Air Products and Chemicals INC.

ESCAMBIA PLANT

INTEROFFICE MEMORANDUM

To: Mr. Lamar Rawson

Date: May 23, 1974

From: B.K. Driver

Copies: A.K. McMillan
R.E. Jones
J.D. Evers
E.A. Primeau
R.R. Spiegelhalter
W.T. Johnson

Re: Trip Report-VCL Monitoring
Seminar held in Houston, Texas
April 25, 1974

RECEIVED
MAY 1974
A. K. McMILLAN

I have just received my copy of the minutes to the VCL meeting I attended back in April. The attendees numbered 40-50 and represented NIOSH (Mr. Charles McCammon), Honeywell Division of Process Analyzers who sponsered the meeting, Monsanto, B.F. Goodrich, Catalytic, Inc., Conoco, G.E., a report from Dow and others. I feel that the meeting was profitable to us and based on what I heard we are quite advanced in our permanent sensor monitoring program compared to the others. BFG has been active since about mid 1973. Our first on-line, 10-point monitor was started March 7, 6 weeks after the first phone call was made to locate the analyzer.

One general statement could express the monitoring program results and I believe this would include all the vinyl manufactures. It is this: Companies were surprised at the high level of VCL that was present when they first monitored, and surprised at how low the level dropped when corrective steps were taken. BFG actually showed the first chart recording they made which had VCL in excess of 1,000 ppm. Later they were able to reduce to less than 50 ppm.

I am not going to write a complete letter of my notes since you will find attached the minutes of the meeting plus other information that should be helpful to Spike.

A similar meeting is planned for June 13, prior to the time that the Permanent Federal Law will be published. I understand that someone from OSHA, NIOSH and EPA will attend.

RECEIVED
MAY 30 1974
A. K. McMILLAN

Since the meeting I have talked with one of the Honeywell representatives who is in charge of setting up the June 13th meeting and indications are that the proposed zero VCL detectable limit will be opposed and probably 5-25 ppm will be asked for. He also said OSHA is preparing to propose limits for T. D. I. which would probably be 50 PPB with excursions not to exceed 200 ppm. He further stated that there seems to be some people who are more immune to T. D. I. and way and means to select these people are being considered. Possibly VCL exposure might be more harmful to some than to others.

In the minutes under BFG monitoring experience there is a reference to 5-6 ppm of background measurement. In our PVC plant here in Pensacola we have found 3-4 ppm of Methane and it remains fairly constant. This could possibly explain BFG's background level. We also found the Methane in a certified VCL calibration cylinder that we had purchased (we didn't ask for the Methane).

This next seminar should be very informative and I plan to tape the entire meeting.

B.K. Driver

BKD:pr

attch.

Honeywell

May 14, 1974

Mr. B. K. Driver
Air Products & Chemical, Inc.
P. O. Box 467
Pensacola, Fla. 32592

Dear Mr. Driver:

Please find enclosed for your information, the minutes of the April 25, 1974 discussion on Vinyl Chloride Monitoring. The tape recording equipment was not operating at the beginning of the discussion, so we have the notes from Jerry Scates as a fill-in.

The permanent proposed Federal Register is out as of Friday, May 10, 1974. It requires monitoring for one part per million levels. I assume you will have 45 days to respond to this requirement.

We talked about another meeting to take place after the Register was released, and prior to your having to respond. Honeywell will still sponsor this meeting if you desire. Please let me know as soon as possible so plans can be made.

Very truly yours,

Ralph Powell

Ralph Powell, Sales Manager
Process Analyzer Center

RP:sk

Enclosure

HONEYWELL INC., 6625 McGREW, HOUSTON, TEXAS 77017, TELEPHONE 713/645-4911

VINYL CHLORIDE MONITORING DISCUSSION

APRIL 25, 1974 AT HOUSTON, TEXAS

Introduction

Holland introduced the Honeywell people attending with other participants identifying themselves and company affilliations.

Powell discussed the purpose of the meeting and emphasized that maximum benefit could best be obtained if all attendees were willing to participate. The listed topics of discussion were presented with resulting requests for six additional topics to be added.

OSHA Requirements

McCammon explained the role of NIOSH and OSHA arriving at standards such as the one relating to exposure to vinyl chloride. NIOSH makes recommendations to OSHA which may or may not be followed. He stated that his particular area of specialization was in gas and vapor sampling. It was emphasized that the emergency temporary standard (Federal Register of April 5, 1974) would be in effect a maximum of 6 months, or that another standard would be out no later than October 5. NIOSH has been and continues to work on the solid adsorption method of sample collection. The use of charcoal as the adsorbent has not been recommended at present, but probably is the preferred material of those evaluated to date.

The acceptable method of taking grab samples is presently to use a 250 cc. glass collecting tube with Teflon stopcocks, sampling for 15 minutes.

Monsanto commented they are presently using the glass tube method but feel the sample time should be reduced from 15 minutes to about 2 minutes due to the changes in VCl concentration in the air over the longer time period.

Carbonized saran spheres were one of the recommended adsorption materials, but were not considered practical from an availability and cost standpoint. NIOSH is presently using coconut charcoal for adsorption studies. The break-through point for 100 mg. of the charcoal is 3000 cc of air sample (0.135 gm. VCl).

A migration effect of the adsorbed VCl within the charcoal tube was discussed. Refrigerated storage prevents the migration. The problem of calibration was discussed, with emphasis on the need to check the desorption of the VCl from the charcoal being used. A desorption coefficient must be included in the calculation method. In desorbing the VCl from the charcoal into carbon disulfide, or THF, better efficiency can be obtained by cooling the CS_2. The efficiency can be increased from a 70 - 75% level to 90 - 95% by cooling to dry ice temperature.

NIOSH had received a request to check another method of sampling, but still lean toward the charcoal tube method due to its being a usable method for OSHA inspectors. The inspectors could perform the tube sampling and send the sealed samples to Salt Lake City for analysis.

Others commented on using a variety of techniques for sampling. including charcoal tubes, air bags, NDIR's and Century total hydrocarbon analyzers.

Summary of MCA Meeting in Philadelphia

Walston reported that most of the monitoring discussion emphasized personnel rather than area monitoring. It was questioned as to how personnel monitoring accomplished the intent of the existing standard in regard to preventing employees from entering, or remaining in, concentrations over 50 ppm VCl.

McCammon commented that he, and others at NIOSH, felt that area monitoring was the more important but that OSHA doesn't always follow all of their recommendations.

Monsanto commented that area monitoring was much more feasible in an enclosed area such as PVC plants, but was a real problem in outside areas where fairly high wind currents existed, such as VCl monomer plants.

McCammon commented that EPA has already been investigating the VCl concentration in ambient air and would undoubtedly increase that activity.

Walston reported on MCA testing being conducted at Biotest labs in Chicago. Mice, rats and hamsters are being tested for exposure to various concentrations of VCl. Mice exposed to 50 ppm VCl for 7 hours a day, 5 days a week for 3 months had developed tumors. No tumors had been noted at that time in rats or hamsters exposed in an identical manner.

Discussion Topics

Since personnel from Dow were unable to attend this meeting, they permitted a reading of their procedure for air sampling, recovery of the VCl, and method of analysis.

Anticipated Regulation Requirements

Holland read an Advance Copy of an OSHA paper entitled "Sampling for VCM", which according to an unofficial OSHA source, may be very similar to the procedure ultimately incorporated in the regulation. The OSHA procedure is as follows:

"Personnel breathing zone samples should be collected from employees. When collected by the CSHO, a Model SP-I Sipin Personnel Sampling Pump shall be used to collect the sample on NIOSH approved charcoal tubes. The flow rate of the pump shall be no more than 50 millliliters per minute, and the total sample size approximately one liter and/or a sampling time of 20 minutes where a concentration of approximately 50 parts per million is suspected. Where concentrations greater than 50 ppm are likely (for example, 100 parts); the sampling time should be 10 minutes.

All measurements should represent the time when exposures are more likely to be the greatest, rather than random exposures throughout the work day. No more than eight tubes per worker, per day, may be submitted for analysis. One or two tubes will suffice, if they represent maximum exposures. A sufficient number of area samples should also be collected to pinpoint high exposure areas for implementation of control measures."

Holland interpreted the phrase "No more than eight tubes per worker, per day, may be submitted ..." as ultimately requiring submission of samples to OSHA's lab in Salt Lake. He also questioned whether the statement "A sufficient number of area samples shall also be collected to pinpoint high exposure areas." did or did not imply a requirement for area monitoring. He also pointed out that the Sipin pump was probably mentioned simply because it is the pump OSHA is presently using, and was not intended to imply that the pump was the only acceptable pump for this procedure.

