal of controlling exposures to occupational hazards. The very fact that we are here in Atlanta, talking about our progress at a symposium rather than undergoing litigatino in a courtroom indicates progress. We have taken a good first step, but we still have a long way to qo.

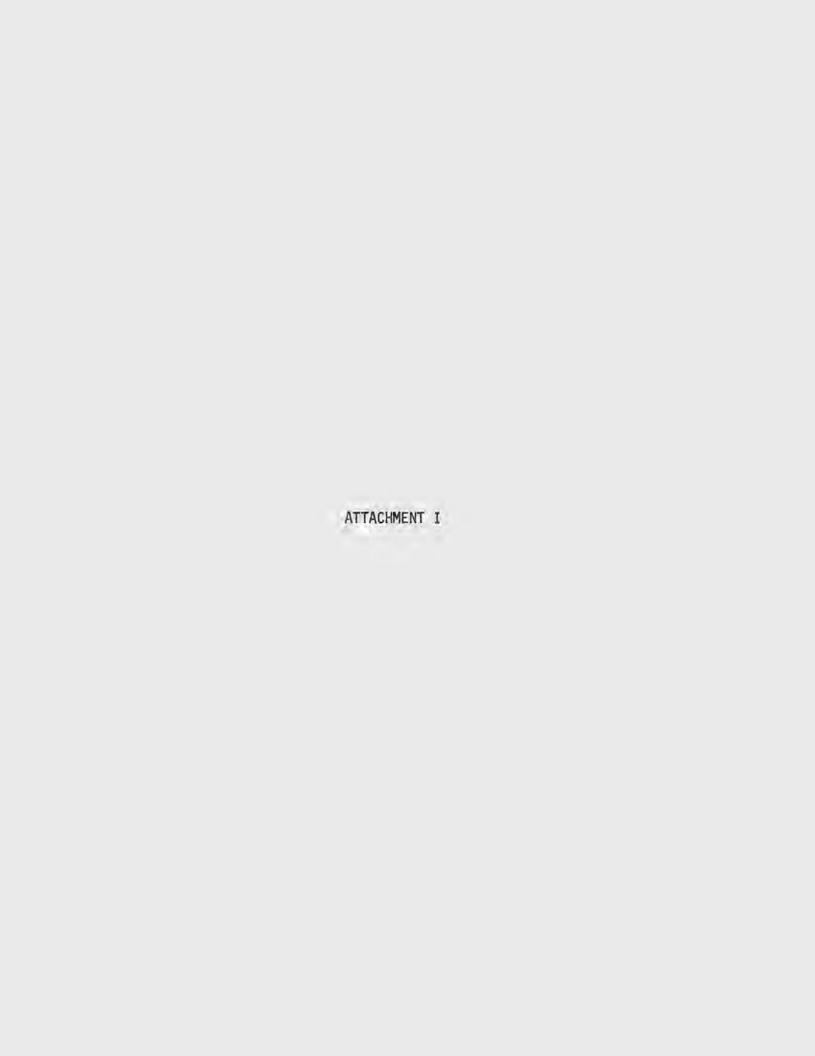
I believe over the next several years we will hear more and more about the issues of energy, transportation, and productivity. The plastics industry, and the chemical industry generally, will be right in the middle of these issues. Your feedstocks come from petroleum and natural gas. Your products will go to make lighter and more efficient automobiles. Your creativity and innovation is a benchmark for much of the rest of industry to follow. Change is going to occur, and we can look at it either as an opportunity or we can attempt to fight it by taking a very defensive posture. I would hope that this symposium has moved all of us closer to working together in a positive manner.

Finally, I would like to acknowledge the large amount of work that has been expended by Dr. Julius Bochinski, Mr. James Gideon, Mr. Donato Telesca, Ms. Gail Ciuoban, Ms. Suzanne Fino, and Ms. Dottie Mathieson in setting up and in conducting this symposium. Also, thanks to each of our speakers for a uniformly excellent program.

APPENDIX A ATTACHMENTS TO R. NICHOLAS WHEELER'S PRESENTATION

ATTACHMENTS

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INTRODUCTION TO REACTIVE CHEMICALS

The Reactive Chemicals Training Program is designed to promote safe work practices through the study and subsequent understanding of those reactive chemicals handled in the Unit. After assignment at the Unit, this training will begin with the issuing of the Basic Reactive Chemicals Manual. Once the Basic Manual study is satisfactorily completed, Specific Reactive Chemical Manuals will be issured for review of the specific reactive chemicals handled in the Unit. The Foreman has the responsibility for providing reactive chemicals training for individual employees.

The manuals are for the instruction and guidance of all persons in the plant who are involved with reactive chemicals. It is for the person who operates the process, transfers the materials or fills the tank car.

The purpose of the Program is to train the new employee and help the experienced employee to improve his/her knowledge and experience by periodic review of specific reactive chemicals.

During this session, we will be providing some insight into the Program content, defining the term, "Reactive Chemical" and reviewing some of the reasons why Reactive Chemical training is so important.

A REACTIVE CHEMICAL is defined as a chemical that has one or more of the following characteristics.

- 1. Will vigorously decompose or react with itself in the pure state.
- Will vigorously decompose or react in the presence of a trace of some other material.
- Will react violently with water.

Many of the chemicals produced and handled at the South Charleston Plant are reactive chemicals. The properties that make them reactive also make them very useful as a means of producing a great number of useful materials. Because of these reactive properties however, they must be given special attention.

Reactive Chemicals may react explosively, violently, slowly or even gently, depending on the chemical and conditions. There is no rule governing the speed or danger of a reaction for all chemicals. For example, one chemical can react so quickly and violently that even the safety devices on equipment provide very little protection. Another may start reacting slowly but as heat is liberated the speed of the reaction is accelerated to a point the vessel or equipment can be ruptured explosively. Still others may react slowly causing the vessel to vent highly flammable vapors with a resulting flash fire from vapor ignitions.

Reactive chemicals become violent and hazardous only when their behavior is allowed to get out of control. By your understanding of this behavior, using appropriate precautions and following safe handling practices, any reactive chemical can be handled safely.

A number of potential hazards are ever-present while processing or handling reactive chemicals. These would include such things as power failure, loss of cooling water, loss of instrument air, loss of blowback, shortages of steam, etc. All these can be critical. Poor temperature control which may be caused by human error, equipment malfunction or failure of warning devices can also be hazardous.

Other causes of reactive chemicals getting out of control include improper cleaning of lines and vessels, improper mixing of chemicals and allowing water to get into the process or equipment. Remember, even a trace amount of a foreign substance can cause a hazardous reaction with a reactive chemical. Some chemicals can even react with the iron in a pipeline with disastrous results.

In order to handle reactive chemicals safely, it is imperative the prescribed Standard Operating Procedures are understood and followed and the reactive characteristics and methods of control are well understood.

Before handling a reactive chemical review the Specific Reactive Chemical Manual.

Remember, there is a safe method for handling the chemical. Any reactive chemical produced or used by Union Carbide can be safely handled or it would not be allowed in the plant.

Once training is initiated at the Unit, you will find it very helpful in all operating situations. You will learn for example, that it is extremely dangerous to pour water in acid but not nearly so dangerous to pour acid in water. You will also learn the reasons why this is true.

You will learn which chemicals react violently with water and which ones react with only a trace of other materials. You will learn what chemicals can react with themselves and the conditions under which this can occur. You will learn why certain chemicals are reactive; why and how they can decompose, and effective measures to control the reactions. In line with this, you will become more familiar with atoms and molecules, chemistry, and some of the laws of physics. It will be directly related to your job and thus much easier to comprehend. The time and effort spent in this program will be very beneficial to you in the "total" job.

SUMMARY

A Reactive Chemical is one what will vigorously decompose or react with itself in the pure state, or will vigorously decompose or react with a trace of some other material, or will react violently with water.

Reactive Chemicals may react explosively, violently, slowly or even gently, depending on the chemical and conditions. However, they become violent and hazardous only when their behavior is allowed to get out of control. By understanding this behavior, using appropriate precautions and following safe handling procedures, any reactive chemical can be safely handled. Always review the Specific Reactive Chemicals Manual before handling a Reactive Chemical and take all necessary safety precautions.

After assignment at the Unit, the Foreman will initiate training in Basic Reactive Chemicals and later with specific chemicals handled in the Unit. This training will be very beneficial in understanding the total job.

South Charleston Plant

"INTRO" PROGRAM

INTRODUCTION TO REACTIVE CHEMICALS PROGRAM

(Review Questionnaire)

ME:_	INSTRUCTOR	
YROL	L:	
TE:_		
	(Complete this copy and turn in to in	structor)
1.	What is the purpose of the Reactive Chemicals Training Prog	gram?
2.	What is a Reactive Chemical?	
3.	List three causes of uncontrolled reactions with reactive ch	nemicals.
4.	Reactive chemicals can be handled safely by	and

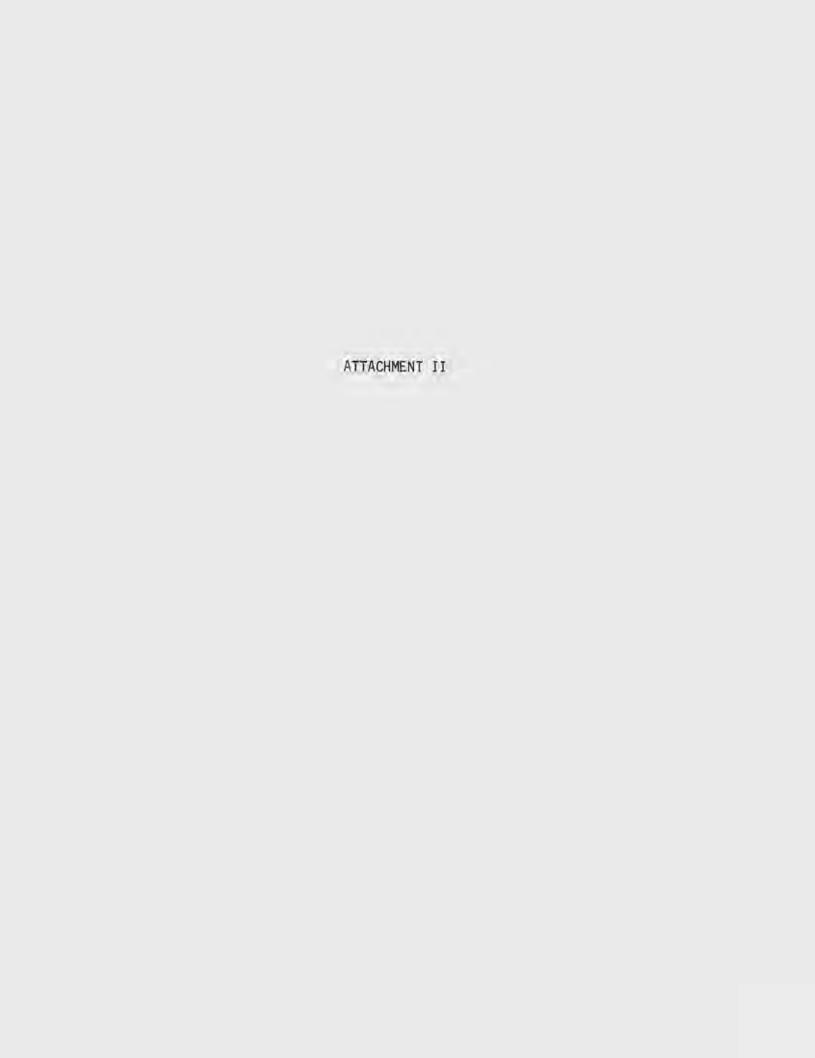
South Charleston Plant

"INTRO" PROGRAM

INTRODUCTION TO REACTIVE CHEMICALS PROGRAM

(Retain this copy for your records)

١.	What is the purpose of the Reactive Chemicals Training Program?	
2.	What is a Reactive Chemical?	
3.	List three causes of uncontrolled reactions with reactive chemicals.	
4.	Reactive chemicals can be handled safely by	and



April 1, 1977

The information and recommendations contained in this memorandum were prepared for the guidance of plant engineering, operations and management, and for persons working with or handling vinyl chloride. The information was compiled from experience and information provided by various manufacturers of vinyl chloride, and from material on vinyl chloride appearing in scientific publications. While the authors believe these sources are reliable and represent the best opinions available on the subject as of April 1, 1977, they nor their companies make no warranty, guaranty, or representation as to the correctness or sufficiency of any information or recommendation herein, and the authors nor their companies assume no responsibility in connection therewith; nor can it be assumed that all necessary warnings and precautionary measures are contained in this memorandum, or that other or additional information or measures may not be required or desirable because of particular or exceptional conditions or circumstances, or because of applicable federal, state, or local law.

PROPERTIES AND ESSENTIAL INFORMATION FOR SAFE HANDLING AND USE OF VINYL CHLORIDE

This presentation is intended to give the reader a general outline to follow in preparing technical training material.

April 1, 1977

BY:

R. N. Wheeler, Jr. John T. Barr Robert W. Laundrie P. J. Snyder

PROPERTIES AND ESSENTIAL INFORMATION FOR SAFE HANDLING AND USE OF

VINYL CHLORIDE

Vinyl chloride monomer is classified by the United States Department of Transportation as a flammable compressed gas. It is easily ignited, producing hazardous combustion gases largely composed of hydrogen chloride, carbon monoxide and carbon dioxide.

Vinyl chloride is believed to be a carcinogen to man. Exposure of three animal species to vinyl chloride has caused a higher frequency of angiosarcoma as well as other respiratory and digestive tumors than in the control groups. Workers in the manufacture of polyvinyl chloride resin have shown a higher incidence of angiosarcoma than expected after long exposure at relatively high concentrations. Acute overexposure affects the central nervous system producing intoxication and dulling of the visual and auditory reponses.

The full text of this chemical safety data sheet should be consulted for details of the hazards of vinyl chloride monomer and suggestions for their control. Appropriate regulations regarding vinyl chloride issued by OSHA, EPA and associated agencies should be carefully reviewed prior to any work related to vinyl chloride.

FIRST AID - SEE PAGE 15

For assistance in the event of any emergency involving this chemical in transportation, call MCA's Chemical Transportation Emergency Center.

CHEMTREC

(800) 424-9300* (Use 483-7616 in District of Columbia)
Toll-free day or night
*Use long distance access number if required.

In CANADA, call Canadian Chemical Producers Association TEAP (Transportation Emergency Assistance Plan)

CHEMICAL SAFETY DATA SHEET

VINYL CHLORIDE

1. NAMES

Chemical Names: Vinyl Chloride Monomer

Chloroethylene Chloroethene

Common Name: Vinyl Chloride, VCM

Formula: CH₂CHC1

2. PROPERTIES

2.1 GRADE: Commercial, sometimes referred to as Technical or Polymerization.

2.2 IMPORTANT PHYSICAL AND CHEMICAL PROPERTIES:

Explosive Limits

(Percent by Volume in Air) Lower 3.6%; upper 33%

Flash Point (Open Cup). -78°C. (-108.4°F.)

Hygroscopicity. None Critical Pressure, psia 775

Light Sensitivity Uninhibited VCM is light sensitive

Melting Point at 1 atm..... - 153.71°C. (-245°F.)

(Freezing Point)

Molecular Weight 62.50

Odor Sweet smelling gas. Inhibited VCM may

have faint phenolic odor.

Physical State Gas at ordinary temperature and pressure.

Liquid under pressure in cylinder or pressure vessel at room temperature.

CHEMICAL SAFETY DATA SHEET

VINYL CHLORIDE

Page Two

2.2	IMPORTANT PHYSICAL AND CHE	MICAL PROPERTIES: (cont.)
	Reactivity	Polymerizes readily in presence of air, sunlight, oxygen or heat. This behavior is due to the presence of a double bond. Otherwise vinyl chloride is quite stable.
	Specific Gravity of Liquid	
	at 4°C. (Water = 1)	0.9121
	Vapor Density of Gas (Air = 1)	2.15
	Vapor Pressure at 68°F	35 psig
	Density, liquid, 1b./cu. ft.	
	at 70°F	56. 71
	at 105°F	54.38
	at 115°F	53.69
	at 130°F	
	OSHA Permissible Exposure Limit	

- 3.1 Employee Education and Training
 - 3.1.1 The supervisor should be thoroughly familiar with the contents of this data sheet, the Occupational Safety and Health Administration Standard for Vinyl Chloride (29CFR §1910.1017) and the Environmental Protection Agency's National Emission Standard for Vinyl Chloride (Part 61 Chapter I Title 40 CFR Subpart F) before undertaking any training of the employees who are engaged in handling or processing of vinyl chloride. Vinyl chloride handling and use are strictly regulated by many governmental agencies but the regulations issued by OSHA and EPA directly affect the content of any training program for vinyl chloride workers. The supervisor should also seek supplementary information and assistance. One recommended reference is the MCA Case Histories to learn of accidents and injuries that have occurred while handling or processing vinyl chloride. If the services of a safety specialist are avialable, the supervisor should consult with him before finalizing a safety review of his operations involving vinyl chloride.
 - 3.1.2 The Occupational Safety and Health Administration Standard for Vinyl Chloride requires that each employee engaged in vinyl chloride or polyvinyl chloride operations shall be provided training in a program including:
 - (a) Nature of the health hazards of vinyl chloride exposure.
 - (b) Specific operations which could result in exposure to vinyl chloride in excess of the permissible exposure limit and necessary protective steps.
 - (c) Purpose, proper use and limitations of the respiratory protective devices.
 - (d) Fire hazard and acute toxicity of vinyl chloride and necessary protective steps.
 - (e) Purpose and description of the monitoring program.
 - (f) Purpose and description of the medical surveillance program.
 - (g) Emergency procedures.
 - (h) Specific information to aid the employee in recognition of conditions which may result in the release of vinyl chloride.

- 3.1 Employee Education and Training (continued)
 - 3.1.2 (i) A review of the OSHA standard for vinyl chloride. This review must be undertaken annually as well as at the employee's first training period.
 - 3.1.3 The Environmental Protection Agency National Emission Standard for Vinyl Chloride requires that Standard Operating Procedures be prepared and implemented for:
 - (a) Loading and unloading line emission control.
 - (b) Slip gauge emission control.
 - (c) Manual venting of gases.
 - (d) Opening equipment emission control.
 - (e) Sample taking, handling and disposition.
 - (f) Leak detection and elimination.
 - 3.1.4 The employee training program should include the following:
 - (a) Process chemistry and objectives.
 - (b) Basic process equipment and operating techniques.
 - (c) Properties and safe handling procedures for the materials involved.
 - (d) Detailed study of the process and process operation.
 - (e) Standard operating procedures for the various plant jobs.
 - (f) Modifications and additions to meet the foregoing EPA and OSHA requirements.
- 3.2 The supervisor should periodically review equipment, materials and procedures in current use. For maximum effectiveness, this review should include the participation or input from selected representatives of operations, maintenance, technical and other related activities. The results and recommendations from this review should be incorporated into employee training programs, standard operating procedures and equipment changes or revisions. All chemical processes and plants, particularly those working with reactive hazardous materials should be updated based on changes in process, changes in materials, past experience and new information.

All significant hazards should be explained together with the precautions to be followed in the standard operating procedures. For example, if eye protection is required while taking a sample, the standard operating procedure should read "Wear splash goggles and sample still number 000". This type of instruction is preferable to requiring that a sample be taken in one part of the standard operating procedure and requiring that goggles be worn in another part.

If there are extremely critical steps in the process where, for example, overcharge of catalyst may cause an uncontrollable reaction, consideration should be given to making these supervisory checkpoints. In a similar vein, if certain process variables are not or cannot be maintained within prescribed limits then the plant or process step should immediately be shut down and the supervisor consulted.

Complete standard operating procedures with safety information are essential to train new employees, to provide guidance for older employees and to demonstrate compliance in certain regulatory agencies. An error by an untrained employee is often regarded as negligence on the employer's part by the courts and by regulatory agencies.

Section 4 HEALTH HAZARDS - MEDICAL MANAGEMENT, FIRST AID AND PROTECTIVE EQUIPMENT

4.1 Health Hazards

4.1.1 Vinyl chloride monomer is believed to be a carcinogen to man. Exposure of three animal species to vinyl chloride has caused a higher frequency of angiosarcoma, as well as other respiratory and digestive tumors than in the control groups. Workers in the manufacture of polyvinyl chloride resin have shown a higher incidence of angiosarcoma than anticipated after long exposure at relatively high concentrations. The long-term effects of short-term and intermittent high concentration exposure have not been studied in animals and man.

Because of the evidence of carcinogenicity, the Occupational Safety and Health Administration and the Environmental Protection Agency have issued regulations that limit the emission of vinyl chloride to the air and the exposure of people to such emissions.

Workers in the PVC industry, primarily reactor cleaners, have been found to have acroosteolytic changes in certain bones, particularly those of the distal phlanges of the fingers. This is largely reversible and has been associated only with high levels of exposure which have been experienced in the past. Certain skin changes suggesting scleroderma have been noted in some patients with occupational acroosteolysis.

Combustion and pyrolysis products of monomeric or polymerized vinyl chloride include hydrogen chloride and other highly irritating gases. Exposure to these gases may cause severe irritation of the mucous linings of the respiratory tract, pulmonary edema and chemical pneumonitis may occur.

Vinyl chloride monomer in gaseous form has no distinctive warning odor in low concentrations nor is it irritating. High concentrations of vinyl chloride has a narcotic effect on the central nervous system and can produce anesthesia. Hazards may be related to impaired judgment or functional ability under these circumstances. The threshold of odor for vinyl chloride varies with purity of VCM and amount of exposure. A two-thousand ppm threshold of odor level has been observed.

4.1.2 Acute Toxicity

Levels on the order of 6,000 ppm for five minutes exposure were required to produce minimal symptoms

4.1 Health Hazards (continued)

4.1.2 Acute Toxicity (continued)

resembling mild alcohol intoxication in humans. Levels of approximately 16,000 ppm for the same length of time will produce varying degrees of intoxication, with lightheadedness, some nausea and a dulling of visual and auditory responses in most humans. Higher levels produce unconciousness.

4.1.3 Chronic Toxicity

Long-term exposure of experimental animals to VCM at concentrations of fifty ppm or greater has produced angiosarcoma of the liver and other evidence of the induction of malignant neoplasms. The incidence of hepatic angiosarcoma among workers exposed to vinyl chloride monomer has been in excess of the predicted incidence based upon control populations. The incidence appears to be dose related in that the disease is most frequent among groups that were exposed to relatively high levels of VCM.

4.2 Medical Management

4.2.1 Physical Examinations

The Occupational Safety and Health Administration Standard for (29CFR \$1910.1017) Vinyl Chloride requires that all employees exposed to a vinyl chloride concentration of 0.5 ppm or more without regard to the use of respirators be provided a program of medical surveillance. This program performed or under the supervision of a licensed physician as stated in the regulation is as follows:

- (1) The the time of initial assignment, or upon institution of medical surveillance;
- (i) A general physical examination shall be performed, with specific attention to detecting enlargement of liver, spleen or kidneys, or dysfunction in these organs, and for abnormalities in skin, connective tissues and the pulmonary system (See Appendix A).
- (ii) A medical history shall be taken, including the following topics:
- (A) Alcohol intake:
- (B) Past history of hepatitis;
- (C) Work history and past exposure to potential hepatoxtic agents, including drugs and chemicals;

- 4.2 Medical Management (continued)
 - 4.2.1 (D) Past history of blood transfusions, and
 - (E) Past history of hospitalizations.
 - (iii) A serum specimen shall be obtained and determinations made of:
 - (A) Total bilirubin;
 - (B) Alkaline phosphatase;
 - (C) Serum glutamic oxalacetic transaminase (SGOT);
 - (D) Serum glutamic pyruvic transaminase (SGPT); and
 - (E) Gamma Glutamyl Transpeptidase.
 - (2) Examinations provided in accordance with this paragraph shall be performed at least:
 - (i) Every six months for each employee who has been employed in vinyl chloride or polyvinyl chloride manufacturing for ten years or longer; and
 - (ii) Annually for all other employees.
 - (3) Each employee exposed to an emergency shall be afforded appropriate medical surveillance.
 - (4) A statement of each employee's suitability for continued exposure to vinyl chloride including use of protective equipment and respirators, shall be obtained from the examining physician promptly after any examination. A copy of the physician's statement shall be provided each employee.
 - (5) If any employee's health would be materially impaired by continued exposure, such employee shall be withdrawn from possible contact with vinyl chloride.
 - (6) Laboratory analyses for all biological specimens included in medical examinations shall be performed in laboratories licensed under 42 CFR Part 74.
 - (7) If the examining physician determines that alternative medical examinations to those required by paragraph (1) of this section will provide at least equal assurance of detecting medical conditions pertinent to the exposure to vinyl chloride, the employer may accept such alternative examinations as meeting the requirements of paragraph (1) of this section, if the employer obtains a statement from the examining physician setting forth the alternative examinations and the rationale for substitution. This statement shall be available upon request for examination and copying to authorized representatives of the Assistant Secretary of Labor for OSHA and the Regional OSHA Director.

4.2 Medical Management (continued)

4.2.1 Physical Examinations (continued)

Appendix A - Supplementary Medical Information

When required tests under paragraph (1) of this section show abnormalities, the tests should be repeated as soon as practicable, preferably within three to four weeks. If tests remain abnormal, consideration should be given to withdrawal of the employee from contact with vinyl chloride, while a more comprehensive examination is made. Additional tests which may be useful:

- (A) For kidney dysfunction: Urine examination for albumin, red blood cells and exfoliative abnormal cells.
- (B) Pulmonary system: Forced vital capacity, forced expiratory volume at one second, and chest roent-genogram (posterior-anterior 14 x 17 inches).
- (C) Additional serum tests: Lactic acid dehydrogenase, lactic acid dehydrogenase isoenzyme, protein determination and protein electrophoresis.
- (D) For a more comprehensive examination on repeated abnormal serum tests: Hepatitis B antigen and liver scanning.

Records of such medical surveillance shall be available to the Assistant Secretary of Labor for OSHA and the OSHA Regional Director. Medical records shall be maintained for the duration of the employment of each employment of each employement of each employee plus twenty years or thirty years, whichever is longer.

4.2.2 Suggestions to Physicians

Treatment for vinyl chloride intoxication is symptomatic; no special procedures are required. In acute overexposures the primary effect is central nervous system depression. In chronic exposure the liver is the principal target with secondary effects possibly in the kidneys and lungs.

Note to Physicians: Avoid use of epinephrine or related drugs in treating acute overexposure cases since vinyl chloride may sensitize the heart to the arrhythmic action of these drugs.

When breathing has ceased due to vinyl chloride narcosis, promptly initiate assisted respiration (e.g., mouth-to-mouth, mechanical resuscitation). Oxygen should be administered. Active ventilation is important to the maintenance of adequate tissue oxygenation and the removal of vinyl chloride to the exhaled air.

4.2 Medical Management (continued)

4.2.2 Suggestions to Physicians (continued)

Oxygen Administration

Oxygen has been found useful in the treatment of inhalation exposures of many chemicals, especially those capable of causing either immediate or delayed harmful effects in the lungs.

In most exposures, administration of 100% oxygen at atmospheric pressures has been found to be adequate. This is best accomplished by use of a face mask having a reservoir bag of the non-rebreathing type. Inhalation of 100% oxygen should not exceed one hour of continuous treatment. After each hour, therapy may be interrupted. It may be reinstituted as the clinical condition indicates.

Some believe that superior results are obtained when exposures to lung irritants are treated with oxygen under and exhalation pressure not exceed 4cm water. Masks providing for such exhalation pressures are available. A single treatment may suffice for minor exposures to irritants. It is believed by some observers that oxygen under pressure is useful as an aid in the prevention of pulmonary edema after breathing irritants.

In the event of an exposure causing symptoms or in case of a history of severe exposure, the patient may be treated with oxygen under 4cm exhalation pressure for one-half hour periods out of every hour. Treatment may be continued in this way until symptoms subside or other clinical indications for interruptions appear.

Caution! It may not be advisable to administer oxygen under positive pressure in the presence of impending or existing cardiovascular failure.

4.3 First Aid

4.3.1 General

First aid should be started at once in the case of acute intoxication with vinyl chloride or in the case of contact with liquid vinyl chloride. Refer all over-exposed patients to a physician and give a detailed account of the accident (OSHA §1910.1017). Each employee exposed to an emergency shall be afforded appropriate medical surveillance.

4.3 First Aid

4.3.2 Contact with Skin

Vinyl chloride in liquid form is a skin irritant and can cause frostbite. All clothing that has become contaminated with vinyl chloride including shoes should be removed immediately and not worn again until properly decontaminated. All affected body areas should be washed thoroughly with warm water and soap. The individual should be referred to a physician promptly.

4.3.3 Contact with the Eyes

If liquid vinyl chloride has entered the eyes, they should be washed promptly with copious quantities of water for at least fifteen minutes. The eyelids should be held apart during washing to ensure contact of the water with all the surface tissues of the eye and lids. Prompt medical attention should be obtained.

4.3.4 Taken Internally

The gaseous nature of vinyl chloride makes the ingestion of significant quantities unlikely. Consult a physician in cases of suspected ingestion.

4.3.5 Inhalation

A worker who has been overcome by vinyl chloride must be carried at once into an uncontaminated atmosphere and if respiration has been slowed or stopped, effective artifical respiration must be initiated immediately. If oxygen inhalation apparatus is available, oxygen should be administered but only by a person authorized for such duty by a physician. The patient should be kept comfortably warm but not hot.

Stimulants will rarely be necessary where adequate oxygenation is maintained. Any such drugs for shock treatment should be given only by the attending physician. Never attempt to give anything by mouth to an unconscious patient.

Exposed persons showing signs of vinyl chloride intoxication should be led to an uncontaminated atmosphere promptly to prevent injury by falling, etc. All exposed persons are to be referred to a physician promptly after exposure.

4.4 Personal Protective Equipment

4.4.1 Availability and Use

Personal protective equipment is not an adequate substitute for good safe working conditions, adequate ventilation and intelligent conduct on the part of employees working with vinyl chloride. It is, however, in some instances the only practical means of protecting the worker, particularly in emergency situations.

The OSHA Standard for Vinyl Chloride specifically requires the use of engineering and work practice controls to reduce employee exposure to vinyl chloride to the permissable level or to the extent feasible. Where such controls are not sufficient to reduce exposure to the permissable exposure limits, a written program shall be established and implemented to reduce employee exposure to the permissable limits or to the greatest extent feasible.

4.4.2 Protective Clothing

Clothing and gloves made of rubber or impervious material should be worn to protect the body skin from accidental contact with liquid vinyl chloride where applicable.