McCammon commented that the OSHA paper sounded more like a recommended sampling procedure for OSHA inspectors, rather than something which would be included in the regulation. He also pointed out that although NIOSH has not recommended charcoal tube sampling, it is possible that OSHA may be considering this technique.

McCammon noted that it is unlikely that the regulation will specify a particular pump. The Sipin pump was developed under a contract from NIOSH, and just happens to be the one OSHA is currently using. Three other companies also have pumps which meet NIOSH specifications for NIOSH/OSHA use: MSA; SKC, Inc. of Pittsburg;

the performance of the unit in the range of 0-100 ppm was questionable. It is felt that the instrument would be adequate for detecting "hot spots".

As a result of these tests, BFG has generally gone to the Century as its portable survey instrument. It is ideal for monitoring levels around valves, flanges, packing, etc., since its response is almost instantaneous.

On the subject of permanent area monitoring, BFG considered three equipment types: infra-red, gas chromatograph, and total hydrocarbon analyzer.

In a "poly" building where vinyl chloride is being used, about 95% of the vapors will be vinyl chloride. Therefore, for ease of maintenance, the total hydrocarbon analyzer was selected. A system was installed last August, and the read-out results have been somewhat surprising. It has become apparent that it is going to take a special type of sampling system to get usable results.

The total hydrocarbon analyzer has a sensitivity of 1 ppm, full scale. Total hydrocarbon was selected over the gas chromatograph due to the feeling at that time that plant personnel lacked the proficiency required for maintenance of the gas chromatograph. The greater cost of the gas chromatograph was also a consideration.

The Wilks Miran II infra-red analyzer was tried, and it was found to be less stable than had been expected. In fact, at the BFG Louisville plant, where mixed monomers are present, the vinyl chloride results were almost worthless. Vinyl chloride discrimination is not good in applications where various other components are present.

When the total hydrocarbon analyzer was first put into operation analyzing a single stream, readings were frequently in the area of 1000 ppm. The average person cannot smell vinyl chloride at concentrations of less than 4000 ppm.

Maintenance steps were initiated immediately to correct the leaks, and as a result, present readings rarely exceed 50 ppm. The current time weighted average is about 15-20 ppm.

It should be noted that these readings were taken in a PVC "poly" plant where mixed vapors are not present. The detector used was a hydrogen flame, and the "background" was suppressed so that the readings are based on the best available clean air vs. that in the "poly" building.

When the total hydrocarbon analyzer was first put into use in August, a 200-foot 1/4-inch stainless steel sample line was used. At successive ranges of up to

1000 ppm, initial analyses (at a sample rate of 1200 cc/minute) showed instances of vinyl chloride concentrations which exceeded each respective full-scale range.

It was found that vinyl chloride stratifies, and moves through the air in waves. With a fixed probe, these waves are detected by the total hydrocarbon analyzer, thus producing occasional full scale excursions. Further experiments showed that installation of about a 1000 cc surge tank just before the instrument provides sufficient mixing of good and bad air to produce a reasonably good record.

It appears that stratification of vinyl chloride eliminates grab sampling as a workable monitoring technique.

Soon after the initial total hydrocarbon analyses, BFG installed a six-stream sampling system, using MSA end-of-line filters and two 40-micron sintered steel filters. Good filtering is essential in order to attain optimum results.

The present system includes a six-point stream switching recorder and the six-stream sampling system, with rotameters on each stream. Flow in the analyzer line is maintained by the analyzer pump, and flow in the other five lines is maintained by a separate pump in the sampling system. The sampling system pump is a Metal Bellows, which pumps about 30,000 cc/minute.

Sample lines are 3/8-inch polypropylene, which has been found to work just as well as stainless steel. Polyethylene will not work due to adsorption. Lines vary in length from 125 to 200 feet, and could probably be longer if necessary.

BFG has approximately 150 people working on the vinyl chloride problem. All technicians are working on a seven-day week and all scientists are working on a six-day week until the problem is solved.

BFG currently has 42 Centurys in use, 14 permanent systems in operation, and has just ordered 42 pumps. In addition, a computer system for readout is planned to handle the resultant load of data. As the system is now configured, a data readout is produced once every two minutes. Readout rates of less than one minute are impractical due to the fact that the system requires 30-40 seconds to stabilize on each point.

The system includes an automatic alarm feature which is activated if the vinyl chloride level exceeds 50 ppm. When an alarm occurs, a man is sent to the respective area with a Century to pinpoint the leak.

At a recent BFG meeting, it was unofficially announced that the maximum vinyl

chloride level in BFG facilities will be 25 ppm, and a time weighted average not to exceed 10 ppm. These are BFG inter-company requirements, and are not necessarily related to OSHA requirements. At present, it is doubtful that any "poly" plant in the country can meet these requirements.

The reason BFG is reducing peak levels from 50 ppm to 25 ppm is because of the tumors found in mice exposed to vinyl chloride for seven hours per day at 50 ppm.

Salzer commented that the concept of personnel monitoring may not be as important as some people think. The weakness of the technique is that a worker could be in a 400 ppm area for one hour, and if he then moves into an area where there is no vinyl chloride, his time weighted average for eight hours will be 50 ppm. Therefore, in order to comply with the requirement that "concentrations above 50 ppm cannot be permitted to occur", some form of permanent monitoring system appears to be necessary.

BFG has made smoke tests in their plants to determine air flow patterns. These tests reveal some surprisingly complex patterns. The pattern of a smoke bomb held at waist level is often entirely different from that of a bomb held at shoulder level.

Again on the subject of personnel monitoring, it appears that the portable Century unit may be usable for this purpose. The unit weighs 10 pounds, and includes a small recorder which can provide a continuous record of exposure over a 10 minute period. This would provide a much more detailed indication of the 10-minute exposure than would a single accumulated sample.

BFG has not abandoned their investigation of charcoal sampling, however they have hopes that the Century approach will prove to be feasible.

It should be mentioned that the Century unit now has a new feature, which consists of a small Porapak chromatographic column which will separate vinyl from other components.

Vinyl Chloride in Dried Resin

Another problem which must be considered is that of unreacted vinyl chloride which is retained in granular resin. BFG is now considering ways to reduce current levels of 10, 50, and 100 ppm down to 1-3 ppm. The implications of retained vinyl chloride are that if a company is extruding water pipe, and if that pipe is being used for drinking water, it is conceivable that the claim may be made that small amounts of

vinyl are being ingested. It is unlikely that this type claim will occur, but it is possible.

Tenneco commented that their research to date indicates that removal of vinyl from resins does not appear to be an impossible task. Their findings thus far are only tentative, but do show promise.

Total Hydrocarbon Analyzer vs. Gas Chromatograph

Initial BFG considerations in selecting the total hydrocarbon analyzer were:

1. Lack of suitably skilled maintenance personnel in their "poly" plants for optimum maintenance of gas chromatographs; and
2. Lower cost of total hydrocarbon analyzer.

If the acceptable level of vinyl is lowered to "very few parts", no choice really exists but to go to the gas chromatograph. Especially in view of the fact that the total hydrocarbon analyzer measures vinyl chloride, plus other components which may be present.

Cost of present BFG sample system is about $3000., and cost of total hydrocarbon analyzer is about $2000. Neither of these is explosion proof.

It should be pointed out that the analyzer cell is not standard, but is specially designed to withstand the corrosive effects of vinyl. In either a total hydrocarbon analyzer or a gas chromatograph, the FID cell should employ a monel or Teflon-coated aluminum bonnet. The corrosive effects of vinyl are more acute in the total hydrocarbon analyzer due to the greater sample volumes used.

In the system BFG put into operation in August, the FID cell has been checked about once every 10 days, and has not failed to date.

BFG is using a computer to compile the data from its six-point system. The computer provides a time weighted eight hour average for each of the six locations being measured. It also provides an hourly average, and the high readings (past 50 ppm) for each probe.

In a plant utilizing four or five analyzers, the volume of data leaves little option but to include a computer for data compilation. The utility of a computer installation is further enhanced by the fact that the regulation may ultimately require data retention for up to five years. With a computer in the loop, a bulk storage medium such as magnetic tape can be readily utilized.

Blood Tests

At BFG, every man working in areas of possible vinyl chloride has had a blood test. It is a test which is intended to detect liver damage. Medical opinions vary as to its effectiveness. So far, there have been no negative comments from workers about the requirement that they take the test.

The only significant problem BFG has had with respect to the blood test is that 50% of prospective new employees fail the test. Other attendees reported similar failure rates in their experience.

Controls imposed on BFG employees before testing included "no alcoholic beverages for 48 hours prior to test", and "no breakfast that morning".

McCammon commented that from a toxicologists viewpoint, it is unlikely that a single-point biochemical test is a reliable means of determining the medical status of an individual. Due to the many variables which affect the test results, it seems that a more realistic approach must necessarily include the compilation of a personal medical history on each individual, including such information as "amount of alcohol normally consumed". This information, along with successive test results, would produce a more meaningful collection of data on which to base a conclusion as to that employee's vinyl exposure and its effects.

Some companies have experienced employee reluctance to taking the test, and other companies have received full cooperation. It appears that the implementation of these tests is best received when preceeded by a good employee information effort. This effort should include pointing out that the test(s) can also detect problems other than vinyl exposure, and that if such problems are detected the employee will be so advised.

The recommended blood test actually includes tests of 12 separate blood characteristics. Urinalysis, pulmonary test, and chest X-rays have also been suggested.

It should be pointed out that the blood test simply detects a possible liver malfunction, which may or may not be the result of vinyl. There are, of course, many other possible causes.

Differences Between Problems of Polymer Plants and Momomer Plants

Shell is conducting eight hour average bag sampling in its monomer plant. Their checks have shown that EDC is more of a problem than vinyl chloride. Vinyl is present only in very small amounts, and increases only when a vessel is opened.

GLC analyses have shown a complete spectrum of componenents. Primary emphasis has been on identifying "safe" and "hazardous" areas, and in re-evaluating procedures accordingly.

At BFG's Calvert monomer plant, a gas chromatograph is being used to sample 10-12 points. Cycle time (pen point) is about 15-16 minutes, which loses a good deal of valuable information. This is a problem which must ultimately be resolved, but for the present, major effort is being focused on the "poly" plant problems.

Conoco is monitoring their Lake Charles and Oklahoma City plants with the Century, air bags, and carbon tubes. At the Aberdeen plant they are using a portable trailer which is equipped with a four-stream total hydrocarbon analyzer. This system is used to monitor levels around the plant on a routine basis. They are monitoring four points in 10 minutes, on a semi-continuous basis. The objective of this program is to determine the operating parameters for a permanent monitoring system. So far, some of their checks have shown the air inside the buildings to be better than the air outside.

Safety Equipment and Procedures

BFG issues coveralls and a charcoal mask to each worker in an area of potentially high vinyl. The mask is worn around the neck continuously for use if an alarm is sounded. When the eight-hour shift is finished, each man from the "poly" area is required to shower. Employees have voiced some complaints about having to wear the mask around the neck continuously.

Tests run by BFG on charcoal masks showed that the charcoal element is exhausted after about three liters of vinyl chloride at about 50 ppm. At this rate, maximum effective life of one element is limited to about one hour. Therefore, BFG procedures call for a change of element after each 45 minutes of use when operating in areas of 50 ppm or greater.

GE commented that the back-pack air mask system weighs about 35 pounds, and each bottle lasts about 30 minutes. In addition, there is a great deal of employee resistance to any more than emergency use of the device. The unit is both heavy and uncomfortable. As a result, it appears that good engineering controls, rather than personal protective devices, are the only way to keep people working on the job.

Relief Devices - What to do with vented materials.

In Catalytic's last continuous PVC project, the PVC reactor had a conventional

relief system consisting of a rupture disc and a relief valve. Vented material was disseminated into the atmosphere at about the 5th floor level. At that time the stringent OSHA requirements were not in effect.

In view of current knowledge, it is apparent that some form of recovery system is going to be necessary.

Conoco commented that they have current plans for installation of flare and recovery systems at their Lake Charles plant.

GE commented that in their plant, all relief systems and bleed systems are routed to a vent gas burner on the roof. This is a water-submerged burner, which presumably solves the problem of combustion of organic materials, but leaves the problem of disposing of the resultant polluted water.

Synoposis of Conclusions from Preceeding Discussions

1. Area monitoring is generally better than personnel monitoring.
2. A need exists for portable personnel monitoring equipment.
3. The regulation limit on vinyl will probably be 50 ppm, and may possibly be as low as 10-25 ppm.
4. October 5, 1974 is anticipated date for the regulation to go into effect.
5. A problem exists in correlating data from personnel monitoring with data from area monitoring systems.
6. Two portable instruments were mentioned, the Century and the Sipin.
7. Infra-red was mentioned for permanent monitoring applications. Comments were made as to its questionable stability.
8. Portable gas chromatograph was mentioned with respect to its use for personnel monitoring.
9. Total hydrocarbon analyzers were discussed for levels above 50 ppm, gas chromatographs were discussed for levels below 50 ppm. Higher cost was mentioned as a drawback to the GC.
10. Recommended sampling systems mentioned were four-streams, six-streams, and 12-streams. Ethyl has 12-stream Miran II (I/R) on order. Several attendees commented their experience with this unit was less than satisfactory. Ethyl reported good experience with these units to date.

It appears that the number of samples collected should be equally divisible into 60 minutes, so that averaging becomes automatic when data is logged. For example, 10 streams produces a six-minute time averaging of the sample; 12 streams is a

five-minute sample; 15 streams is a four-minute sample, etc. Thus, the sample system configuration might best be a trade-off between averaging and speed of analysis.

Honeywell commented that time involved with using the gas chromatograph is 30 seconds for vinyl chloride and 75-80 seconds for vinyl chloride and EDC.

11. Sample system costs can be reduced significantly by using polypropylene tubing rather than stainless steel.

12. There is a need for some means of bulk data storage. Suggestions included computers, magnetic tape and microfilm. Paper tape was also mentioned as a possible medium for intermediate storage, followed by voice-line data transmission to a central computer.

13. Surge tanks appear necessary to avoid problems of stratification. The question was raised as to whether OSHA will accept the results of sample systems which incorporate this type of "smoothing" feature.

14. Most employees express no reluctance to taking the blood tests, especially if the benefits are pointed out in a good employee information program.

15. Blood tests are non-conclusive, with respect to vinyl exposure, due primarily to the fact that the results merely indicate the status of liver function. Pre-test controls of employee activities (eating, drinking, etc.) are necessary in order to achieve meaningful results.

16. Potentially dangerous components detected to date include vinyl chloride, EDC, and vinylidene chloride. OSHA's list includes about 400 components. At Dow-Freeport plant, Dow is analyzing for 10-12 different chlorinate hydrocarbons. Dow posts daily results for employee information purposes. This is made possible by their use of a computer-based area monitoring system.

17. Equipment mentioned included a trailer-mounted monitoring system, alarm systems, protective clothing, charcoal air masks, back-pack air systems, etc.

18. The "after-the-fact" nature of the personnel monitoring concept appears to negate its use in preventing employees from entering hazardous areas.

19. Honeywell presented chromatographic runs indicating:

    a. If specificity of vinyl chloride is desired, and a 90-second analysis cycle is acceptable, the only valve required is a sample valve, assuming that no components "heavier" than 1,2-Dichloroethane (EDC) - b.p. of 83.5°C - are present in the air sample.

b. If both specificity and rapid analysis cycles are desired, the addition of a backflush-to-vent valve allows analysis every 40 seconds, and is a safeguard against components "heavier" than EDC.

Based on subsequent tests, Honeywell stated that these analysis times can be reduced to 75-80 seconds and 30 seconds, respectively. With the 90-second cycle, 960 analyses can be run in a 24-hour day. With the 40-second cycle, 2160 analyses can be run in a 24-hour day. It was pointed out that the analysis can be programmed to run at a less frequent rate, and if an excursion is detected, the frequency can be automatically increased to provide a better profile of critical levels.

The objective of the chromatographic runs was to demonstrate the feasibility of making a very precise measurement within the limitations of a minute, if this capability becomes a requirement for area monitoring.

Anticipated Future Action and Meeting Summary

Honeywell will act as a distribution point for dissemination of the results of this meeting, and of any subsequent information provided by attendees. Maximum follow-up information from each company will be necessary in order to make this effort worthwhile. Any information of this type should be forwarded to Honeywell by about May 24. Honeywell will plan to distribute any resultant input to all attendees on or about June 1. In the interim, any information of an urgent nature will be sent out in bulletin form. The objective of this effort is information-sharing between all concerned parties.

It was agreed that additional meetings of this type be held on a regular basis until the immediate urgency of the vinyl problem is resolved. McCammon (NIOSH) suggested that NIOSH, OSHA, and EPA be represented at future meetings.

Manno (Honeywell) suggested that the meetings might be most effective if kept at a workable size, rather than issuing a blanket invitation to all agencies concerned.

Manno also suggested that it might be prudent to advise OSHA at this time, of the deficiences of personnel monitoring which were noted at this meeting. It appears that the only effective long-range solution to the problem lies in utilizing high quality, well calibrated permanent area monitoring systems, with personnel monitoring used on a supplemental basis for special cases.

Personnel mentioned as being involved with various aspects of the vinyl problem were:

Dr. Don Lassiter; Washington, D.C.; Phone 202-961-3878; Department of Labor representative working with OSHA in writing standards and in getting them in print.

Thomas Curry; Houston, Texas; Director of OSHA-Houston office.