Protective garments are required for employees who are engaged in hazardous operations such as cleaning polyvinyl chloride residue on vessel walls. These garments shall be selected for the operation and possible exposure conditions when liquid vinyl chloride is not involved

All protective garments shall be provided clean and dry for each use.

4.4.3 Foot Protection

Footwear with built-in steel toe caps are recommended for all industrial operations. For added protection against chemical contact and liquid vinyl chloride, safety footwear or overshoes worn over leather shoes are recommended. It is important to thoroughly clean or discard contaminated footwear.

4.4.4 Eye Protection

Spectacle-type safety glasses meeting ANSI standard 287.1 with metal or plastic frames are recommended as minimum protection against eye injuries from flying particles.

4.4 Personal Protective Equipment (continued)

4.4.4 Eye Protection (continued)

When there is danger of splashing or material is under pressure, splash goggles and/or plastic shields (full length, eight-inch minimum) with forehead protection should be worn where complete fact protection is desirable.

Where liquid vinyl chloride is involved or there is likelihood of exposure to vinyl chloride at concentrations exceeding the permissable exposure limit, appropriate respiratory protection is required by OSHA. Use of a full-face piece respirator provides adequate eye protection without supplementary devices.

4.4.5 Respiratory Protection

Where employees are provided or are required to wear respiratory protective devices a respiratory protection program meeting the requirements of OSHA \$1910.134 shall be established and maintained. Respirators selected for vinyl chloride shall be as follows:

	Atmospheric Concentration of Vinyl Chloride	Required Apparatus	
(i)	Unknown, or above 3,600 ppm.	 Open-circuit, self-contained breathing apparatus, pressure demand type, with full face- piece. 	
(ii)	Not over 3,600 ppm	(A) Combination type C supplied air respirator, pressure demand type, with full or half face-piece and auxiliary self-contained air supply; or	
		(B) Combination type C, supplied air respirator continuous flow type, with full or half facepiece, and auxiliary selfcontained air supply.	
(iii)	Not over 1,000 ppm	. Type C, supplied air respirator, continuous flow type with full or half facepiece, helmet or hood.	
(iv)	Not over 100 ppm	(A) Combination type C supplied air respirator demand type, with	

full facepiece and auxiliary self-contained air supply; or

4.4 Personal Protective Equipment (continued)

4.4.5 Respiratory Protection (continued)

Atmospheric Concentration of Vinyl Chloride Required Apparatus (iv) Not over 100 ppm (continued). . . (B) Open-circuit, self-contained breathing apparatus with full facepiece, in demand mode; or (C) Type C supplied air respirator, demand type, with full facepiece. (v) Not over 25 ppm (A) A powered air-purifying respirator with hood, helmet, full or half facepiece, and a canister which provides a service life of at least four hours for concentrations of vinyl chloride up to 25 ppm; or (B) Gas mask, front-or backmounted canister which provides a service life of at least four hours for concentrations of vinyl chloride up to 25 ppm. (vi) Not over 10 ppm (A) Combination type C suppliedair respirator, demand type, with half facepiece and auxiliary self-contained air supply; (B) Type C supplied-air respirator, demand type, with half facepiece; or (C) Any chemical cartridge respirator with an organic vapor cartridge which provides a service life of at least one hour for concentrations of vinyl chloride up to 10 ppm.

Respirators shall be selected from among those jointly approved by NIOSH and MESA under the provisions of 30CFR Part 11.

Employee entry into unknown concentrations of vinyl chloride or concentrations greater than 36,000 ppm may be made only for life rescue. Entry into concentrations ranging from 3,600 to

4.4 Personal Protective Equipment (continued)

4.4.5 Respiratory Protection (continued)

36,000 may be made only for life rescue, firefighting or securing equipment so as to prevent a greater hazard.

When air purifying respirators are in use a continuous monitoring and alarm system must be provided when vinyl chloride concentrations may reasonably be expected to exceed the maximum allowable concentration for the devices in use. Such a system shall be used to alert employees that the vinyl chloride concentration exceeds that allowable for the respirator in use.

Where air purifying canisters or cartridges are used they shall be replaced prior to the expiration of their service life or at the end of the work shift in which they were used, whichever occurs first.

4.4.6 Head Protection

Hard hats are recommended for protection from falling objects, overhead liquid leaks and chemical splashes.

Section 5 FIRE HAZARDS AND FIRE FIGHTING

5.1 Fire Hazards

Vinyl chloride is extremely flammable. Its explosive limits are between 3.6 and 33% by volume in air for the vapor or gas. Vinyl chloride is most often handled as a liquid under pressure; thus, a one-gallon spill of liquid vinyl chloride quickly produces 45 cubic feet of flammable gas which produces over 1,000 cubic feet of explosive gas-air mixture. Vinyl chloride when burning produces carbon monoxide and hydrogen chloride. Burning is usually accompanied by the production of a dense black smoke.

The hazards of vinyl chloride with regard to fire are summarized as follows:

Fire - Vinyl chloride is highly flammable. Vapors from a liquid spill spread quickly.

Explosion - Flammable vapor from a liquid spill if ignited cause a gas explosion hazard indoors, outdoors and sewers. Containers and/or tanks of liquid vinyl chloride may explode due to the heat from a fire.

Health - Contact with liquid may cause burns to skin and eyes. Vapors may cause dizziness or unconciousness. Fire will produce irritating, poisonous gases.

5.2 Fire Fighting

Carbon dioxide or dry chemical agents extinguish small fires effectively, but no extinguisher is known to be suitable for large fires. Control of large fires is confined to eliminating the source of fuel and to reducing fire damage by cooling structures and tanks with water spray. Extinguishing a vinyl chloride fire from a major leak source such as a broken pipeline may lead to explosive reignition if all sources of spark and flame are not eliminated.

Some guidelines for major spills or fires are:

Immediate Action

Evacuate area.

Keep upwind. Define and isolate hazard area.

Wear self-contained breathing apparatus and protective clothing.

Eliminate all open flames, flares, smoking and internal combustion engines if there is a vapor cloud.

5.2 Fire Fighting (continued)

Followup Action

Let fire burn unless leak or emission can be stopped immediately.

Cool tanks and containers with water from maximum distance until after fire is out. Use unmanned spray systems, monitor nozzles and hoses for major fires. Impound the water to prevent spread of the hazard. Do not let water enter the sewage collection system. Stay clear of tank and container ends. Evacuate immediately in case of a rising noise from venting safety device.

5.3 Special Hazards

All persons exposed to vinyl chloride or its combustion products should be checked by a physician. (See Section 4 of this data sheet.)

Entry into fire area after the fire is out should be limited to persons wearing self-contained breathing apparatus until the absence of vinyl chloride, hydrogen chloride and other hazardous gases is confirmed by test.

Section 6 INSTABILITY AND REACTIVITY HAZARDS AND CONTROLS

Vinyl chloride is a reactive monomer and will undergo addition and polymerization reactions which are characteristic of the ethylenic double bond. Under normal conditions of handling and storage uninhibited vinyl chloride is relatively stable. Vinyl chloride polymerizes exothermally in the presence of light, air, oxygen or free radical initiators to yield polyvinyl chloride. To prevent polymerization in transit or storage it is important that the monomer be protected at all times from contact with air, oxygen, moisture, catalytic impurities and light. Heat along does not initiate hazardous polymerization until temperatures of 250°C or more are reached, though vinyl chloride will become hazy if stored for long periods at temperatures over 20°C indicating that some polymerization does take place.

Vinyl chloride will react with air or oxygen to form vinyl chloride polyperoxide which is shock sensitive and will detonate under some conditions. It will also catalyze polymerization of the monomer. Polyperoxides have been found as a grey-white powdery mass in equipment where vinyl chloride is exposed to small amounts of air or oxygen such as recovery systems for vent gases, etc. When the presence of polyperoxides is suspected, treatment with caustic solutions will usually suffice for their destruction.

To stop polymerization or to prevent polymerization small amounts of phenol, hydroquinones, phenothiazine, tert butyl catechol, isoprene, styrene and styrene derivatives will act as inhibitors or short stops if thoroughly mixed with the vinyl chloride.

Section 7 ENGINEERING CONTROL OF HAZARDS

7.1 Building Design

- 7.1.1.1 Equipment and vessels containing vinyl chloride should preferably be isolated from other facilities by walls and floors of fire resistive construction or by adequate spacing.
- 7.1.1.2 Standard fire walls are recommended for isolation of larger equipment and storage tanks, while partitions of plaster and expanded metal lath may be used to isolate smaller equipment from other combustible materials.
- 7.1.1.3 Not less than two means of exit should be provided from each separate room or building in which VCM is stored, handled or used. No portions of such a room or building should be farther than 75 feet from the nearest exit. Additional exits should be provided depending upon the number of persons in the building (see NFPA Standard #101 Life Safety Code or OSHA Standard 28 CFR 1910 Subpart E).
- 7.1.1.4 All exit doors should open out in the direction of travel and should be provided with panic hardware. Fire doors should open out in the direction of travel and be an approved type.
- 7.1.1.5 For multistory buildings consideration should be given to the use of escape slides or external ramps instead of stairways or ladders from the higher levels. Most injuries have resulted from ignition of flammable vapor clouds or uncontrollable reactions. Escape from these hazards requires the utmost speed on the part of personnel.
- 7.1.2 In processes where large quantities of vinyl chloride are involved only those portions of the process requiring weather protection should be housed. Process vessels and storage tanks not requiring weather protection or close operating supervision should be located in the open.
- 7.1.3 Operations where large quantities of vinyl chloride are used should preferably be housed in one-story buildings or partially enclosed in critical areas only. Newer PVC plants with large reactors often have only the top portion of the reactors enclosed for a control room.
- 7.1.4 Explosion vents may be used to reduce destructive damage to buildings particularly those where a large leak or operating error could result in explosive concentrations of flammable vapors.

7.1 Building Design (continued)

- 7.1.4.1 Explosion venting windows, roof wall panels, skylights, light windows, diaphragms, etc. may be used to minimize building damage due to explosion pressures.
- 7.1.4.2 Since the required area of explosion vents depends upon such factors as the intensity of an explosion, vapor temperature, type of structure, the type of vent closure, etc. the determination of vent ratios should be made by experienced engineers and fire and safety protection specialists. (Reference NFPA Fire Codes Vol. 9-#68).
- 7.1.4.3 Vinyl chloride processing buildings equipped with internal water deluge and emergency ventilation systems controlled by flammable gas monitors are preferred for dissipation of flammable vapor clouds resulting from equipment failures within the building.
- 7.1.5 Adequate spacing of other process and service building from process buildings involving vinyl chloride is desirable to minimize damage from explosion and to insure the availability of critical services for fire fighting and control of uninvolved equipment.
- 7.1.6 Fire resistive stairwells with automatic fire doors may be specified for hazardous operation on upper floors but these are less desirable than slides or ramps leading away from the building.
- 7.1.7 Floor drains and process drains should be segregated from sanitary sewer systems to minimize the sewer explosion hazard and to minimize the amount of waste water to be treated for vinyl chloride removal as required by the Environmental Protection Agency regulations.
- 7.1.8 The vinyl chloride process building design should include a breathing air supply system for respirators, an open head automatically controlled fire water sprinkler system and an adequate forced ventilation system as well as emergency showers and eye wash facilities.

7.2 Equipment Design

7.2.1 Materials of construction considered hazardous for equipment in vinyl chloride service are copper, zinc, aluminum and alloys containing these materials. Copper is excluded due to the possibility of traces of acetylene reacting to form explosive copper acetylides. Zinc and aluminum are excluded due to their reactivity with vinyl chloride. Other materials such as steel, stainless steel, nickel, glass, Teflon, compressed asbestos and ceramics are acceptable. Most elastomers swell and lose strength in vinyl chloride service.

7.2 Equipment Design (continued)

7.2.2 Special Equipment and Design

The design of vinyl chloride piping and equipment is highly specialized because of the reactive, flammable and toxic properties of the material. Prior to the start of any plant or equipment design the Occupational Safety and Health Administration Standard for Vinyl Chloride (29 CFR §1910.1017) and the Environmental Protection Agency National Emission Standard for Vinyl Chloride (40 CFR 61f) as well as any other pertinent regulations should be thoroughly understood. The EPA Standard in particular requires specific equipment items. The technical problems of designing equipment, providing adequate ventilation and formulating operating procedures which ensure maximum safety and economy can be handled best by experienced engineers and safety and fire protection specialists.

- 7.2.3 In handling of vinyl chloride or the operation of any type of vinyl chloride system, all valves, pipelines, vents, safety devices, etc. should be located that they can be readily inspected and repaired. Consideration should be given to redundant facilities in critical areas. All handling and storage equipment should be located away from any source of sparks, flames, heated surfaces and other sources of ignition. The use of excess flow valves, valves with fusible links and remotely operated valves should be considered on large tanks in the case of fires or major leaks near these vessels. Bottom connections are to be avoided if practical.
- 7.2.4 Safety requires that equipment be used and maintained as recommended by the manufacturer or within design limits such as the ASME Pressure Vessel Code. All process equipment including safety devices should have regularly scheduled testing and inspection.

7.3 Ventilation

7.3.1 Good ventilation is essential in rooms or confined areas where vinyl chloride is handled to prevent the unsafe accumulation of toxic or explosive concentrations. Consideration should also be given to emergency ventilation to remove dangerous concentrations resulting from leaks and/or equipment failures. Good practice indicates that a normal ventilation system should yield at least fifteen air changes per hour for enclosed processing areas.

7.3 Ventilation (continued)

7.3.1 Many companies also provide emergency ventilation rates of thirty air changes per hour controlled by automatic analyzers in the work space air.

Pressurized control rooms or buildings with ventilation air intakes located upwind or some distance from sources of contamination can be used to provide a "safe" area for operating personnel where respirators need not be worn.

Good ventilation is a valuable tool in achieving the required one ppm or lower concentration in the work space air, but it is effective only when used in conjunction with good equipment and process design and proper equipment maintenance. In the design of a good mechanical ventilation system, consideration should be given to employee comfort and to control of the system; i.e. under what conditions should it operate normally, when should it be off, when should emergency speed be used and should control be automatic or manual.

7.3.2 Air Analysis-Monitoring

Analysis of the air for vinyl chloride in the work area is required by the EPA Standard (40 CFR 61.60F) as a means of detecting and measuring emissions to the air. The standard requires a system which obtains air samples from one or more points on a continuous sequential basis and analyzes the samples with gas chromatography or by alternative methods. The OSHA standard (29 CFR 1910.1017) requires that when employees are wearing air purifying respirators a continuous monitoring and alarm system be in use if there is a likelihood of exceeding the vinyl chloride concentration allowable for the respirator in use. In addition, these analyzers are invaluable in providing data for work in meeting the OSHA permissable exposure limits.

Flammable gas detectors are also used to indicate danger from fire or explosion and may activate water deluge as well as mechanical ventilation systems.

Automatic analyzers are complicated pieces of equipment and should be checked and maintained to meet the EPA standard requirements as a minimum.

The OSHA Standard also requires monitoring employee exposures to vinyl chloride on a specific basis. Sampling and analysis may be done in any fashion so long as acceptable levels of accuracy are achieved. This type of monitoring requires the consultation with a trained industrial hygienist.

7.4 Electrical Equipment

7.4.1 Vinyl chloride is normally handled in closed systems and all work areas should be ventilated and controlled to low concentrations of vinyl chloride. Flammable concentrations may exist in emergency cases. Under normal condition, electrical equipment approved for Class I Division 2 locations may be used.

The selection of electrical equipment for a plant requires skilled evaluation by a competent process engineer as well as an electrical engineer. All equipment and wiring should be purchased and installed to meet the appropriate sections of the National Electric Code.

- 7.4.2 Separate power supply to lights, analyzers and automatic control systems is provided by many companies in their plants. These separate power supplies are often backed up by auxiliary generators or batteries for critical control items.
- 7.4.3 Static electricity is generated when vinyl chloride or polyvinyl chloride flows through or is discharged from a pipe. To drain off static charges and avoid spark discharges, a continuous path from the point of generation to ground should be provided. This is best accomplished by electrically interconnecting all vessels and piping (bonding), by grounding all vessels and piping or by a combination of bonding and grounding.

Bonds or grounds for static electricity protection may be of any conductor size and any ground that is adequate for power or lightning protection is more than adequate for grounding static electricity. Ground wiring should be of sufficient size to provide reasonable protection against physical wear. Periodic checks of continuity to ground should be made. Systems using non-conductors such as glass, plastic and ceramic piping or coatings should be carefully checked for continuity. Some types of Teflon lined plug valves have required electrical bonds between the plug and the body to reduce sparking.

For a more complete discussion of static electricity see NFPA #77.

8.1 Storage

8.1.1 General

Vinyl chloride storage areas should always be selected to comply with all applicable local codes and regulations, especially those involving occupational health, environmental control, hazardous materials and fire prevention. Organizations such as The National Fire Protection Association, The National Board of Fire Underwriters and the Factory Insurance Association can be consulted about proper site selection.

8.1.2 Conditions of Storage

(A) Vinyl chloride is a very volatile, toxic and flammable gas at normal atmospheric conditions. Vinyl chloride may be stored for reasonable periods of time (one year) without danger from the hazardous decomposition or polymerization of vinyl chloride when kept in contact with ferrous materials and in the absence of air, oxygen, water, light or excessive heat.

Containers and vessels used for handling vinyl chloride at ambient temperatures are usually under pressure. Nitrogen blanketing may be employed to increase the storage pressure in order to facilitate tank pumping operations. Refrigeration can be used to maintain the storage temperature within an acceptable range - below 50° and preferably between 0°C and 20°C.

Vinyl chloride, properly stored, uninhibited either under refrigeration or at normal atmospheric temperature, should be checked regularly for the presence of polymers.

(B) All piping, instrument leads, storage tanks, relief devices and other equipment employed to handle vinyl chloride should be constructed of recommended materials. (See Section 7.2) This equipment should be designed to withstand a full vacuum, if practical, or a working pressure of at least 100-150 psi conforming to the ASME code for unfired pressure vessels or any code applying to the locale of planned storage. Vapor recompression or refrigerated storage tanks can be designed, however, for lower operating pressures.

Shut-off valves and control valves should be of steel or a suitable alloy not containing copper, and these valves should be designed for working pressures of at least 150 psi. All welded construction is recommended to insure a

8.1 Storage (continued)

8.1.2 Conditions of Storage (continued)

leakproof integrity. Wherever possible, all liquid inlet lines should enter the bottom or extend to the bottom of the storage vessels. This contributes to the guarding against the accumulation of static electricity. All equipment should be properly grounded and bonded with resistance to ground never exceeding 25 ohms. The stand leg should have an opening in it near the top of the tank to act as a vacuum breaker and to help prevent blowback. All electrical wiring, lighting and equipment should comply with NEC requirements. Vinyl chloride tanks should be painted with white or other heat reflective paint.

(C) All storage areas should have installed an appropriate water spray system or automatic sprinkling system or other special fire extinguishing systems which are suitable for use with Class B fires. Portable fire extinguishers of the carbon dioxide or dry chemical type should be readily accessible to personnel in these areas. (See Section 5)

Diking and/or draining to a safe location should be provided in all storage areas to completely confine and dispose of the liquid in the event of a major spill or vessel rupture.

8.1.3 Isolation

Vinyl chloride storage areas should be selected and constructed in accordance with local codes or authorities having jurisdiction. Such highly volatile and flammable materials should be stored outside of buildings. Preferably, vinyl chloride storage tanks should be segregated away from major process units. Process units such as furnaces or reactors, which have a higher than average fire or explosion risk potential, should be situated as far from such storage tanks as practical. All potential ignition sources should be eliminated from such storage areas. Cylinders containing vinyl chloride should be stored in a vertical position, outside of buildings and in an isolated and well ventilated area. It is best to store cylinders in the open, but provision should be made to shield them from the sun's direct rays and to prevent the accumulation of dirt, snow, water or ice on their valves or safety devices. Vinyl chloride storage areas should be restricted to authorized personnel only and are often classified as "regulated areas" per OSHA.

8.1 Storage (continued)

8.1.4 Regulatory Aspects

(A) 20 CFR 1910.1017 outlines the scope, application and specific requirements of the Occupational Safety and Health Standard for Vinyl Chloride.

Specific sections of this standard provide for personnel exposure limits, regulating areas to authorized individuals, environmental monitoring, respiratory protection, labeling, etc. A vinyl chloride program must be established and comply with all the requirements of 29 CFR 1919.1017.

(B) 40 CFR Part 61 "The National Emission Standards for Hazardous Air Pollutants" outlines the rules and regulations governing vinyl chloride emissions that have been established by the Environmental Protection Agency. The provisions of this standard should be complied with by the owner or operator of a vinyl chloride plant.

8.1.5 Compatible and Dangerously Reactive Materials

Vessels used for vinyl chloride should be only used for vinyl chloride. They must be purged with a dry inert gas until free of oxygen (<1,000 ppm) prior to filling. VCM is generally non-corrosive at normal atmospheric temperatures when dry (moisture free). However, mild to appreciable corrosion has been reported when vinyl chloride is wet even at ordinary temperatures. This may be due to the presence of impurities. In contact with water at elevated temperatures vinyl chloride accelerates corrosion of iron and steel. Acetylene as an impurity in vinyl chloride may form an explosive compound (acetylide) when exposed to copper or copper alloys.

8.2 Labeling and Identification

The statements and items listed below summarize the major labeling requirements; however, they are not necessarily complete or comprehensive. It is recommended that the Federal Code of Regulations be consulted for the specific details and labeling requirements of the Department of Transportation, OSHA and the Coast Guard.

- 8.2.1 Department of Transportation Requirements Coast Guard.
- 8.2.1.1 Cylinder by Water, Land or Air
- 49 CFR 172.101 Each container and overpacked cylinder containing vinyl chloride (including tank cars) shall carry a label "Flammable Gas" and a name "Vinyl Chloride" as shown on the outside of any shipping container and on any shipping papers.

8.2 Labeling and Identification (continued)

49 CFR 172-417 - Small cylinders should have a four-inch "Flammable Gas" label which is red in color and has black printing and cylinder marked with "Vinyl Chloride".

§172.417 FLAMMABLE GAS label.

(a) Except for size and color, the FLAMMABLE GAS label must be as follows:



(b) In addition to complying with \$172.407, the FLAMMABLE GAS label must be red. The printing and symbol must be black.

49 CFR 173-306 - Exceptions from Department of Labor labeling requirements.

49 CFR 172.400 - General labeling requirements, placement of labels.

49 CFR 172.326 - Any portable tank (cylinder) containing more than 1,000 pounds of vinyl chloride must be marked in letters two inches or more in size with the shipping name "Vinyl Chloride" and have the Flammable Gas label affixed.

Any truck moving the portable vinyl chloride containing tank must be placarded on the two sides as well as front and rear with "Flammable Gas" placard. (Paragraph 172.515 and Appendix B)

The square on the point placard should be made from tagboard and have a size 10 3/4" by 10 3/4". It should withstand thirty days open weather exposure. The letters on this placard should be red in color with white lettering.

- 8.2 Labeling and Identification (continued)
 - 8.2.1.2 Barge in Bulk
 - 46 CFR 151.45-2 (e) Cargo Signs and Cards. Warning signs shall be displayed on the vessel, port and starboard facing outward without obstructions at all times except when the vessel is gas free
 - 46 CFR 151.45-7 Shipping Papers. Each barge carrying dangerous cargo shall have on board a bill of lading manifest or shipping document giving the shipper, loading point location and the kind, grade and approximate quantity by compartment of each cargo in the barge . . .
 - 46 CFR 151.50-34 (h) The words "Cancer-Suspect Agent" must be added to the warning signs required by 46 CFR 151.45.2 (e).
 - 8.2.1.3 Ship in Bulk
 - 46 CFR 35.30-1 (b) General Safety Rules. A sign shall be displayed to warn persons approaching the gangway while a vessel is moored or anchored unless it is empty and gas-freed. The sign shall state in letters not less than two inches high substantially as follows:

WARNING

NO OPEN LIGHTS

NO SMOKING

NO VISITORS

46 CFR 151.45-2 (e) 3 A cargo Information Card for each cargo regulated by this subchapter shall be carried on the bridge or in the pilot house of the towing vessel readily available for use by the person in charge of the watch . . .

46 CFR 40.15-1 (b) and (c) The words "Cancer-Suspect Agent" must be added to the warning sign required by 46 CFR 35.30-1 (b). Signs bearing the legend:

Cancer-Suspect Agent in This Area

Protective Equipment Required

Authorized Personnel Only

must be posted whenever hazardous operations, such as tank cleaning, are in progress.

8.2.1.4 Portable Tanks. Portable tanks are not authorized for use with vinyl chloride.

8.2 Labeling and Identification (continued)

8.2.2 MCA Recommended Label

8.2.2.1 The Manufacturing Chemists Association recommends that all containers of vinyl chloride should bear a label as shown. The text of the label is designed for the product as shipped for industrial use. It should be used in addition to or in combination with any specific wording required by law. Since individual statutes, regulations or ordinances may require that particular information be included in a label, that certain information be displayed in a particular manner, or that a specific label be affixed to a container, the use of this label will not necessarily insure compliance with such laws.

VINYL CHLORIDE

DANGER! EXTREMELY FLAMMABLE LIQUID AND GAS UNDER PRESSURE

HARMFUL IF INHALED

MAY POLYMERIZE VIOLENTLY UNDER FIRE CONDITIONS OR LOSS OR REMOVAL OF INHIBITOR

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid breathing vapor.

Avoid contact with skin.

Keep cylinder out of sun and away from heat.

Container should be grounded when being emptied.

Never drop cylinder.

FIRST AID: If inhaled, remove to fresh air. If not breathing give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.

In case of:

Fire - Use water spray, dry chemical, or CO2.

Spill or Leak — For small spills, evacuate area and permit to evaporate. For large spills or leaks, evacuate area. Dike or flush to ground and let evaporate. Do not flush to sewer because of explosion hazard.

MCA Chemical Safety Data Sheet SD-56 available.

- 8.2 Labeling and Identification (continued)
 - 8.2.3 OSHA Labeling Requirements
 - 8.2.3.1 The Occupational Safety and Health Administration (OSHA) is authorized by the Occupational Safety and Health Act of 1970 to establish occupational safety and health standards.
 - 29 CFR Part 1910.1017 lists all the requirements for the control of employee exposure to vinyl chloride. The requirements of this health standard include environmental monitoring, the establishment of regulated areas, training and use of specific signs and labels.
 - 8.2.3.2 Entrances to regulated areas* shall be prominently posted with legible signs bearing the legend:

Cancer-Suspect Agent Area

Authorized Personnel Only

8.2.3.3 Areas containing hazardous operations or where an emergency** currently exists shall be posted with legible signs bearing the legend:

Cancer-Suspect Agent in This Area

Protective Equipment Required

Authorized Personnel Only

8.2.3.4 Containers of polyvinyl chloride resin waste from reactors or other waste contaminated with vinyl chloride shall be legibly labeled:

Contaminated with Vinyl Chloride

Cancer-Suspect Agent

8.2.3.5 Containers of polyvinyl chloride shall be legibly labeled:

Polyvinyl Chloride (or Trade Name)

Contains

Vinyl Chloride

Vinyl Chloride is a Cancer-Suspect Agent

*Regulated areas means any area where vinyl chloride concentrations may be in excess of the permissable exposure limit.

^{**}Emergency means any occurrence such as, but not limited to, equipment failure or operation of a relief device which is likely to or does result in massive release of vinyl chloride.

- 8.2 Labeling and Identification (continued)
 - 8.2.3 OSHA Labeling Requirements (continued)
 - 8.2.3.6 Vinyl chloride shall be legibly labeled either

Vinyl Chloride

Extremely Flammable Gas Under Pressure

Cancer-Suspect Agent

or in accordance with 49 CFR Parts 170-189 with the additional legend applied near the label or placard

Cancer-Suspect Agent

8.2.3.7 No statement shall appear on or near any required sign, label or instructions which contradicts or detracts from the effect of any required warning, informations or instructions.

All transportation equipment (tank trucks, tank cars, barges or ships) not subject to labels as specified above shall be labeled in accordance with the requirements set forth in applicable Department of Transportation and United States Coast Guard regulations.

Department of Transportation Requirements - Each container of vinyl chloride including tank cars shall carry an identifying label.

The proper shipping name, Vinyl Chloride, as shown in the commodity list (172.101) must be used and shown on the outside shipping container per paragraph 172.300.

Unless excepted each individual container must bear the FLAMMABLE GAS label as described in paragraph 172-417.

Department of Transportation 172.328 requires that tank motor vehicles transporting vinyl chloride shall be marked on both sides and at the front and rear with letters at least four inches high with words "Vinyl Chloride". The words "Flammable Gas" must be displayed on other motor vehicles transporting 1,000 pounds or more gross weight per paragraph 177.823 (a).

Each railroad car must bear the "Flammable Gas" placard per paragraph 177.823 (a).

Paragraph 173.29 (f) specifies that an "Empty" label must be applied to containers which have been emptied and on which the old label has not been removed, obliterated or destroyed. It must be so placed on the container to completely cover the old label.

- 8.2 Labeling and Identification (continued)
 - 8.2.3 OSHA Labeling Requirements (continued)
 - 8.2.3.7 Paragraph 172.510 (c) specifies that a "Flammable Gas-Empty" placard shall replace or cover the "Flammable Gas" placard on the railroad tank car which has been emptied.

The labels used should also conform with all other Federal, State and Local regulations relating to vinyl chloride such as the Federal Insecticide, Fungicide and Rodenticide Act; The Federal Hazardous Substances Act; The Federal Food, Drug and Cosmetic Act and other similar state and local legislations.

8.2.3.8 The Manufacturing Chemists Association also provides cards (Chem-Cards) containing information concerning the material as well as suggestions for safety precautions and emergency procedures. A copy of such a card is shown. These are of particular value accompanying bulk shipments.

CC-46 February 1976

VINYL CHLORIDE

Compressed, liquefied gas; sweet odor. Gas is heavier than air.

HAZARDS

(CANCER SUSPECT AGENT)

FIRE

Extremely flammable. May be ignited by heat, sparks or open flame. Burning releases hydrogen chloride gas which is extremely irritating and corrosive. Fire may cause violent rupture of tank.

EXPOSURE

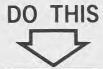
Vapor harmful. Liquid may cause skin or eye injury similar to frostbite.

IN CASE OF ACCIDENT

IF THIS HAPPENS



For assistance, phone
CHEMTREC
toll free, day or night
800-424-9300



SPILL or LEAK

Shut off ignition. No smoking or flares. Keep people away. Keep upwind. Shut off leak if without risk. Wear self-contained breathing apparatus and full protective clothing. Flush area with water spray. Run-off to sewer may create explosion hazard; notify authorities.