Bruce Simpson; Houston, Texas; Assigned by Curry to handle OSHA liaison with Houston area companies.

Charles McCammon, Mr. Crable, Dr. Alex Teass, Dr. George Carson, Dr. Harris; NIOSH-Cincinatti, Ohio:

Mr. Crable is Administrator of the Physical and Chemical Analysis Branch in the Division of Laboratories and Criteria Development. His group is responsible for development of analytical methodology. Dr. Teass, who works for Mr. Crable, is more directly involved with the day-to-day operations of the group.

Mr. McCammon is involved with generation of standards pertaining to sampling. He is responsible to Dr. Carson, whose particular area of specialization is "particulate sampling". Dr. Carson is not currently involved directly with the vinyl problem.

Dr. Harris is Director of the Division of Laboratories and Criteria Development. The division makes recommendations to OSHA, which OSHA may or may not choose to follow. All final regulation requirements are determined exclusively by OSHA.

Bob Stevens, Andy O'Keefe; Contacts at the Environmental Protection Agency;

Research Triangle, N. C.

Table of Sorbents for Contaminants Listed in ACGIH 1970 Threshold Limit Values

American Industrial Hygiene Association and the American Conference of Governmental Industrial Hygienists Joint Committee on Respirators

Introductory Statement

THE AIHA-ACGIH RESPIRATOR COMMITTEE has prepared this table of sorbents for airborne contaminants in response to questions from users of respirators. There is an apparent mystery about what is in a gas mask or chemical cartridge respirator that magically purifies the inspired air. Therefore, the primary purpose of this table is to serve as an educational aid to respirator users by eliminating some of the mystery about respiratory protection. The table may also be used in the laboratory to aid in selecting sorbents for gases and vapors.

This printing updates the first list of sorbents that appears on pages 56 to 58 in *Respiratory Protective Devices Manual*, published by AIHA-ACGIH in 1963. The manual lists gases and vapors for which ACGIH assigned TLV values in 1961. This new table includes all contaminants in the 1970 TLV list. As emphasized in the Manual, the actual capacity of a sorbent for any specific contaminant is dependent upon many factors. Any list of sorbents must therefore be interpreted only as a guide. Users should refer to respirator manufacturers for information on specific respirators for specific contaminants.

Sorbent Code

1. Activated carbon
2. Soda lime
3. Combination of activated carbon and soda lime
4. Silica gel
5. Hopcalite (with drier)
6. Impregnated carbon; example, carbon treated with metalic salt to absorb ammonia
7. Special sorbent (manufacturers proprietary mix)
8. Filter, for highly toxic dusts
9. Filter, for toxic dusts

Notes:

(1) Where two or more sorbent code numbers are listed after a substance, the sorbents are in decreasing order of preference. Where a plus (+) sign is used, both are required.

(2) Very strong oxidizing substances in low concentrations may be sorbed by activated or impregnated carbon; however, carbon should not be used because of a possible explosion hazard with these combinations. For respiratory protection against very strong oxidizers, a self-contained breathing apparatus should be used.

List of Contaminants with Sorbent Code

Substance	Sorbent
Abate	9
Acetaldehyde	1
Acetic acid	1,2
Acetic anhydride	3,2
Acetone	1
Acetonitrile	3,1
Acetylene dichloride, see 1,2-Dicloroethylene	1
Acetylene tetrabromide	1
Acrolein	1
Acrylamide – Skin	1,6
Acrylonitrile – Skin	3,1
Aldrin – Skin	8+1
Allyl alcohol – Skin	1
Allyl chloride	1,3
Allyl glycidyl ether (AGE)	1
Allyl propyl disulfide	3

Substance	Sorbent
2-Aminoethanol, see Ethanolamine	
2-Aminopyridine	1,7
Ammonia	7,6,4
Ammonium sulfamate (Ammate)	9
n-Amyl acetate	1
sec-Amyl acetate	1
Aniline – Skin	1,7
Anisidine (*o,p*-isomers) – Skin	9+1
Antimony & compounds (as Sb)	9
ANTU (Alpha naphthyl thiourea)	9+1
Arsenic & compounds (as As)	6+9
Arsine	6,7
Azinphos-methyl – Skin	9+1
Barium (soluble compounds)	9+6
Benzene (benzol) – Skin	1
Benzidine – Skin	8+1
p-Benzoquinone, see Quinone	
Benzoyl peroxide	9+1
Benzyl chloride	1,3
Beryllium	8
Biphenyl, see Diphenyl	
Boron oxide	9
Boron tribromide	5+3
Boron Trifluoride	5+3
Bromine	3
Bromine pentafluoride	2,7
Bromoform – Skin	1
Butadiene (1,3-butadiene)	1
Butanethiol, see Butyl mercaptan	
2-Butanone	1
2-Butoxy ethanol (Butyl cellosolve) – Skin	1
Butyl acetate (*n*-Butyl acetate)	1
n-Butyl acetate	1
sec-Butyl acetate	1
tert-Butyl acetate	1
Butyl alcohol	1
sec-Butyl alcohol	1
tert-Butyl alcohol	1
Butylamine – Skin	7,6,4
tert-Butyl chromate (as CrO_3) – Skin	8
n-Butyl glycidyl ether (BGE)	1
Butyl mercaptan	1
p-tert-Butyltoluene	1
Cadmium (metal dust and soluble salts)	9,6
Cadmium oxide fume	8
Calcium arsenate	9
Calcium oxide	9
Camphor	9+1
Carbaryl (Sevin)	9+1
Carbon black	9
Carbon dioxide	2
Carbon disulfide – Skin	1
Carbon monoxide	5
Carbon tetrachloride – Skin	1
Chlordane – Skin	9+1
Chlorinated camphene – Skin	1
Chlorinated diphenyl oxide	1
Chlorine	3,6
Chlorine dioxide	2,7
Chlorine trifluoride	2,7
Chloroacetaldehyde	1
Chloracetophenone (phenacylchloride)	1
Chlorobenzene (monochlorobenzene)	1
O-Chlorobenzylidene malononitrile (OCBM)	3,1
Chlorobromomethane	1
2-Chloro-1,3-butadiene, see Chloroprene	
Chlorodiphenyl (42% chlorine) – Skin	1,3
Chlorodiphenyl (54% chlorine) – Skin	1,3
1-Chloro-2,3-epoxypropane, see Epichlorohydrin	
2-Chloroethanol, see Ethylene chlorohydrin	
Chloroethylene, see Vinyl chloride	
Chloroform (trichloromethane)	1
1-Chloro-1-nitropropane	1
Chloropicrin	1
Chloroprene (2-chloro-1, 3-butadiene) – Skin	1
Chromic acid and chromates (as CrO_3)	8+2
Chromium, soluble chromic or chromous salts as Cr	9
Metal & insol. salts	9
Coal tar pitch volatiles (benzene soluble fraction) anthracene, BaP, phenanthrene, acridine, chrysene, pyridine)	9+1
Cobalt, metal fume & dust	8
Copper fume	8
Dusts and mists	9
Cotton dust (raw)	9
Crag herbicide	9+1
Cresol (all isomers) – Skin	1
Crotonaldehyde	1
Cumene – Skin	1
Cyanide (as CN) – Skin	9+2
Cyanogen	3
Cyclohexane	1
Cyclohexanol	1
Cyclohexanone	1