FIRE

Do not put out fire until leak has been shut off. On small fire use dry chemical or CO₂. On large fire use water spray. Wear self-contained breathing apparatus. Tanks in massive flame contact may rupture violently unless cooled by straight streams of water. Use unmanned monitor nozzle. Apply from side. Keep clear of tank ends. Otherwise, withdraw from area and let fire burn.

EXPOSURE

Remove to fresh air. If unconscious, call a physician. If not breathing, apply artificial respiration, oxygen. In case of contact with liquid, thaw frosted parts with water. In case of exposure to gas from fire, administer oxygen if breathing is difficult.

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Printed in USA

8.3 Non-Bulk Containers

8.3.1 General

In many of the specific steps involved in the handling, loading, sampling and process of vinyl chloride, there are points of potential employee exposure to vinyl chloride monomer. Each facility working with vinyl chloride should identify what potential exposure points may exist and perhaps be peculiar to their individual plant operations. When necessary, engineering, work practice and personel protective controls must be provided as outlined by the OSHA vinyl chloride standard to control employee exposures to, at or below the permissable exposure limit.

8.3.2 Cylinders

- 8.3.2.1 Cylinders should not be filled except with or by the consent of the owner and then only in strict accordance with the applicable Department of Transportation and OSHA regulations.
- 8.3.2.2 Areas where cylinders are connected or stored should have sufficient ventilation to prevent vinyl chloride concentrations from exceeding the OSHA permissable exposure limit.
- 8.3.2.3 Valve protection caps must always be kept securely in place except when the vinyl chloride containers are connected to piping, apparatus or equipment. As soon as the cylinder is disconnected the protective cap must be replaced. Empty vinyl chloride cylinders must be securely closed and capped. Air must not be allowed to enter the vessel.
- 8.3.2.4 Full or partly emptied cylinders should not be returned without permission of the supplier. Such cylinders must be shipped as full vinyl chloride cylinders and correspondingly handled, labeled and tagged.
- 8.3.2.5 In shipping vinyl chloride cylinders, the bill of lading should give cylinder identification number. For each cylinder shipped, show the name of the cosignee and indicate whether the cylinder is empty or full.
- 8.3.2.6 Department of Transportation approved cylinders containing vinyl chloride shall be legibly labeled in accordance with the requirements of OSHA and the Department of Transportation. (See Section 8.2)
- 8.3.2.7 Magnets or slings should never be used to unload cylinders. When transporting by crane or derrick a suitable platform, cradle or boot should be used.
- 8.3.2.8 Care should be exercised not to drop cylinders or otherwise handle them roughly.

8.3 Non-Bulk Containers (continued)

- 8.3.2.9 Cylinders may be moved by tilting and rolling them on their bottom edge. Dragging and sliding them should be avoided.
- 8.3.2.10 When cylinders are transported by hand truck, they should be held securely in position by means of a locking clamp, chain or other suitable holding device.
- 8.3.2.11 Cylinders should never be used as rollers for moving any object or material.
- 8.3.2.12 Avoid disturbing the fusible plug. The safety device should be tagged in order to differentiate it from the discharge connection.
- 8.3.2.13 Check valves must be installed in feed lines from the cylinder to prevent the reactants from entering the cylinder.
- 8.3.2.14 Cylinders should be provided with pressure regulators as recommended by the supplier.
- 8.3.3 Sample (Bomb) Cylinders

Where applicable, the recommendations set forth for cylinders in the preceding section also apply to sample bombs.

- 8.3.3.1 Stainless steel sample pressure bombs meeting the requirements of Department of Transportation regulation 3B-400 should be used to take quality control vinyl chloride monomer samples. Samples must be taken in bombs that are dedicated to vinyl chloride service. A closed loop sampling system which is designed to include the sample container is preferred in order to minimize the venting of vinyl chloride to the atmosphere.
- 8.3.3.2 Person(s) directly involved in the collection or analysis of vinyl chloride samples for quality control purposes should wear NIOSH/MESA approved respiratory protection consistent with the requirements of the OSHA vinyl chloride standard. The type of respiratory device utilized should reflect actual or reasonably anticipated vinyl chloride exposure levels.
- 8.3.3.3 All quality control testing and analyzing should be performed in a laboratory equipped with a chemical laboratory hood having a capture velocity adequate to collect vinyl chloride vapors under conditions prevailing in the laboratory. The discharge from the laboratory hood and from the analytical test instruments shall be designed so that vinyl chloride vapors do no re-enter a nonregulated area.
- 8.3.3.4 All quality control sampling containers (bombs) should be routinely inspected to assure the integrity of the valves and for leakage.

8.4 Bulk Transport

8.4.1 General

In many handling and unloading steps there are potential points of exposure to vinyl chloride monomer. Consult with the technical service staff of the supplier regarding where monomer unloading exposure points may be in your plant. Check also for other exposure points that are peculiar to individual plant operations.

Design of bulk transport facilities varies and unloading procedures are usually specified by the supplier. Complete understanding between the supplier and the user with regard to equipment and procedures is essential to safety of the transfer operation.

Loading or unloading bulk containers should be considered a hazardous operation and OSHA regulations regarding signs, barricades and respirator use followed.

- 1. EPA does not approve control devices. The control device used must meet the emission levels.
- 2. Allow no vehicular traffic in the area during transfer. If this cannot be done, minimize and control traffic by temporary road blocks.
- 3. If a sample is required before transfer for testing purposes, a stainless steel sample bomb meeting the Department of Transportation's requirements and dedicated to vinyl chloride service should be used. A closed loop sampling system is preferred. The operator taking the sample must use a suitable respirator and appropriate personal protective equipment during the period of sampling.

Bulk containers delivered with defective valves or other equipment should be held pending instructions from the owner. Only such actions should be taken that will provide for control of immediate safety problems such as obvious leaks and spills.

8.4 Bulk Transport

8.4.1 General

In these cases remove sources of ignition. Kepp people away. Control the leak by plugs, valves or patches to the extent that the immediate hazard is controlled. Personnel potentially exposed to vinyl chloride vapor should wear NIOSH/MESA approved air supplied respirators.

8.4.2 Miscellaneous Items

Where access to the top of the tank car or truck is needed, the spot should be provided with stairs and a platform of noncombustible construction. Overhead piping and equipment should be counterbalanced for ease of handling.

Allow no vehicular traffic in the area during transfer. If this cannot be done, minimize and control traffic by temporary road blocks.

An emergency shower and eye bath should be directly accessible and within twenty-five feet of the loading or unloading spot.

Fittings - The packing and lubricant for valves and piping must be of a material recommended for vinyl chloride handling.

Pumps and compressors must be equipped with double mechanical seals on packing glands. Space between the seals must be vented to an EPA-accepted control device or purged with a pressurized fluid so that there is no external leakage of vinyl chloride.

Unloading or loading piping should be provided with excess flow check valves to control spills in the event of a line bread. All unloading or loading piping must be attached to an EPA-accepted control system to limit atmosphere emissions to 0.13 FT³ at STP for each disconnect.

The use of slip gauges is forbidden unless EPA-accepted control devices are provided to control the emissions.

8.4.3 Tank Trucks

- 8.4.3.1 Tank trucks should be visually inspected for leaks and to confirm the contents before they are allowed to enter the plant. Unloading or loading should be performed only during daylight unless the working areas are adequately lighted.
- 8.4.3.2 The tank truck pad should provide two feet clearance on each side of the truck and four feet at each end. The pad should be sloped to drain spills away from the truck and exposed structures. Tank truck wheels should be blocked and brakes set to prevent movement during loading or unloading and the engine stopped. If the tractor must be separated from the trailer, this must be done before making any connections and place an adequate brace under the front end.

- 8.4.3.3 Static electricity is often generated by the tank truck in transit or it may be generated by the loading or unloading operation. All piping, tanks and structures should be electrically bonded by conductors that are adequate for power or lightning protection before any work is initiated. (See NFPA #77).
- 8.4.3.4 All sampling must be done with EPA-accepted systems to minimize vinyl chloride emissions to the atmosphere.
- 8.4.3.5 Unloading or loading operations should conform to the owner or operators instructions. On completion of the operation, loading or unloading hoses must be evacuated as noted previously and wheel blocks removed.
- 8.4.3.6 The truck engine should be started and the truck removed only after all connections are severed and the absence of flammable gases confirmed by test.

8.4.4 Tank Cars

Tank cars are the most commonly used bulk container for vinyl chloride shipment. All are unloaded from the top through one or both of the liquid eductor tubes. A third valve provides access to the vapor space of the car for purposes of padding or pressurizing the car to prime the unloading pump. Sampling slip gauging and unloading hose emissions are subject to the same EPA limitations noted for tank trucks.

- 8.4.4.1 Shippers and/or owners instructions should always be followed and all caution markings on both sides of the tank and dome should be read and observed. If inspection shows the car has faulty equipment or is leaking, the shipper should be contacted for instructions. Shippers' plants and procedures vary; thus, instructions should be obtained regarding loading or unloading a vinyl chloride tank car.
- 8.4.4.2 The car unloading track should be level and the engine crew should accurately spot the car at the unloading lines.
- 8.4.4.3 The tank car brakes must be set and the wheels blocked prior to hookup of the pipelines. Unless the car is protected by a closed locked switch, derails should be placed approximately one car length from each end of the car.
- 8.4.4.4 Caution signs and warning lights prescribed by Department of Transportation regulations must be placed at the derails on the track to warn persons or trains approaching the car from open end or ends of the siding. These must remain in place until the car is ready to be moved.

8.4.4.5 The contents of the car should be verified by checking the car number with the shipping papers. Many companies also sample the contents for analysis. Failure to verify the car contents can lead to serious and hazardous mixing of reactive chemicals.

8.4.4.6 Typical Unloading Situation

Tank cars of vinyl chloride are filled with liquid up to no more than 86% of the water weight capacity of the tank. Vinyl chloride vapor occupies the space above the liquid. Air or oxygen must not be introduced during unloading or storage to prevent formation of a flammable mixture or premature polymerization. Purge all lines thoroughly with nitrogen before hooking up. Use nitrogen with a masimum of ten ppm oxygen. Nitrogen purging can be minimized by sealing the line and alternately pressurizing with nitrogen and bleeding off the nitrogen to a remote recovery system or incinerator.

Remove the threaded pipe plugs on the liquid and gas valves cautiously and connect the liquid unloading line and the vapor padding line. The vapor pressure is needed to prime the centrifugal forwarding pump, if one is used. To reduce pressure drop, locate the pump as close to the tank car as possible. Some installations have a compressor on the vapor line from the storage tank in addition to the pump. In warm climates, a compressor may be used alone without a pump, but in cold weather a pump is usually needed - with or without the compressor - to facilitate unloading. The vapor pressure used for padding should not exceed 225 psig. Never apply heat to accelerate the unloading of a vinyl chloride tank car.

To obtain flexibility in the unloading system, either stainless steel hose or steel pipe with flexible joints can be used. The flows of vinyl chloride from the tank car should be regulated by a valve in the transfer line. If the discharge rate suddenly becomes too great, an excess flow check valve in the tank car will close. To re-open this valve, close the unloading connection valve until the pressure is equalized.

Start unloading by slowly opening the vapor padding connection valve to the car. If it is necessary to discontinue unloading for any reason, close all valves tightly and disconnect all unloading connections.

The lines leading from the unloading connection valve and the padding connection valve should be purged with nitrogen so that the vinyl chloride monomer vapor in those lines is transferred to the recovery system.

8.4.4.6 Check the storage tank frequently to determine when the tank car is almost empty. Completely unload the tank car; it should not be used for storage.

A pressure gauge on the unloading line is the best way to indicate when all the liquid has been emptied from the car.

After the car is emptied, stop the transfer pump. Close the padding connection valve and then the unloading connection valve at the top of the car. After this, close all other valves in the vinyl chloride line.

The lines leading from the unloading connection valve and the padding connection valve should be purged so the vinyl chloride monomer vapor in those lines is transferred to the recovery system.

Check the vinyl chloride monomer concentration to make sure there are no invisible leaks from valves. Wear respiratory protection if there is any leakage. Take care of leaks as recommended.

Do not allow tank car to stand with unloading connections attached after unloading has been completed. Remove all lines from the car and disconnect grounding wires.

Reverse the "Flammable Gas" placard on the car so that it reads "Flammable Gal-Empty".

IMPORTANT Leave at least 5-10 psig of vinyl chloride vapor pressure in the empty tank car being returned after closing and sealing all openings. The pressure is necessary to prevent air from entering the car.

8.5 Shipping

8.5.1 Department of Transportation Classification and Regulations

Vinyl chloride is classified by the United States Department of Transportation as a flammable gas. When shipped by rail, water or highway it must be packaged in authorized containers and shippers must comply with Department of Transportation regulations regarding packaging, loading, handling, labeling, marking and placarding. (R. M. Graziano's Tariff No. 31, 1977 is a source of condensed Department of Transportation Regulations for Hazardous Materials.)

8.5 Shipping (continued)

8.5.2 Shipping Containers - Type and Size Title 49 CFR Transportation Part 173.304

Cylinders - 4B150, 4BA225, 4BW225, 3A150, 3AA150, DOT-25 and 3E-1800.

Cylinders with brazed seams are not permitted.

Maximum filling density - 84%.

Title 49 CFR Transportation Part 173.315 Requirements for Compressed Gases in Cargo Tanks MC-330 and 331.

Maximum filling density - 84%.

Title 49 CFR Transportation Part 173.314 Requirements for Compressed Gases in Tank Cars DOT 106A500X

Maximum filling density - 84%.

DOT 105-200W

Maximum filling density - 87%.

DOT 112A340W

Maximum filling density - 86%.

DOT 114A340W

Maximum filling density - 86%.

8.6 Transportation Emergencies

8.6.1 Assistance Available

8.6.1.1 CHEMTREC (CHEMical TRansportation Emergency Center)

This center, located in Washington, D. C. at the offices of the Manufacturing Chemists Association, is manned 24 hours per day, seven days a week, and provides by telephone immediate response/action information for police, fire fighters and others concerned with the control of chemical transportation emergency situations.

8.6.1 Assistance Available (continued)

8.6.1.1 CHEMTREC (continued)

For assistance, dial:

- *(800) 424-9300 in the 48 contiguous States of the USA.
- *(800) 483-7616 in District of Columbia.
- *(200) 483-7616 in Alaska.

In Canada, call Canadian Chemical Producers Association's TEAP (Transportation Emergency Assistance Plan).

*Use long distance prefix if needed.

8.6.1.2 Company Mutual Aid

A number of vinyl chloride manufacturing companies voluntarily participate in a mutual-aid organization under which, in the event of a transportation accident, the closest company vinyl chloride plant will dispatch a qualified adviser to the scene of the accident if requested to do so by the shipper of the commodity.

8.6.2 Emergency Control

8.6.2.1 Personnel Attending Accident Scene

Shippers' representatives do not take charge of emergency operations. They are present as advisers only.

8.6.2.2 Recommended Emergency Kit

The following are considered essential:

- a. Explosion meter
- NIOSH/MESA approved self-contained breathing apparatus
- c. Wood plugs and wood mallet
- d. Data sheet and pencil
- e. Camera and film
- f. Flashlight (Bureau of Mines approved)
- g. Rubber gloves
- h. Slicker suit
- i. Rubber overshoes
- j. Safety lines (braided stainless, plastic covered) and harness

8.6.2 Emergency Control (continued)

8.6.2.2 Recommended Emergency Kit (continued)

- k. Goggles
- 1. Safety hat
- m. O-rings
- n. Strap wrench
- o. Ten-inch adjustable wrench
- p. Screwdriver
- q. Ground continuity meter
- r. Large first aid kit and collapsible water container, approximately fifty gallons. The water container should be filled at the emergency site and be available for eye wash or treatment of chemical skin contacts.

8.6.2.3 Recommended Procedures

Leaks of Vinyl Chloride

I. Controllable Leaks

- a. Small holes: Drive wooden plugs.
- b. Larger holes: Neoprene patch, bonded or chained to tank. Special rigs should be left to the judgment of the man at the scene.
- c. Jagged holes are difficult to close.
- d. Potassium bicarbonate will extinguish a vinyl chloride fire but reignition often occurs. Use it around valves if it appears that a leak can be subsequently controlled.

II. Uncontrollable Leaks - No Fire

- a. Evacuate area and isolate.
- b. Remove sources of ignition.
- c. Control spread of vapors by water spray.

III. Uncontrollable Leaks - Fire

- a. Evacuate and isolate area.
- b. Keep adjacent cars cool, if possible, with water spray.
- c. Keep nonessential personnel away.
- d. Treat a non-burning tank car in vicinity of fire as if it is about to rupture.
- e. If vinyl chloride gets to a sewer, evacuate area and flush sewers with fire hoses.

8.6.2 Emergency Control (continued)

8.6.2.4 Spilled Vinyl Chloride

Spilled vinyl chloride should not be deliberately ignited.

8.6.2.5 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and extent of car damage, vinyl chloride may be recoverable, but recovery should not be the determining factor in controlling the situation.

- a. If car condition permits, transpfer contents to empty tank car using nitrogen pressure.
- b. If car is ruptured, attempt to use pump with flooded suction.
- c. If pumping is impractical, use water or oil to float out remainder of vinyl chloride.
- d. Fill empty tank with water or nitrogen.
- e. If a vinyl-ice mixture forms, keep a water stream on the tank until it dissipates.
- f. Handling of vinyl chloride in a damaged car can be influenced by weather conditions. At low temperatures, since vaporization is reduced, patch tank, if possible, so that it can be moved.

8.6.3 Marine Emergencies

8.6.3.1 United States Coast Guard regulations (reference Vinyl Chloride Coast Guard Standard, i.e. Parts 40, 151, and Chapter 1 of Title 46 CFR. . .) require that a cargo information card for vinyl chloride be carried aboard the tank barge mounted near a warning sign and in such a position as to be easily read by a man standing on the deck of the barge. The cargo information card shall also be carried on the bridge or in the pilot house of the towing vessel. Copies are available from the Manufacturing Chemists Association.

8.6.3.2 Special Safety Equipment

In addition to normal safety equipment provided at the dock, the following special items should be available:

- a. NIOSH/MESA approved self-contained breathing equipment (at least two and two spare bottles).
- b. Explosimeters.
- c. Ground continuity meter.

8.6.3 Marine Emergencies (continued)

- 8.6.3.2 Special Safety Equipment (continued)
- d. Water with an appropriate number of nozzles.
- e. Dry chemical fire extinguisher.
- f. MCA Chemical Safety Data Sheet SD-56 and Cargo Information Card CIC-80.

8.6.3.3 Recommended Emergency Procedures

8.6.3.3.1 Leaks of Vinyl Chloride

- I. General Activate Alarm
- II. Controllable Leaks No Fires
 - a. Evacuate area of nonessential personnel and isolate leak from source.
 - b. Eliminate ignition source.
 - c. Control spread of vapors by water fog.
 - d. Attempt to repair leak using adequate safety protection procedures.

III. Uncontrollable Leaks or Rutpures - No Fires

- a. Evacuate area of nonessential personnel and isolate area.
- b. Remove all sources of ignition.
- c. Use water spray to prevent accumulation of liquid and to dissipate vapor cloud. It is not recommended that the ship's fire water supply be hooked into the city water supply.

IV. Uncontrollable Leaks - Fire

- a. Isolate area.
- b. Evacuate area except for emergency personnel.
- c. Use water fog on fires and fumes (do not extinguish fire unless leak can be controlled).
- d. Use copious amounts of water to keep adjacent areas cool.
- e. Treat adjacent tanks as if about to rupture.
- f. Make provisions to minimize the mixing of air with vinyl chloride vapor in confined spaces and the burning tanks or line (water, N₂ or inert gases).

8.6.3.3.2 Spilled Vinyl Chloride

Spilled vinyl chloride should not be deliberately ignited.

- 8.6 Transportation Emergencies (continued)
 - 8.6.3.3 Recommended Emergency Procedures (continued)
 - 8.6.3.3.3 Recovery or Removal of Vinyl Chloride

Depending upon circumstances and the extent of the tank damage vinyl chloride may be recoverable but provisions must be made to keep air out of the tank.

- a. If tank condition permits, transfer contents to an empty tank or back to shore.
- b. If tank cannot be patched and it does not have a deep well pump or the deep well pump cannot be used, sparge heated nitrogen into the bottom of the tank to vaporize the vinyl chloride.

Section 9 WASTE DISPOSAL GUIDELINES AND SPILL CONTROL

9.1 Waste Disposal Regulations

9.1.1 Federal, state, interstate and local regulations governing waste disposal make it essential for the producers and users of vinyl chloride to be fully aware of viable alternatives for the safe ultimate disposal of waste vinyl chloride and to select and practice a disposal method or process which assures compliance with all applicable regulations. Consideration must be given to air, water (surface and ground) and land pollution potential. MCA Technical Guides SW-1 (Landfill), SW-2 (Contract Disposal) and SW-3 (Incineration) may be helpful in fulfilling environmental responsibilities.

9.1.2 Discharges into Navigable Waters

Discharges are controlled by regulations (State, Interstate, Local or Federal) promulgated under the Federal Water Pollution Control Act (Public Law 92-500). Point source discharges must be in compliance with the effluent limitations set forth in the NPDES permit for that point source.

The Federal EPA Standard for emission of Vinyl Chloride (see 40 CFR Part 61 Sub-part F) stipulates as a work practice that in process waste water that contains over ten ppm of vinyl chloride must be stripped to ten ppm or less before:

- a. Being exposed to the atmosphere.
- b. Being discharged to a waste treatment plant.
- c. Being discharged untreated as a wastewater.

Any vinyl chloride stripped from such waste waters must be directed to a primary control device that emits less than ten ppm of vinyl chloride to the atmosphere.

9.1.3 Discharges to Municipal Sewage

Vinyl chloride or waste waters contaminated with vinyl chloride should never be discharged to public or private sewage treatment plants.

9.1.4 Air Emissions

Under the authority of Section 112 of the Federal Clean Air Act (see 42 U.S.C. 1857 et seq.), the Federal

9.1 Waste Disposal Regulations (continued)

9.1.4 Air Emissions (continued)

Environmental Protection Agency declared that vinyl chloride was a hazardous air pollutant and promulgated a National Emission Standard for Vinyl Chloride (see 40 CFR Part 61 Sub-part F). Essentially, the standard regulates the equipment and work practices to be used to meet:

- a. Point source discharges
- b. Mass emission levels

Although the Federal EPA has preempted the regulation of vinyl chloride emission, States may also regulate vinyl chloride emissions as long as the State regulations are at least as restrictive as the Federal regulations.

9.1.5 Land Application

At the present time environmental regulations for other than air and water pollution control are of a non-federal nature; however, Federal guidelines have been promulgated in some instances (land fill and incineration) and strict compliance with those and local, state and regional requirements is necessary.

9.2 Spill and Leak Control

9.2.1 General

Prevention of leaks and spills must be the keynote in the handling of either liquid or gaseous vinyl chloride. Nothing takes the place of carefully designed and well-maintained equipment operated by competent, trained and skilled operators. Standard safe startup, operating and shutdown procedures should be spelled out and their use enforced.

The prevention of spills, leaks and emissions should not result in operating procedures or plant designs that in any way interfere with the proper operation of emergency venting either by rupture disc, relief valve or manual vent. The polymerization of vinyl chloride can be rapid and highly exothermic making control of a polymerization a major objective in any emergency.

Large spills of liquid vinyl chloride are especially hazardous. The heat of vaporization keeps a great deal of the material liquid so that it penetrates porous fill, runs into sewers and depressions where it can generate large volumes of flammable gas. (Ten gallons of liquid

9.2 Spill and Leak Control (continued)

9.2.1 General (continued)

vinyl chloride will produce a flammable cloud fifty feet in diameter.) In designing plants, consideration should be given to this fact. Handle large spills of liquid vinyl chloride with extreme caution.

9.2.2 Control of Leaks and Spills

The National Emission Standard for Vinyl Chloride (see 40 CFR Part 61 Sub-part F) delineates much of the equipment and practices considered by the Environmental Protection Agency to be the best available control technology (BACT). Among recommended practices of the standard are:

1. The use of sealless pumps, double mechanical seals on pumps, or the equivalents.

2. A proscription against manual discharge valve and relief valve discharges except as a last resort in

emergency situations.

3. The use of add-on devices to control vinyl chloride discharges - possibilities suggested include incinerators, absorbers, refrigerated vents, strippers, recovery units and gasholders.

4. The use of continuous sequential monitoring for leaks

and emissions in stacks and buildings.

5. Provision for reducing volume of vinyl chloride in vessels prior to opening of such vessels and directing such vinyl chloride gas or liquid to a control device.

6. The use of leak patrols on a periodic basis.

7. The incorporation of a leak detection program into the standard operating procedures.

9.2.3 Handling Vinyl Chloride Leaks and Spills

The greatest danger from vinyl chloride leaks is:

- a. The damage that results from a fire and/or explosion.
- b. The exposure of personnel and the public to the effects of inhalation.

The explosion limits for vinyl chloride are 3.60% to 33.00% by volume in air.

Practical considerations in the event of a leak of vinyl chloride should include:

1. The use of proper protective clothing (see 4.4.2, 4.4.3, 4.4.4) and appropriate respiratory equipment (see 4.4.5).

9.2 Spill and Leak Control (continued)

9.2.3 Handling Vinyl Chloride Leaks and Spills (continued)

2. The sounding of a gas alarm and evacuation of all but personnel required to preserve life and property.

3. The use of emergency ventilation.

- 4. The valving off of the sources of the leak (isolation).
- 5. The use of the deluge system or other source of water mist to dilute the atmosphere. Such water should be drained to open ponds or diked areas, not to underground sewage collection systems because it may create an explosion hazard.
- 6. The shutting down of all ignition sources in the immediate area - such as autos, switch engines, trucks, electrical switchgear, boilers, etc. No ignition sources within twenty yards of the vapor cloud should be permitted.
- 7. The warning and evacuation of the public that may be in the path of a vapor cloud. Evacuation should be upwind and 2,000 feet from the sources if possible.

When the immediate danger from a leak or spill has been controlled each incident should be carefully investigated and medical surveillance provided to those involved. Federal and state regulations should be consulted and the required reports made to the regulatory agencies promptly.

10.1 Preparation for the Job

The inherently hazardous nature of vessel entry is increased by the flammability and toxicity of vinyl chloride and by the possibility of the presence of peroxide residues in a vessel that has contained vinyl chloride. Only experienced and trained workers should be assigned this duty and then only under the direct supervision of an experienced foreman. All work should be done in compliance with an adequate vessel entry procedure that provides for training, the use of suitable protective equipment, health safeguards and a written checklist or work practice guideline for each step.

10.2 Preparation of the Tank or Equipment

- 10.2.1 The Environmental Protection Agency regulation (40 CFR Part 61 Sub-part F) on vinyl chloride has sharply restricted the allowable emissions to the environment from vessel openings. Vessels over 25-gallon capacity are allowed to release no more than 2% of the vessel volume as vinyl chloride vapor or 25 gallons upon opening, whichever is greater. Reactors are limited to twenty pounds of vapor per million pounds of product. Therefore, special control methods must be used.
- 10.2.2 Any liquid vinyl chloride should be transferred to another suitable vessel insofar as possible. The remaining heel should then be evacuated or allowed to evaporate to a lower pressure system which leads eventually to a recovery or emission abatement system capable of moving the final effluent to less than ten parts per million concentration of vinyl chloride. The model method recommended by EPA is to use water to displace the vapor to a recovery or abatement system. The water so used becomes contaminated and must be stripped to less than ten ppm vinyl chloride concentration before release to the environment. Alternate methods are repeated evacuation and repressurization with an inert gas or continual purging with inert gas or steam with the exhaust gas being treated by recovery or abatement equipment in either case. When the vinyl chloride content has been reduced to less than 2% of the standard volume of the vessel or 25 gallons it may be opened to the atmosphere and further action is not regulated by EPA, but OSHA rules still apply. (See 40 CFR Part 61, Sub-part F).
- 10.2.3 Peroxide residues should be assumed to exist if the vessel has contained recovered vinyl chloride or if there has been any possibility that oxygen and moisture have been present.

10.2 Preparation of the Tank or Equipment (continued)

- 10.2.3 Sufficient 10% sodium hydroxide should be added to cover any solid deposits in the lower section of the vessel and this should remain in contact for three to six hours. This time may be shortened to two hours if the temperature can be raised above 60°C (145°F). This should be done before an attempt is made to disconnect any lines on the bottom of the vessel to avoid detonation of this sensitive material. Care should be taken in handling, removing and disposing of this solution to prevent caustic burns. Refer to the MCA Data Sheet Number SD-9 on sodium hydroxide for recommended precautionary measures.
- 10.2.4 All process piping should be disconnected, slip blanket or blinded so that there is no opportunity of process materials or utilities re-entering the vessel. Local regulations regarding the method of installing blinds should be followed. It is not sufficient to valve off these lines or to only insert blinds in the line. An open section should exist between the vessel and the line if there is any question as to the integrity of the blinds.
- 10.2.5 As soon as the vessel is open to the atmosphere, positive ventilation should be applied to remove the remaining vinyl chloride vapor. Sources of ignition should be eliminated from the work area until tests show that the concentration throughout the area and inside the vessel are well below the flammable limits. Care should be taken that all dead spots are eliminated and that the exhaust gases are dispersed adequately.
- 10.2.6 All persons in the work area during the vessel preparation steps should be equipped with impermeable clothing until one is assured that no liquid vinyl chloride remains in the vessel or its associated piping and should wear suitable NIOSH/MESA approved air-supplied respirators until tests have shown that the vinyl chloride concentration has been reduced to the point where other methods of protection are adequate.
- 10.2.7 After adequate dispersion of vinyl chloride vapors the interior of the vessel should be washed as free as possible of wall fouling or loose debris to prevent desorption of vinyl chloride back into the work atmosphere.

10.3 Vessel Entry

10.3.1 General [Consult OSHA Regulations 1910.1017(h)]

A written work permit must be prepared before tank preparation and entry. It must describe work procedures to be used, hazards which may be encountered and procedures and equipment

10.3 Vessel Entry (continued)

10.3.1 General (continued)

to be used to protect against these hazards. The permit must be prepared, reviewed and signed by the supervisor to whom the tank is assigned after he has satisfied himself that tank entry and repair work can be done safely and applicable regulations met.

As a minimum this permit procedure must assure that proper protective equipment is used, mechanical and electrical lockout procedures followed, the vessel atmosphere has been tested, and adequate rescue capabilities are available. A new authorization or permit is required at each shift change.

10.3.2 Special ventilation providing a continuous supply of fresh air is required during the entire time personnel are inside the tank.

It is preferable that vapors be exhausted from the bottom of the tank with fresh air being admitted at the top. In the case of the tanks having a top opening only this can be accomplished by extending a flexible air duct to the bottom of the tank. Care must be taken to avoid recycling exhaust gases into the tank.