Substance	Sorbent
Cyclohexene	1
Cyclopentadiene	1
2,4-D	9+1
DDT – Skin	9+1
DDVP – Skin	9+1
Decarborane – Skin	9+7
Demeton – Skin	8+1
Diacetone alcohol (4-methyl-2-pentanone)	1
1,2-Diaminoethane (Diazomethane), see Ethylenediamine	
Diborane	7
1,2-Dibromoethane (ethylene dibromide) – Skin	1
Dibutyl phosphate	8+1
Dibutylphthalate	1
Dichloroacetylene	3,7
o-Dichlorobenzene	1
p-Dichlorobenzene	1
Dichlorodifluoromethane	1
1,3-Dichloro-5-dimethyl hydantoin	3
1,1-Dichloroethane	1
1,2-Dichloroethane	1
1-2-Dichloroethylene	1
Dichloroethyl ether – Skin	1
Dichloromethane, see Methylene chloride	
Dichloromonofluoromethane	1
1,1-Dichloro-1-nitroethane	3
1,2-Dichloropropane, see Propylenedichloride	
Dichlorotetrafluoroethane	1
Dieldrin – Skin	9+1
Diethylamine	7,6,4
Diethylamino ethanol – Skin	7
Diethylene triamine – Skin	7,6,4
Diethylether, see Ethyl ether	
Difluorodibromomethane	1
Diglycidyl ether (DGE)	1
Dihydroxybenzene, see Hydroquinone	
Diisobutyl ketone	1
Diisopropylamine – Skin	7,6,4
Diphenyl amine	9+7
Dimethoxymethane, see Methylal	
Dimethyl acetamide – Skin	1
Dimethylamine	7,6,4
Dimethylaminobenzene, see Xylidene	
Dimethylaniline (N-dimethylaniline) – Skin	7
Dimethylbenzene, see Xylene	1
Dimethyl-1,2-dibromo-2, 2-dichloroethyl phosphate, (Dibrom)	9+1
Dimethylformamide – Skin	1
2,6-Dimethylheptanone, see Diisobutyl ketone	
1,1-Dimethylhydrazine – Skin	7,6,4
Dimethylphthalate	1
Dimethylsulfate – Skin	1,3
Dinitrobenzene (all isomers) – Skin	9+3
Dinitro-*o*-cresol – Skin	9+3
Dinitrotoluene – Skin	9+3
Dioxane (diethylene dioxide) – Skin	1
Diphenyl	1
Diphenyl amine	9+1, 7
Diphenylmethane diisocyanate, see methylene bisphenyl isocyanate (MDI)	
Dipropylene glycol methylether – Skin	1
Di-*sec*-octyl phthalate (Di-2-ethylhexyiphthalate)	1+8,9
Endosulfan (Thiodan®)	8+1
Endrin – Skin	8+1
Epichlorohydrin – Skin	1
EPN – Skin	9+1
1,2-Expoxypropane, see Propylene-oxide	
2,3-Epoxy-1-propanol, see Glycidol	
Ethanethiol, see Ethylmercaptan	
Ethanolamine	7,6,4
2-Ethoxyethanol – Skin	1
2-Ethoxyethylacetate (Cellosolve acetate) – Skin	1
Ethyl acetate	1
Ethyl acrylate – Skin	1
Ethyl alcohol (Ethanol)	1
Ethylamine	7,6,4
Ethyl *sec*-amyl ketone (5-methyl-3-heptanone)	1
Ethyl benzene	1
Ethyl bromide	1
Ethyl butyl ketone (3-Heptanone)	1
Ethyl chloride	1
Ethyl ether	1
Ethyl formate	1
Ethyl mercaptan	1
Ethyl silicate	1
Ethylene chlorohydrin – Skin	1
Ethylenediamine	7,6,4
Ethylene dibromide, see 1,2-Dibromoethane	
Ethylene dichloride, see 1,2-Dichloroethane	
Ethylene glycol dinitrate and/or Nitroglycerin – Skin	1

Substance	Sorbent
Ethylene glycol monomethylether acetate, see Methyl cellosolve acetate	
Ethylene imine – Skin	7,6,4
Ethylene oxide	1
Ethylidine chloride, see 1,1-Dichloroethane	
N-Ethylmorpholine – Skin	1
Ferbam	9+3
Ferrovanadium dust	9
Fluoride (as F)	9+3
Fluorine	3,2
Fluorotrichloromethane	1
Formaldehyde	1
Formic acid	1
Furfural – Skin	1
Furfuryl alcohol	1
Gasoline	1
Glycidol (2,3-Epoxy-1-propanol)	1
Glycol monoethylether, see 2-Ethoxyethanol	
Guthion, see Azinphosmethyl	
Hafnium	9
Heptachlor – Skin	9
Heptane (*n*-heptane)	1
Hexachloroethane – Skin	1
Hexachloronapthalene – Skin	9+1
Hexane (*n*-hexane)	1
2-Hexanone	1
Hexone	1
sec-Hexyl acetate	1
Hydrazine – Skin	7,6,4
Hydrogen bromide	2,3+9
Hydrogen chloride	2,3+9
Hydrogen cyanide – Skin	2,7
Hydrogen fluoride	2,3,7
Hydrogen peroxide, 90%	2,7
Hydrogen selenide	6
Hydrogen sulfide	3,6
Hydroquinone	9+1
Indene	1
Indium and compounds, as In	8
Iodine	9+1
Iron oxide fume	9
Iron salts, soluble, as Fe	9
Isoamyl acetate	1
Isoamyl alcohol	1
Isobutyl acetate	1
Isobutyl alcohol	1
Isophorone	1
Isopropyl acetate	1
Isopropyl alcohol	1
Isopropylamine	7,6,4
Isopropylether	1
Isopropyl glycidyl ether (IGE)	1
Ketene	1
Lead	9
Lead arsenate	8
Lindane – Skin	9
Lithium hydride	8
L. P. G. (Liquified petroleum gas)	1
Magnesium oxide fume	9
Malathion – Skin	9+1
Maleic anhydride	9+3
Manganese	9
Mercury – Skin	6,7
Mercury (organic compounds) – Skin	8+6,7
Mesityl oxide	1
Methanethiol, see Methyl mercaptan	
Methoxychlor	9+1
2-Methoxyethanol, see Methyl cellosolve	
Methyl acetate	1
Methyl acetylene (propyne)	1
Methyl acetylene-propadiene mixture (MAPP)	1
Methyl acrylate – Skin	1
Methylal (dimethoxymethane)	1
Methyl alcohol (methanol)	1
Methylamine	7,6,4
Methyl amyl alcohol, see Methyl isobutyl carbinol	
Methyl isoamyl ketone	1
Methyl *n*-amyl ketone (2-Heptanone)	1
Methyl bromide – Skin	1
Methyl butyl ketone, see 2-Hexanone	
Methyl cellosolve – Skin	1
Methyl cellosolve acetate – Skin	1
Methyl chloride	1
Methyl chloroform	1
Methylcyclohexane	1
Methylcyclohexanol	1
o-Methylcyclohexanone – Skin	1
Methyl ethyl ketone (MEK), see 2-Butanone	
Methyl formate	1
Methyl iodide – Skin	1
Methyl isobutyl carbinol – Skin	1
Methyl isobutyl ketone, see Hexone	
Methyl isocyanate – Skin	1
Methyl mercaptan	1
Methyl methacrylate	1
Methyl propyl ketone, see 2-Pentanone	

Substance	Sorbent
Methyl silicate	1
Methyl styrene	1
Methylene bisphenyl isocyanate (MDI)	8+1
Methylene chloride (Dichloromethane)	1
Molybdenum (soluble compounds) (insoluble compounds)	9 9
Monomethyl aniline – Skin	1,7
Monomethyl hydrazine – Skin	7,6,4
Morpholine – Skin	1
Naphtha (coal tar)	1
Naphthalene	1
β-Naphthylamine	7,6,4
Nickel carbonyl	3+5
Nickel, metal and soluble compounds	9
Nicotine – Skin	1
Nitric acid	2,3
Nitric oxide	3
p-Nitroaniline – Skin	1
Nitrobenzene – Skin	1
p-Nitro-chlorobenzene – Skin	1
Nitroethane	1
Nitrogen dioxide	2,7
Nitrogen trifluoride	2,7
Nitroglycerin – Skin	1
Nitromethane	1
1-Nitropropane	1
2-Nitropropane	1
N-Nitrosodimethylamine (Dimethyl-nitrosoamine) – Skin	7,6,4
Nitrotoluene – Skin	1
Nitrotrichloromethane, see Chloropicrin	
Octachloronaphthalene – Skin	1
Octane	1
Oil mist (mineral)	9+1
Osmium tetroxide	8
Oxalic acid	9+3
Oxygen difluoride	3,6
Ozone	7
Paraquat – Skin	9+7
Parathion – Skin	8+1
Pentaborane	7,1
Pentachloronaphthalene – Skin	9+1
Pentachlorophenol – Skin	9+1
Pentane	1
2-Pentanone	1
Perchloroethylene	1
Perchloromethyl mercaptan	1
Perchloryl fluoride	2,7
Petroleum distillates (Naphtha)	1
Phenol – Skin	1
p-Phenylenediamine – Skin	7
Phenylether (vapor)	1
Phenylether-biphenyl mixture (vapor)	1
Phenylethylene, see Styrene	
Phenyl glycidyl ether (PGE)	1
Phenylhydrazine – Skin	7,6,4
Phosdrin (Mevinphos) – Skin	8+1
Phosgene (Carbonyl chloride)	3,6
Phosphine	6
Phosphoric acid	9+1
Phosphorus (yellow)	8+2
Phosphorus pentachloride	9+3
Phosphorus pentasufide	9+3
Phosphorus trichloride	9+3
Phthalic anhydride	3
Picric acid – Skin	8+3
Pival (2-Pivalyl-1,3-indandione)	8
Platinum (soluble salts)	8
Polytetrafluoroethylene decomposition products	8+3
Propane	1
β-Propiolactone	1
Propargyl alcohol – Skin	1
n-Propyl acetate	1
Propyl alcohol	1
n-Propyl nitrate	1,7
Propylene dichloride	1
Propylene imine – Skin	1
Propylene oxide	1
Propyne, see Methylacetylene	
Pyrethrum	9
Pyridine	1
Quinone	1
RDX – Skin	8
Rhodium, metal fume and dusts, Soluble salts	8 8
Ronnel	9+1
Rotenone (commercial)	9+1
Selenium compounds (as Se)	8
Selenium hexafluoride	3
Silver, metal and soluble compounds	8
Sodium fluroacetate (1080) – Skin	8
Sodium hydroxide	9
Stibine	6
Stoddard solvent	1
Strychnine	8
Styrene monomer (Phenylethylene)	1
Sulfur dioxide	2