- 10.3.3 During the course of the work, frequent tests should be made to determine that the atmosphere in the tank is being maintained within the safe range. This precaution is necessary because residues not completely removed by washing may recontaminate the tank atmosphere.
- If flammable vapors are detected over 10% of the LEL, the cleaning process should be repeated until the tank or vessel is free of vapor. The air should also be tested for oxygen content.
- 10.3.4 The electrical supply to any agitation within the vessel, and to any moving equipment nearby shall be locked out in the off position according to local codes and the key kept in the possession of the man inside the vessel or his foreman. The starting switch should be activated to be sure the proper circuit has been deactivated. The switch may also be disabled by a rod or lock in the "off" position, although this should not be the only lockout protection.
- 10.3.5 Danger signs should be prominently placed to indicate when workmen are in the tank.

10.3 Vessel Entry (continued)

- 10.3.6 No one should enter a tank or vessel that does not have a manhole opening large enough to admit him while wearing his safety harness, life line and respiratory protective equipment. It should be ascertained that the tank or vessel can be left by the original entrance. In some cases, it is advisable to have a block and tackle positioned on a tripod or otherwise fastened above the manhole.
- 10.3.7 No one should enter a tank or confined space until a work permit has been signed by an authorized person indicating that the area has been tested and found to be safe. Before directing men to enter a tank, an inspection of the interior should be made by the foreman who should be equipped with a positive pressure (or continuous flow) air line mask or self-contained breathing apparatus, together with rescue harness and life line. Another person should be on guard during the inspection.
- 10.3.8 Workers entering vessels should wear boots or rubbers over safety shoes, eye protection, hard hat and a NIOSH/MESA approved supplied air respirator. Impermeable clothing is needed if the walls are fouled with polymer. A wrist harness and safety line are also required and at least one other person similarly equipped for vessel entry should be stationed at the entrance of the vessel at all times. At least one other employee must be within audible hailing distance at all times.
- 10.3.9 All ladders, scaffolds or other large equipment shall be tied off properly and secured to prevent slipping or falling during the work assignment. Care must be taken to avoid tangling of air hoses and rescue lines with other equipment.
- 10.3.10 Any lights or electrically powered tools shall be inspected for proper insulation and grounding, and local codes shall be followed in regard to the permissible voltage to be used inside vessels. Refer to 29 CFR 1910.309 (OSHA regulation).

10.4 Emergency Rescue

10.4.1 It is essential that one or more attandants be present at the point of entry whenever another person is in the tank, depending upon the mechanical aids provided for removing a man from the tank. If work is being done in an isolated area, arrangements should be made to have additional assistants available at all times. Each person entering a tank should wear an approved safety harness or wristlets with a rope attached. An individual rope must be provided at the manhole cover for each person.

10.4 Emergency Rescue (continued)

Additional supplied-air respirators (hose mask) or self-contained breathing apparatus, together with rescue harness and life-line should always be located outside the tank entrance for rescue purposes regardless of the type of respiratory equipment or air supply which is provided for employees inside the tank. The air intake of the hose mask should be kept in an uncontaminated area.

- 10.4.2 Under no circumstances should a rescuer enter a tank to remove a victim of overexposure without proper respiratory protection (canister respirators are not proper equipment), a safety harness and an attached life line or before he has summoned additional assistance.
- 10.4.3 If a workman is overcome be fumes, he should be removed to fresh air immediately. Artificial respiration should be applied if breathing has stopped and a physician or ambulance summoned at once.

An injured worker should leave the vessel under his own power if possible, but if not he may be assisted by the attendent lifting on the rescue line or by means of the block and tackle. Only as a last resort should one person try to carry another up a ladder or out of a manway. Victims of a fall who have a suspected back or neck injury should only be moved in a basket litter.

Refer to Section 4 for treatment of overexposure to vinyl chloride.

10.5 Cleaning and Repairs

- 10.5.1 No repairs should be attempted until the vessel has been completely freed of polymer and peroxide residues. Care should be taken to avoid any exposure to vinyl chloride that may be entrapped in the solids. Protective foot, head and hand covering shall be required as a minimum, in addition to the previously recommended air-supplied respirators, while engaged in cleaning.
- 10.5.2 Any burning or welding may cause the formation of hydrogen chloride due to the decomposition of polymer. Adequate respiratory protection shall be used and sufficient ventilation is supplied to compensate for the oxygen demand of the welding operation.
- 10.5.3 No burning, welding, grinding or other operation that provides a potential source of ignition shall be allowed until

10.5 Cleaning and Repairs (continued)

10.5.3 (continued)

- a hot-work permit has been issued by a responsible supervisor who has determined that the work can be done safely. Both the conditions in the work area and the possibility of flammable vapor from adjacent areas must be considered. Continued testing of the work space must be done as described in Section 10.3.3.
- 10.5.4 All repairs to a vessel must be done in accordance with the appropriate ASME codes.
- 10.5.5 Careful attention should be given to the condition of nozzles and flanges, especially those bearing the safety relief devices. All residues and buildup should be removed while the vessel is open.

REFERENCES AND OTHER DATA SOURCES

- 1. Chemical Safety Data Sheet SD-56, Vinyl Chloride, Revised 1972, Manufacturing Chemists Association.
- EPA National Emission Standards for Hazardous Pollutants-Standard for Vinyl Chloride (40 CFR Part 61 Subpart F).
- 3. OSHA Exposure to Vinyl Chloride (29 CFR 1910.1017).
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- Vinyl Chloride, Code of Practice for Health Precautions, Health and Safety Executive, London, 1975.
- 7. Work Practice Standard for Manufacture of Synthetic Polymer Containing Vinyl Chloride, MCA Vinyl Chloride Technical Task Group, 1974.
- 8. Occupational Safety and Health Work Practice Standard for the Manufacture, Storage and Loading of Vinyl Chloride Monomer-Unpublished, Dr. Z. Bell, PPG Industries, 1974.
- 9. Vinyl Chloride Reactive Chemicals Data Sheet, Unpublished. Union Carbide Corporation, 1976.
- 10. Proposed Regulation Vinyl Chloride, Final Environmental Impact Statement Occupational Safety and Health Administration, 1974.
- 11. Economic Impact Studies of the Effects of Proposed OSHA Standards for Vinyl Chloride, Foster D. Snell, 1974.
- 12. Scientific and Technical Assessment Report on Vinyl Chloride and Polyvinyl Chloride, U. S. Environmental Protection Agency, 1975.
- Standard Support and Environmental Impact Statement, Promulgated Emission Standard for Vinyl Chloride, U. S. Environmental Protection Agency, 1975.
- 14. Recommended Standard for Occupation Exposure to Vinyl Chloride, NIOSH. U. S. Department of Health, Education and Welfare, 1974.
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- 21. Polyvinyl Chloride, L. Kardos, Stanford Research Institute, California, 1965.
- 22. Vinyl Chloride, Yu-Ren Chin and K. E. Linde. Stanford Research Institute, California, 1975.
- 23. Vinyl Resins, Dr. W. Mayo Smith, Rhienhold, 1958.
- 24. Vinyl Chloride Monomer Handling and Properties, PPG Industries, 1975.
- 25. Control of Vinyl Chloride Emissions in Distribution Operations, M. E. Sutherland, R. N. Wheeler, Jr., Chemical Engineering Progress, 1975.
- 26. Comments on Environmental Protection Agencies Proposed Standard for Vinyl Chloride, Society of the Plastics Industries, New York, 1975.
- 27. Coast Guard Regulations CFR 46 Chapter 1, Parts 40 and 151.

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CHEMICALS AND PLASTICS

P. O. BOX 8004, SOUTH CHARLESTON, WEST VIRGINIA 25303

To (Name)

Division Location See Attached List

Date November 3, 1978

Originating Dept.

Copy to

Subject OSHA Standard Acrylonitrile (CFR 1910.1045) Training Package

The OSHA Standard for Acrylonitrile requires that employees be trained at the time of initial assignment for new employees and prior to January 2, 1979 for existing employees. All employees shall be trained annually thereafter. The training shall consist of the following:

- (A) The information in appendixes A and B.
- (B) The quantity, location, manner of use, release or storage of AN and the specific nature of operations which could result in exposure to AN as well as any necessary protective steps.
- (C) The purpose, proper use and limitations of respirators and protective clothing.
- (D) The purpose and a description of the medical surveillance program required.
- (E) The emergency procedures developed as required.
- (F) Engineering and work practice controls, their function and the employees relationship to these controls.
- (G) A review of this standard.

In an effort to reduce your work or training, a general package has been assembled to fulfill a part of your training needs. This package will take care of the requirements in (A), (D), and (G), as well as part of (C). For your particular location you will have to provide training material for the rest of (C), (B), (E), and (f). These items will vary with the process and local practices.

The training package consists of the following items:

- 1. Fifty two (52) 2 x 2 slides numbered from one to fifty-two in the order of presentation.
- A magnetic tape cassette containing commentary on the slides. The tapes and the slides may be used with a Singer Caramate projector. In this case the tape contains the necessary

- 2. signal to automatically change the slide in sync with the tape talk. The Caramate need only be turned on and off at the start and finish of the talk. Naturally at the end of each presentation the tape must be rewound and the slide tray reset to zero. If a Caramate is not used then the tape may be played on any suitable reproduction equipment and the slides projected by a semi automatic projector. The tape sound track contains a brief 400 cycle beep indicating when the slide should be changed manually.
- A copy of the OSHA Standard for Acrylonitrile is attached.
 This must be reproduced and a copy given each trainee.
- 4. A summary copy of the OSHA Standard covering the main points. This should be reproduced and given each trainee though this is not required by law.

The slide presentation requires approximately 20 minutes, thus there should be no problem in setting time for training in the specialized items noted earlier.

The training presentation appears to meet OSHA's requirements in the areas it covers, however, OSHA's approval has neither been obtained or sought.

Very truly yours,

R. N. Wheeler. Jr.

RNWJr:ke Ext. 2164

Attachments

ACRYLONITRILE STANDARD TRAINING SCRIPT

Set slide tray on "0" Music 10 sec.



Acrylonitrile has been declared a suspect chemical carcinogen by OSHA.

It is in all employees best interests as well as required by law to be trained in the properties, hazards, and safety procedures for acrylonitrile.



Over the next few minutes we will be talking about Properties and Characteristics of AN.

Call attention to the items.

The standard is the Occupational Safety and Health Standard effective November 2, 1978.

2



Acrylonitrile is poisonous whether you inhale it, drink it, or apply it to your skin.

3



If a cage of rats is exposed to 300 to 600 ppm AN concentration in air, half of the rats will be dead in four hours.

4



Acrylonitrile is a white to yellowish liquid which is not normally handled in pressure vessels, etc



The AN boiling temperature is $77^{\circ}C$; close to ethanol, isopropanol, vinyl acetate, and ethyl acetate to name a few materials that are similar.

6



Acrylonitrile is flammable; any time it is exposed to air and a spark above 30°F or -1°C a fire may result.

7



Acrylonitrile vapor mixed with air in a range of 3% to 17% is explosive.

Note comparison with gasoline and others. 3% equals 30,000 ppm. Most of this discussion will be in ppm.

8



AN has a mild pungent odor described by some as like bitter almond and peach seed centers. It is nauseating. Most people can detect the odor at the 21 to 22 ppm level.

9



AN vapor is heavier than air thus releases of high concentrations are likely to collect in pits, trenches, and low spots unless there is good ventilation or a wind blowing.

10



At UCC, AN is classed as a reactive chemical. In the presence of peroxides or strong caustics it can react violently.



The fact that AN is a reactive chemical makes it useful to manufactur latexes. synthetic fibers, plastics, and synthetic rubber. We should not forget, however, that 1 lb. of AN reacting with itself produces enough heat to boil 1/2 lb. of water.

12



Other than fire and reactivity, the short term hazards of AN are that it will cause death at high concentrations in air. Lower concentrations cause nausea, headache, vomiting, and light headedness. Prolonged skin contact by AN will cause blistering (contaminated shoes are a problem.

Repeated skin contact will cause scaling dermatitis.

13



The suspected hazard from long term exposure was the reason for the current OSHA standard. Laboratory animals (rats) exposed to low levels, such as 50 ppm, for long periods (for 12 to 24 months) developed central nervous system cancer.

DuPont reported an apparent cancer excess in a South Carolina fiber plant (lung and colon).

Studies are continuing, for the data are not clear; however, close control of AN exposure is believed to be best at the present time.

14

Briefly, let's review these key facts. AN is:

- Toxic 1.
- Flammable
- 3. Will vaporize readily to produce excessive concentrations.
- If you can smell AN, put on a respirator or leave the area immediately.

15

for ACRYLONITRILE

For your protection UCC provides the following approved respirators in AN areas. There are others approved and changes may be made for special cases.



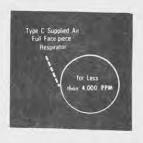
17

For work situations where the AN concentration is 4000 ppm or more, when you do not know the concentration, or for emergency escape or entry, the self-contained breathing apparatus with full-face piece operating in the positive pressure mode is required.

In other words, in case of doubt use this respirator or leave the area immediately.



18



19

For many work situations, such as tank entry and cases where AN concentration is less than 4000 ppm or 0.4%, the supplied air type C respirator is used with full face piece.



The fresh air mask has no bulky tank and no limit on the air supply. Its disadvantage is that the work area is limited by the length of the air hose. Auxiliary air tanks are sometimes used with these respirators to permit escape or movement of the hose supply to another outlet.

20



21

For low concentrations of AN, 100 ppm or less, the organic vapor cannister gas mask is acceptable and it has the advantage of greater portability.



In using cannister gas masks one should always remember that the cannister cleans up the air and does not provide air. Thus, if the work space contains no air the cannister gas mask cannot be used. Never enter a confined space with a cannister mask.

For escape from a contaminated area, use any available respirator.

Now, let's talk about the OSHA standard.



As a result of the suspected carcinogenic properties of AN, OSHA issued an ETS in January 1978 and a permanent standard in October 1978. Copies of the permanent standard will be provided for you at the end of this training session.

The permanent standard is effective November 2, 1978.



The OSHA standard applies to all AN occupational exposure such as storage, handling, reacting, packaging, laboratories, etc.

It applies to both employer and the employee.

It doesn't apply to products made from acrylonitrile such as ABS plastics and fibers. It does not apply to finish UCC latexes and polymer polyols.



The standard specifically forbids employee exposure in excess of 2 ppm averaged over an 8 hour period or 10 ppm maximum. If exposure averages below 1.0 ppm, certain parts of the standard don't apply.

When there is potential exposure to liquid AN, protective clothing and equipment must prevent skin or eye contact.



There are many other aspects of the standard which OSHA requires and will enforce. We will discuss some of the principal items.

24

25

Exposure Monitoring



Determinations shall be made from air samples that are representative of each employee's exposure to AN over an 8 hr. period, regardless of whether he is wearing a respirator. If exposure is less than the action level, no further monitoring is needed. If 2 ppm or less, quarterly checks are required. If over 2 ppm, monthly checks are needed.

These tests will be done with a carbon tube and sample pump worn by the employee.



Where exposures are high or variable automatic monitors will be used to give direct readings as well as provide records. Systems such as these are often required by EPA. EPA has not prepared a regulation yet.

28

27



The primary objective is to prevent excessive exposure to AN, therefore, surveys of potential leak sources and contaminated materials and plant areas will be conducted as necessary.

29

(I an Employee is Exposed to Concentrations Exceeding the Permissible Limits, He is Entitled Notification Within 5 Days.

All AN exposure measurements are available for an affected employee to see. Additionally, he will be notified if his exposure exceeds the permissible limits.



The standards require that all employees must be trained in the content of the standard and must be retrained yearly. New employees are to be trained prior to assignment to the AN area.

31



All employees exposed to AN must be trained by January 2, 1979.

32



The training will concentrate on personal hygiene and proper use of protective clothing and equipment.

33



AN is a liquid at normal temperatures and pressures; therefore, when there is potential for exposure, personal cleanliness, showering and washing are required.

Similarly, clean protective equipment is essential.

34

TRAINING Framing Must be Provident in the Hazards and Proper Protective Actions as Regards Accylements Training in the various hazards from AN, and protective actions are also necessary. This is why the discussion on AN properties is required.



Plant surfaces shall be kept free of accumulations of liquid AN. Waste AN, scrap and debris shall be decontaminated before being put into the general waste disposal system.

36



Emergency procedures must be established to control and to prevent excessive employee exposure to AN.

37



While we cannot promise that all jobs involving AN will be like this one, every effort is to be made to use engineering control and work practice procedures to control and reduce employee AN exposure.

38



The employer will post signs, such as this one, to clearly indicate work areas where AN exposures exceed permissible limits:

DANGER
ACRYLONITRILE (AN)
CANCER HAZARD
AUTHORIZED PERSONNEL ONLY
RESPIRATORS MAY BE REQUIRED

39

Areas where permissible AN exposures are exceeded, regulated areas will be established, such as this one for vinyl chloride. UCC does not expect to need regulated areas, however, the potential for excessive exposure will be carefully considered.





Precautionary labels such as this are to be affixed to all containers of AN and to containers of polymers where there is likelihood of excessive AN exposure.

41

DANGER
CONTAINS ACRYLONITRILE (AN)
CANCER HAZARD

The Employer Must Have a Written Plan to Reduce Employee Exposures to the Permissible Limits. If the work place exposure exceeds the permissible exposure limits the employer must have written plans to reduce exposures to the permissible range no later than November 2, 1980. UCC does not expect to have such areas if present data are correct.

42

MEDICAL SURVEHLANCE PROGRAM A Medical Surveillance Program. Including Periodic Physical Exama Must be Esteblished. The employer must establish a program of medical surveillance for employees working with AN.

43



This program is to be made available to all employees whose exposure exceeds the action level of 1.0 ppm averaged over 8 hours.

44

FREQUENCY
Opportunity for Examination
will be Provided Annually
Employee Examined, Given a
Statement Regarding His/Her
Suitability for
Continued Exposure.

Medical examinations will be offered to these employees annually

The employee and the employer will be given a statement as to whether the employee should continue to work in areas where AN is present.

45

A lameral Physical Economistion
A Medical Hosting
Lumplete Blook Cloud
Hostone Unitalizats
Pétrodic Deest X Rays
Periodic Polimenary Fair Host Tests
Periodic Vision and Elascolna Tests
Periodic Electrocardingrams
Periodic Audurans

RECORDS adical Records we kept Indefinitely 46

The medical examination will at least consist of a general physical examination, a medical and work history, complete blood analysis, urinalysis, a chest X-ray, pulmonary function testing, vision and glaucoma testing, electrocardiograms for older workers, and a hearing test. Additional tests may be used if the doctor believes them necessary.

Medical and AN exposure records will be maintained indefinitely for each employee working with AN.

These confidential records are available for use by the employee or his private physician.

MEDICAL RECORDS

Normally Confidential
But
Must Be Made
Available to:
Asst. Sec. of Labor
and NIOSH

48

47

As with all records these days, governmental representatives (OHSA and NIOSH) may have $\underline{\text{full}}$ access.

PERMISSIBLE EXPOSURE LEVELS:

«FPPM Max. Averaged.

«FPPM Max.
Action Leval also FPM
Manitoring of Exposure
Work Precision
Medical Surveillance

To review parts of the standard that most directly affect you and your job: The permissible exposure level is 2 ppm averaged over 8 hours or 10 ppm maximum. The action level for the standard is 1.0 ppm (8 hr. avg.). Your exposure will be checked on a regular basis as required by the standard.

Some changes in work practices and rules will be made.

The current UCC medical program will be changed slightly to conform with the standard.

Technical and Financial
Responsibility
...
Aid and Cooperation to
Regulatory Body

As far as the standard is concerned UCC expects to provide all necessary technical and financial resources needed to comply. UCC expects each supervisor and employee to make a personal commitment to carry out its requirements. As in the past this facility will cooperate and work with NIOSH, OSHA and other governmental regulatory agencies.

50

49

Text. Wheeler
R. N. Wheeler
Narration...
Frank Stowers
Graphics...
Jim McClure

51

52

This training unit was prepared by the South Charleston Plant.

Do not forget to pick up your copy of the OSHA acrylonitrile standard before you leave. A summary is also provided for easy reference.

SUMMARY

OCCUPATIONAL EXPOSURE TO ACRYLONITIRLE (VINYL CYANIDE) 29 CFR 1910

Item 1910.1045 Acrylonitrile

A. Scope and Application

- 1. This section applies to all occupational exposures to acrylonitrile, except as provided in paragraphs (a)(2) and (a)(3) of this section.
- 2. This section does not apply to exposures which result solely from the processing, use, and handling of the following:
 - (1) ABS resins, SAN resins, nitrile barrier resins, solid nitrile clastomers, and acrylic and modacrylic fibers
 - (ii) Materials made from and/or containing AN for which objective data is reasonably relied upon to demonstrate that the material is not capable of releasing AN in airborne concentrations in excess of 1 ppm as an 8-hour time weighted average, under the expected conditions of processing, use, and handling which will cause the greatest possible release, and
 - (iii) Solids materials made from and/or containing AN which will not be heated above 170°F during handling, use, or processing.

B. Definitions

"Action level" means a concentration of AN of 1 ppm as an 8-hour time weighted average.

"Decontamination" means treatment of materials and surfaces by water washdown, ventilation, or other means to assure that the materials will not expose employees to airborne concentrations of AN above 1 ppm.

"Emergency" means any occurrence such as, but not limited to, equipment failure, rupture of containers, or failure of control equipment, which results in an unexpected massive release of AN. Exceeding the 15 minute ceiling value of acrylonitrile in the work-space air does not necessarily mean an emergency per se.

"Liquid AN" means AN monomer in liquid form, and liquid or semi-liquid polymer intermediates, including slurries, suspensions, emulsions, and solutions produced during the polymerization of AN.

C. Permissible Exposure Limits

1. <u>Inhalation</u>. The employer shall assure that no employee is exposed to an airborne concentration of acrylonitrile in excess of two parts per million as an 8 hour time weighted average.

Ceiling limit. The employer shall assure that no employee is exposed to an airborne concentration of acrylonitrile in excess of 10 ppm as averaged over any 15 minute period during the working day.

2. Dermal and eye exposure. The employer shall assure that no employee is exposed to skin contact or eye contact with liquid acrylonitrile.

D. Notification and Regulated Areas and Emergencies

- 1. Regulated areas. Within 30 days following the establishment of a regulated area pursuant to paragraph (F) of this section, the employer shall report the necessary information to the OSHA area office.
- 2. Emergencies. Emergencies and the facts obtainable at that time shall be reported with 72 hours of the initial occurrence to the OSHA area office.

E. Exposure Monitoring

- 1. General. Determination of airborne exposure levels shall be made from air samples that are representative of each employee's exposure to AN over an 8-hour period.
- 2. <u>Initial monitoring</u>. Each employer who has a place of employment in which AN is present shall monitor such workplace and work operation to accurately determine the airborne concentrations of AN to which employees may be exposed.
- 3. Frequency. If the monitoring required by this section reveals employee exposure to be below the action level, the employer may discontinue monitoring for that employee. If the monitoring required reveals employee exposures above the action level but below the permissible exposure limits, the employer shall repeat such monitoring for each employee at least quarterly. If the monitoring reveals employee exposure in excess of the permissible exposure limits, the employer shall repeat these determinations for each employee at least monthly.
- 4. Additional monitoring. Whenever the employer has any reason to suspect a change which may result in new or additional exposures to AN, additional monitoring shall be conducted.
- 5. Employee notification. Within 5 working days after the receipt of the results of monitoring, the employer shall notify each employee in writing of the results which represent that employee's exposure.

F. Regulated Areas

The employer shall establish regulated areas where AN concentrations are in excess of the permissible exposure limits.

G. Methods of Compliance

- 1. Engineering and work practice controls. By November 2, 1980 the employer shall institute engineering and work practice controls to reduce and maintain employee exposures to AN, to or below the permissible exposure limits, except to the extent that the employer establishes that such controls are not feasible.
- 2. Compliance program. The employer shall establish and implement a written program to reduce employee exposures to or below the permissible exposure limits solely by means of engineering and work practice controls. Written plans for these compliance programs shall include at least the description of each operation and process resulting in employee exposure to AN above the permissible limits and outline the nature of the engineering controls and work practices to be applied, a report of the technology considered in meeting the permissible exposure limits, a schedule of the implementation of engineering and work practice controls for the operation or process, and any other relevant information.

H. Respiratory Protection

- 1. General. The employer shall assure that respirators are used where required to reduce employee exposure to within the permissible exposure limits. Respirators shall be used in the following circumstances:
 - (i) During the time necessary to install and implement feasible engineering and work practice controls.
 - (ii) In work operations, such as maintenance and repair activities in which the employer establishes that engineering and work practice controls are not feasible.
 - (iii) In work situations where feasible, engineering and work practice controls are not yet sufficient to reduce exposures to or below the permissible exposure limits.
 - (iv) And in emergencies.
- 2. Respirator selection. For acrylonitrile concentration less than or equal to 100 ppm, the respirator type shall be a full face piece respirator with an organic vapor cartridge, a supplied air respirator with full face piece or a self-contained breathing apparatus with full face piece. For concentrations less than or equal to 4,000 ppm, a supplied air respirator operated in the positive pressure mode with full face piece, helmet, suit, or hood. For concentrations greater than 4,000 ppm or for unknown concentrations, the respirator type shall be supplied air with auxiliary self-contained breathing apparatus having full face piece or a self-contained breathing apparatus with full face piece in the positive pressure mode. For escape purposes, any organic vapor respirator or self-contained breathing apparatus is acceptable.

Emergency Situations

- 1. Written plans. A written plan for emergency situations shall be developed for each workplace where liquid acrylonitrile is present and appropriate portions of this plan shall be implemented in the event of emergency.
- 2. Alerting employees. Where there is the possibility of employee exposure to AN in excess of the ceiling limit, a general alarm shall be installed and used to promptly alert employees of such occurrence.

J. Protective Clothing and Equipment

Provision and use. Where eye or skin contact with liquid acrylonitrile may occur, the employer shall assure that employees wear impermeable protective clothing or other equipment to protect any area of the body which may come in contact with liquid acrylonitrile.

K. Housekeeping

All surfaces shall be maintained free of visible accumulations of liquid acrylonitrile. In operations involving liquid acrylonitrile the employer shall institute a program for detecting leaks and spills of liquid acrylonitrile, including regular visual inspections. Where spills of liquid acrylonitrile are detected, the employer shall assure that all surfaces contacted by liquid acrylonitrile are decontaminated.

L. Waste Disposal

Acrylonitrile waste, scrap, debris, bags, containers, or equipment shall be decontaminated before being incorporated in the general waste disposal system.

M. Hygiene Facilities and Practices

Where employees are exposed to airborne concentrations of acrylonitrile above the permissible exposure limits, or where employees are required to wear protective clothing or equipment, the facilities provided shall include clean change rooms and shower facilities for use of those employees. The employer shall assure that the employees wearing protective clothing or equipment for protection from skin contact with liquid acrylonitrile shall shower at the end of the work shift. The employer shall also assure that in the event of skin or eye exposure to liquid acrylonitrile, the affected employee shall shower immediately to minimize the danger of skin absorption.

N. Medical Surveillance

The employer shall institute a program of medical surveillance for each employee who is or will be exposed to acrylonitrile at or above the action level. The employer shall provide each such employee with an opportunity for medical examinations and tests in accordance with this regulation. The employer shall obtain a written opinion from the examining physician

which shall include the results of the medical examination and tests performed, the physician's opinion as to whether the employee has any detected medical condition which would place the employee at an increased risk of material impairment of the employee's health and exposure to acrylonitrile, any recommended limitations upon the employee's exposure to acrylonitrile, and a statement that the employee has been informed by the physician of the results of the medical examination and any medical conditions which require further examination or treatment. The employer shall provide a copy of the written opinion to the affected employee.

O. Employee Information and Training

By January 2, 1979, the employer shall institute a training program for, and assure participation of all employees exposed to acrylonitrile above the action level, all employees whose exposures are maintained below the action level by engineering and work practice controls, and all employees subject to potential skin or eye contact with liquid acrylonitrile. Training shall include information contained in Appendixes A and B, the quantity, location, manner of use, release or storage of acrylonitrile, and the specific nature of operations which could result in exposure to acrylonitrile as well as any necessary protective steps. Training shall also provide information on the purpose, proper use and limitation of respirators, and protective clothing. Other training items include the purpose and description of the medical surveillance program, the emergency procedures, engineering and work practic controls, their functions and employee's relationship to these controls, and a review of this standard.

P. Signs and Labels

The employer shall post signs to clearly indicate all workplaces where AN concentrations exceed the permissible exposure limits. These signs shall bear the following legend:

DANGER

ACRYLONITRILE (AN)

CANCER HAZARD

AUTHORIZED PERSONNEL ONLY

RESPIRATORS MAY BE REQUIRED.

The employer shall assure that precautionary labels are affixed to all containers of liquid acrylonitrile and acrylonitrile-based materials not exempted. The labels shall bear the following legend:

DANGER
ACRYLONITRILE (AN)
CANCER HAZARD

Q. Recordkeeping

- 1. Objective data for exempted operations. Where processing, use, and handling of materials made from or containing acrylontrile are exempted, the employer shall establish and maintain an accurate record of objective data reasonably relied upon in support of the exemption.
- 2. Exposure monitoring. The employer shall establish and maintain an accurate record of all monitoring required by this regulation. The employer shall maintain this record for at least 40 years or duration of employment plus 20 years, whichever is longer.
- 3. Medical surveillance. The employer shall establish and maintain an accurate record of each employee subject to medical surveillance as required of this regulation. This record shall include a copy of the physician's written opinions, any employee medical complaints related to exposure day in, a copy of the information provided to the physician, and a copy of the employee's medical and work history.
- 4. Availability. The employer shall make all records required to be maintained for this regulation available on request to the Assistant Secretary and the Director for examination and copying. The employer shall make records required available on request for the examination copying to the affected employees, former employees, or their designated representative.

R. Observation and Monitoring

The employer shall provide affected employees or their designated representatives an opportunity to observe any monitoring of employee exposure to acrylonitrile conducted pursuant to this regulation. Monitoring and medical surveillance conducted since January 17, 1978, under the provisions of the emergency temporary standard may be relied upon by the employer to meet the initial monitoring and initial medical surveillance requirements of this regulation. Training programs must be implemented by January 2, 1979. Engineering and work practice controls required by this regulation shall be implemented no later than November 2, 1980.

S. Appendixes

The information contained in the appendixes is not intended by itself to create any additional obligations not otherwise imposed or to detract from any obligation.

R. N. Wheeler/ke 10-16-78 (3005/511)

APPENDIX B

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