Substance	Sorbent
Sulfur hexafluoride	3
Sulfuric acid	2
Sulfur monochloride	9+3
Sulfur pentafluoride	3
Sulfuryl fluoride	7,3
Systox, see Demeton	
2,4,5-T	9
Tantalum	9
TEDP – Skin	8+1
Teflon decomposition products	8+3
Tellurium	8
Tellurium hexafluoride	3
TEPP – Skin	8
Terphenyls	1
1,1,1,2-Tetrachloro-2,2-difluoroethane	1
1,1,2,2-Tetrachloro-1,2-difluoroethane	1
1,1,2,2-Tetrachloroethane – Skin	1
Tetrachloroethylene, see Perchloroethylene	
Tetrachloromethane, see Carbon tetrachloride	
Tetrachloronaphthalene – Skin	9+1
Tetraethyl lead (as Pb) – Skin	8+1
Tetrahydrofuran	1
Tetramethyl lead (TML) (as Pb) – Skin	8+1
Tetramethyl succinonitrile – Skin	1
Tetranitromethane	3
Tetryl (2,4,6-Trinitrophenyl-methylnitramine) – Skin	9+3
Thallium (soluble compounds) – Skin	8
Thiram	9+1
Tin (inorganic compounds, except SnH_4 and SnO_2)	9
Tin (organic cmpds)	8+1
Titanium dioxide	9
Toluene (toluol)	1
Toluene-2,4-diisocyanate (TDI)	9+1
o-Toluidine – Skin	1
Toxaphene, see Chlorinated camphene	
Tributyl phosphate	9+3
1,1,1-Trichloroethane, see Methyl chloroform	
1,1,2-Trichloroethane – Skin	1
Trichloroethylene	1
Trichloromethane, see Chloroform	
Trichloronaphthalene – Skin	9+1
1,2,3-Trichloropropane	1
1,1,2-Trichloro-1,2,2-trifluoroethane	1
Triethylamine	7,6,4
Trifluoromonobromomethane	1
Trimethyl benzene	1
2,4,6-Trinitrophenol, see picric acid	
2,4,6-Trinitrophenylmethylnitramine, see Tetryl	
Trinitrotoluene – Skin	9+1
Triorthocresyl phosphate	8+3
Triphenyl phosphate	9+3
Tungsten & compounds, as W Soluble	9
Insoluble	9
Turpentine	1
Uranium (natural) soluble & insoluble compounds as U	8
Vanadium (V_2O_5 dust)	8
(V_2O_5 fume)	8
Vinyl benzene, see Styrene	
Vinyl chloride	1
Vinylcyanide, see Acrylonitrile	
Vinyl toluene	1
Warfarin	8
Xylene (Xylol)	1
Xylidine – Skin	1
Yttrium	9
Zinc chloride fume	9
Zinc oxide fume	9
Zirconium compounds (as Zr)	9

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A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere

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Industrial hygienists have generally sampled for industrial solvent vapors either by taking grab samples or by measuring the concentrations with bulky equipment such as the Davis halide meter. A convenient method is described for the determination of solvent vapors in atmospheric samples. A glass tube packed with activated charcoal is used to take an integrated sample. A standard volume of 10 liters is sampled, and the tube is capped and returned to the laboratory for analysis. The activated charcoal is desorbed with carbon disulfide, and an aliquot is introduced into a gas chromatograph equipped with a flame ionization detector. Optimum operating conditions have been established on the gas chromatograph for the separation and analysis of selected solvent vapors of occupational health interest. Data are presented on both the adsorption and the desorption efficiencies of selected solvent vapors determined by this method. The solvents were benzene, n-butyl acetate, 2-butanone, carbon tetrachloride, chloroform, p-dioxane, ethanol, ethyl ether, iso-octane, perchloroethylene, pyridine, toluene, trichloroethylene, and xylene.

Introduction

ANALYSIS OF SOLVENT VAPORS in the industrial atmosphere for the determination of worker exposure levels has been a difficult problem for industrial hygiene chemists.[1] In evaluating occupational hazards,[2,3] industrial hygienists have generally sampled for solvent vapors by taking grab samples or by measuring the concentrations with bulky equipment such as the Davis halide meter.

The collection and concentration of atmospheric samples for analysis have been the most troublesome aspects in the assessment of solvent vapor hazards. Several specialized collection-concentration techniques have been reported. The usual methods involve absorption in solvents[4-6] or adsorption on coated or noncoated solid adsorbents,[7-18] with desorption in the laboratory by heat[7,19] or a suitable solvent,[7,14] and subsequent analyses of the resulting samples by gas chromatographic procedures.[4,12-14] As predicted by Ruehing[9] in 1958, the gas chromatograph has proven to be a valuable analytical instrument for making qualitative and quantitative solvent vapor measurements.

The method of Coleman and Guy,[12] which indicated that adsorption of organic vapors could be accomplished by using activated charcoal with desorption by carbon disulfide, holds great promise for application in collecting and describing organic solvent vapors. Liquid desorption is advantageous, since multiple analyses of the same sample are possible. The collection efficiency of activated charcoal is not affected by variations in relative humidity, since water is easily displaced by organic vapors.[8,18] Variations in the mesh sizes and types of charcoal (assuming adequate charcoal section length) apparently exhibit no significant difference in the collection and desorption efficiencies.[12,13] A sampling system

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having a pump capable of drawing a measurable amount of air through a charcoal tube is necessary. The charcoal tubes are easy to make, seal, handle, transport, and store. Optimum operating parameters on the gas chromatograph have normally been established for each compound to be determined.[4,12-14]

Experimentation conducted in this laboratory during the past several years indicates that a solvent vapor is rarely found by itself in the industrial atmosphere. Therefore, an analysis is desired that requires a minimum of time and effort to simultaneously separate and quantitatively measure all the compounds in a solvent vapor mixture. Optimum operating conditions on the gas chromatograph for the separation and analysis of fourteen selected solvent vapors of occupational health interest are presented. Data are given on both the adsorption and desorption efficiencies of these compounds, singly and in matrix, as determined by the sampling procedure of Otterson and Guy.[12] For purposes of this paper, the word matrix will be used to include the total solution environment.

Experimental Apparatus and Reagents

Perkin-Elmer Model 900 gas chromatograph equipped with dual flame ionization detectors.
Datex DIR-1 digital integrator (not required).
Honeywell Electronik 194 dual-pen strip chart recorder.
Column (20 ft × ⅛ in.) with 10% FFAP stationary phase on 80/100-mesh acid-washed DMCS Chromosorb W solid support.
Bureau of Mines Grade A helium.
Prepurified hydrogen.
Filtered compressed air.
Pyrex glass tubing, 6 mm O.D., 4 mm I.D.
Activated charcoal, 20/40 mesh.
Spectrograde, spectroquality, and reagent-grade solvents.
Glass-stoppered microcentrifuge tubes.
Hamilton syringes, 10, 25, and 100 μl.
Test chamber, 3540 liters, with 3540-lpm flush system.
Nominal 1-lpm stainless-steel limiting orifices.
Five-port, valved manifold.
Gast vacuum pump.
Associated laboratory hardware and supplies.

Preparation of Standard Curves

The following equation[15] relates the parts per million by volume to the number of milligrams of compound present in that volume of air at 25°C.

$$\text{Parts per million} = \frac{24{,}450 \times \text{milligrams per liter}}{\text{molecular weight}}$$

Because a standard air sample volume of 10 liters is to be taken, the amount of compound (in milligrams) necessary to make standards at values of one-half the current TLV, the TLV, twice the TLV, 20, 40, 60, 80, 100, and 200 ppm concentration are calculated by this formula for each solvent. The solvents were benzene, *n*-butyl acetate, 2-butanone, carbon tetrachloride, chloroform, *p*-dioxane, ethanol, ethyl ether, isooctane, perchloroethylene, pyridine, toluene, trichloroethylene, and xylene. A microliter syringe is used to inject the calculated amount of solvent into exactly 1 ml of carbon disulfide in a glass-stoppered volumetric flask. Ten times the calculated amount may be injected into 10 ml of carbon disulfide to minimize the error due to the volatility of the carbon disulfide. *Caution:* Carbon disulfide is toxic and should be handled in a hood. The standard solutions should be stored in a refrigerator; they are useful for 2 days only. Any standard containing ethanol should be utilized soon after preparation, owing to the rapid loss of ethanol from the solution.

A 5-μl aliquot is withdrawn from the flask with a microliter syringe and introduced into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the needle of the injection syringe, the solvent flush injection technique is employed.[16] The syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent is drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and

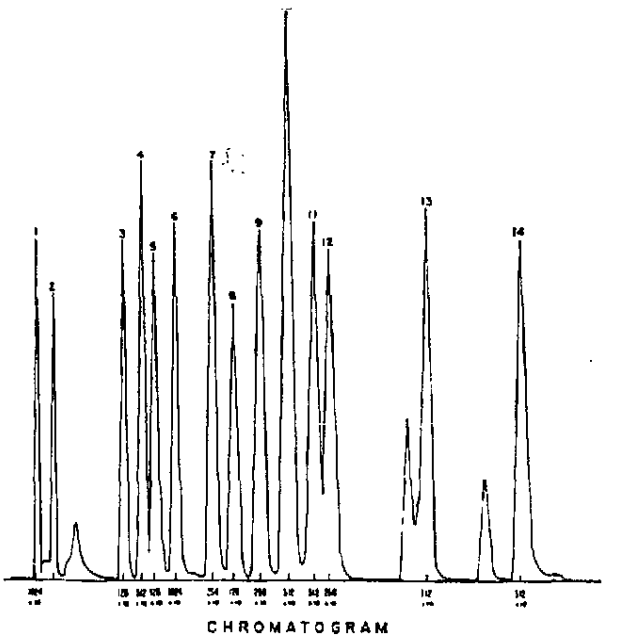

FIGURE 1. Chromatogram (0 to 10 minutes, programmed from 100° to 140°C)

the plunger is pulled back about 0.5 μl to separate the solvent flush from the sample with a pocket of air. The needle is then immersed in the sample, and the 5-μl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back to minimize evaporation of the sample from the tip of the needle.

The standard curves are established for these fourteen compounds by using the same operating conditions on the gas chromatograph as are used for the unknown samples. Curves are established with a strip chart recorder by plotting concentration versus average peak area. Peak area is determined by multiplying the height of the peak by the width at half-height. Triplicate injections are made, and the average peak area is calculated. When an electronic digital integrator is employed, concentration is plotted against the average number of counts. Figure 1 is a representative chromatogram of a 100-ppm standard that contains all fourteen solvents and has been programmed from 100° to 140°C. Table I lists the retention data (when programmed from 100° to 140°C) and boiling points for the fourteen compounds.

Experimental Procedure

Sampling Tube Preparation

Fire-polished straight glass tubes 6 inches long, 4 mm I.D., were packed with two 1-inch sections (180 mg each) of 20/40-mesh activated charcoal. The two sections were separated with a plug of fiberglass and re-

TABLE I
Retention Data and Boiling Points

Compound	Retention Time (seconds)	Boiling Point (°C)	Retention Volume (ml)
Ethyl ether	89	35	125
Cyclohexane	97	69	136
Carbon disulfide	120	46	168
Carbon tetrachloride	142	77	227
2-Butanone	181	80	253
Ethanol	190	78	266
Benzene	215	80	298
Trichloroethylene	248	87	347
Chloroform	266	61	372
Perchloroethylene	293	121	410
Toluene	321	111	450
n-Butyl acetate	344	127	482
p-Dioxane	362	101	507
p-Xylene	445	138	620
m-Xylene	456	139	648
o-Xylene	542	144	725
Pyridine	560	115	795

tained with plugs of fiberglass at each end. Both ends were flame-sealed in such a manner that they could be easily broken in the field. These tubes were used to take an integrated atmospheric sample.

Test Chamber Sampling

Known concentrations were generated in a 3540-liter test chamber by evaporating a calculated volume of solvent into the chamber. A fan was used to thoroughly mix the vapors in the chamber (Figure 2). Five tubes were positioned in different areas of the chamber;

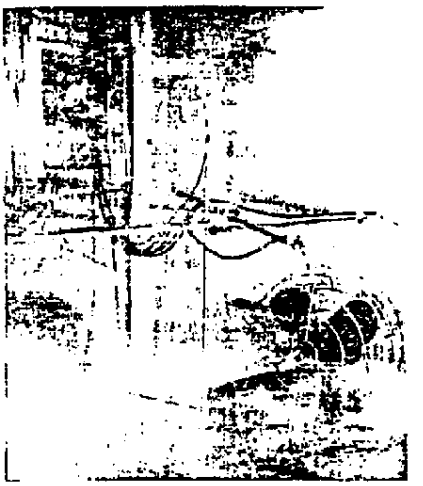

Figure 2. Test chamber, 3540-liter capacity

the ere connected by rubber tubing to a five-port, valved manifold with five nominal 1-lpm limiting orifices (Figure 3). An electrically powered Gast vacuum pump provided a constant rate of flow through these orifices (Figure 4).

Before each experiment the chamber walls were saturated with the solvent vapor or vapors at a given concentration. The test chamber was then flushed at a rate of 3540 lpm for 5 minutes to remove the solvent. Test chamber concentrations at values of one-half the current TLV, the TLV, and twice the TLV were then generated, both singly and in matrix, to determine the adsorption coefficients. A standard volume of 10 liters was sampled, and the tubes were sealed and returned to the laboratory for analysis. To assess the effect of sampling rate and volume on the adsorption coefficient, 25 liters of petroleum ether and acetonitrile (concentration 100 ppm) were sampled at rates of 0.5, 1, 1.5, and 2 lpm.

Desorption Tube Preparation

Activated charcoal equivalent to one section in the sampling tube (180 mg) was measured into a 2-inch, 4 mm I.D. glass tube sealed at one end and capped with Parafilm. A known volume of solvent was injected directly into the activated charcoal with a microliter syringe, and the tube was capped off with more Parafilm. Volumes of all fourteen solvents equivalent to concentrations of one-half TLV, TLV, 2 TLV, 60 ppm, 100 ppm, and 200 ppm in 10 liters of air were injected into the activated charcoal.

To determine the effect of a matrix on the desorption coefficient, various matrixes of four, seven, and fourteen compounds were injected into a number of tubes. The tubes were allowed to stand for 1 day to assure complete adsorption of the solvent(s) by the charcoal. The activated charcoal in the desorption tubes was desorbed in exactly the same manner as each of the charcoal sections in the sampling tube.

Analytical Procedure

Desorption of the organic materials was accomplished by using 1 ml of carbon disul-

fide per 1-inch section of activated charcoal. Each section was analyzed separately; the one nearest the pump was designated as section B, and the other was marked section A. Each section of activated charcoal was placed in a glass-stoppered microcentrifuge tube. One milliliter of carbon disulfide was added to the charcoal. Experimentation has indicated that desorption is accomplished in 30 minutes if the sample is shaken repeatedly or otherwise agitated.

The resulting carbon disulfide solution was analyzed by introducing a 5-µl aliquot into a gas chromatograph. Either dual-column, differential operation or the uncompensated mode of operation can be used in the analysis. A Honeywell Electronik 194 dual-pen strip chart recorder was used to record the peaks. Although the Datex DIR-1 electronic digital integrator was used for a number of determinations, it is not required.

The operating parameters for the Perkin-Elmer Model 900 gas chromatograph have been designed to be optimum for all fourteen compounds. The concentration of any or all of these solvents can be determined from the same chromatogram. Temperature programming is not necessary for this procedure, but it can be utilized to shorten the time required for analysis of a sample that contains xylene and pyridine.

Operating conditions for the Perkin-Elmer gas chromatograph are:

1. 85 cc/min (70 psig) helium carrier flow
2. 65 cc/min (24 psig) hydrogen gas flow to detector
3. 500 cc/min (50 psig) air flow to detector
4. 200°C injector temperature
5. 200°C manifold temperature (detector)
6. Oven temperature
   - *a* Isothermal
     - (*i*) 100°C
   - *b* Temperature program
     - (*i*) 100°C initial temperature for 6 minutes
     - (*ii*) 20°C per minute program from 100 to 140°C

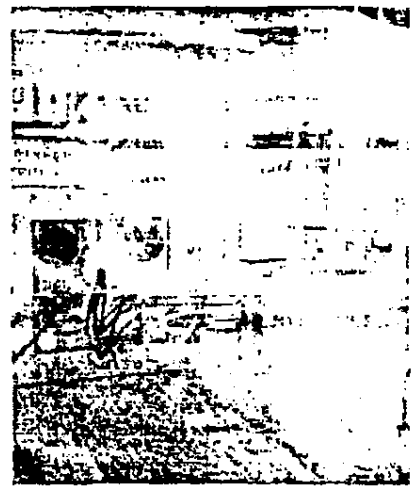

FIGURE 3. Air pump and limiting orifices.

Triplicate injections were made, and the average peak area for each compound was calculated from the chromatograms. By referring the average area back to the standard curves, the concentration in parts per million and the total weight of each solvent were easily determined. The percent desorption is calculated by dividing the solvent weight that was determined experimentally in the desorption tube charcoal by the solvent weight that was injected into the charcoal, multiplied by 100.

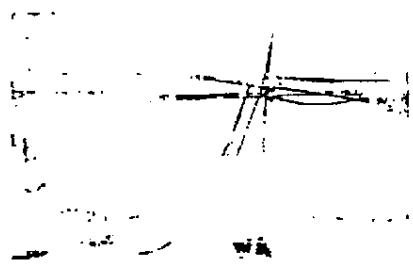

TABLE II
Chamber Desorption Perce[illegible]es

Compound	TLV (ppm)	½ TLV (av. range)		TLV (av. range)		2 TLV (av. range)	
No. of Components:			7		7		7
Benzene	25	99	97–100	96	94–100	93	91–94
2-Butanone	200	96	94–97	96	94–98	90	88–96
n-Butyl acetate	150	96	93–99	94	88–97	95	92–97
Carbon tetrachloride	10	98	95–101	101	96–113	98	96–99
Chloroform	50	97	93–105	100	98–101	96	87–103
p-Dioxane	100	85	78–87	88	84–93	94	91–96
Ethanol	1000	35	51–71	67	64–72	69	67–71
Ethyl ether	400	91	88–95	90	86–96	87	86–88
Iso-octane	400	94	85–97	95	92–97	98	96–104
Perchloroethylene	100	93	88–95	96	95–97	99	99–100
Pyridine	5	57	56–60	48	46–50	56	51–61
Toluene	200	96	93–98	96	95–99	98	96–100
Trichloroethylene	100	92	89–93	97	93–99	98	96–100
Xylene	100	97	91–105	90	97–100	94	92–96

Discussion

Several columns were compared experimentally to determine which column would effect a complete yet rapid separation of the fourteen compounds. The groups of compounds represented are alcohols, acetates, amines, aromatics, ketones, ethers, halogenated hydrocarbons, hydrocarbons, and halogenated olefins. A 20-ft × ⅛-in. stainless-steel FFAP column fulfilled these requirements. This column has 10% FFAP stationary phase on 80/100-mesh acid-washed DMCS chromosorb W solid support.

Desorption percentages determined for the fourteen compounds at chamber concentrations of one-half TLV, TLV, and 2 TLV are given in Table II. Table III shows the desorption percentages for 60, 100, and 200 ppm concentrations in different matrixes. The percentages represent the average value of three to twelve determinations. These solvents have desorption percentages of over 90%, with the exception of ethanol and pyridine. Matrixes of three different random sets of seven or all fourteen components apparently do not significantly affect the desorption efficiencies of any of these compounds. As was also noted by Otterson and Guy,[12] larger sections of activated charcoal appear to cause a decrease in desorption efficiencies.

Several desorption tubes that contained all fourteen solvents adsorbed at 100 ppm concentrations on the activated charcoal were desorbed with carbon disulfide. These samples were not shaken, stirred, or agitated in any manner. Aliquots from these samples were injected into the gas chromatograph at 30-min intervals. Maximum desorption percentages were reached 3 hours after desorption began. Table IV shows the desorption efficiency variations for each solvent under these conditions. Experimentation indicated that maximum desorption can be accom-

TABLE III
Standard Desorption Percentages

Compound	60 ppm				100 ppm				200 ppm			
	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range	Av.	Range
No. of Components	1		2		1		7		14		4	
Benzene	94	83–97	94	91–95	95	90–98	99	97–102	92	88–97		
2-Butanone	98	91–105	92	89–94	99	96–106	96	95–97	91	85–100		
n-Butyl acetate	95	94–97	94	92–96	94	86–98	96	95–97	93	91–99		
Carbon tetrachloride	99	94–109	99	96–100	99	93–116	98	87–101	97	91–103	97	95–99
Chloroform	99	96–102	99	99	98	97–100	96	81–103	93	88–99		
p-Dioxane	93	90–95	90	81–91	92	85–98	86	83–99	95	86–96		
Ethanol	72	68–75	51	49–52	67	63–69	61	58–64	61	51–68	60	57–63
Ethyl ether	94	86–99	94	86–98	101	97–105	98	92–101	103	94–111		
Iso-octane	96	96	86	82–90	95	91–99	99	98–100	97	93–100		
Perchloroethylene	99	96–109	99	99	98	93–106	96	94–97	96	93–102	99	99–100
Pyridine	70	69–71	61	60–66	68	65–69	69	65–72	66	60–71		
Toluene	92	85–100	92	90–95	100	97–102	95	93–96	94	88–97		
Trichloroethylene	94	81–100	96	93–105	99	96–103	97	91–99	95	91–98	92	85–96
Xylene	95	79–103	93	91–95	94	91–96	98	97–100	94	89–96		

plished in 30 minutes if the sample is repeatedly shaken or otherwise agitated.

Test runs with petroleum ether and acetonitrile (concentration 100 ppm) at sampling rates from 0.5 to 2 lpm indicate that these rates do not affect the adsorption efficiency of the activated charcoal tube.

Tubes with four 1-inch sections of activated charcoal were used to sample and collect each of the solvent vapors at chamber concentrations of twice the current threshold limit value. All solvent vapors were adsorbed on the first two 1-inch sections of activated charcoal. Based on the recovery data obtained from the chamber experiments (Table II), the overall efficiency was found to be equivalent to the efficiency of the desorption standard (Table III); thus the sampling adsorption efficiencies were determined to be 100%. These results indicate that a single tube (two 1-inch sections of activated charcoal) can be used to sample and efficiently collect each of the fourteen solvent vapors up to concentrations of at least twice the threshold limit value.

A small, portable Willson Casella pump capable of aspirating an accurately measurable amount of air through a single charcoal tube has been employed to take a large number of samples in the field. Analysis of these tubes indicated that many of the fourteen solvents can be determined with the flame ionization detector in the parts-per-billion concentration range by volume in the air. It is not necessary to alter the above-mentioned analytical procedure or any of the parameters for these determinations. This method was inadequate for the analysis of acetone and methanol.

Polar compounds tend to be displaced from the first onto the second 1-inch section of the charcoal tube when sampled in the presence of high concentrations of nonpolar organic solvents. Approximately 25% of the acetonitrile was displaced onto the second section when an equal concentration (100 ppm) of petroleum ether was present, regardless of the difference in sampling rate (0.5 to 2 lpm). 2-Butanone, chloroform, and ethanol were affected in a similar manner when tested in three random matrixes of seven components at concentrations of TLV and greater.

TABLE IV
Desorption Percentage Variation with Time

Compound	30 minutes	3 hours*
Benzene	85	94
2-Butanone	83	91
n-Butyl acetate	91	99
Carbon tetrachloride	93	100
Chloroform	88	99
p-Dioxane	88	96
Ethanol	54	64
Ethyl ether	95	100
Iso-octane	93	99
Perchloroethylene	91	98
Pyridine	61	69
Toluene	88	96
Trichloroethylene	84	99
Xylene	86	96

*Nonagitated, unstirred, sampled regularly.

Depending on the matrix, a 1-inch section of charcoal has a saturation limit of 28 to 45 mg (1000 to 1500 ppm) of total solvents. The saturation limit of a single solvent on a 1-inch section of activated charcoal is 28 to 30 mg (600 to 1500 ppm). Each charcoal section efficiently collects the solvent vapors passing through it until the saturation limit is reached.

Summary

Fourteen selected atmospheric solvent vapors can be collected efficiently on activated charcoal prior to simultaneous separation and analysis by using a gas chromatograph equipped with a flame ionization detector.

A matrix of seven or fourteen components apparently does not significantly affect the desorption efficiencies of any of these compounds. Recovery data showed that the overal efficiency was equivalent to the efficiency of the desorption standards for each solvent vapor; therefore the sampling adsorption efficiency was determined to be 100% for these solvents. Sampling rate and volume apparently do not affect the adsorption efficiency.

The study also indicates that a single charcoal tube can be used to sample and efficiently collect each of the fourteen solvent vapors at a concentration twice the current TLV.

Acknowledgments

We wish to acknowledge the excellent assistance of Ceola Moore, who prepared the charcoal tubes. The assistance of John V. Crable and Cathryn Dawson is also appreciated.

(c) The Deputy Administrator, Veterinary Services, upon request to him, may approve other identification systems in specific cases and under such conditions as he may prescribe if he determines that such systems provide the necessary information to allow for traceback of the swine to their herd of origin.

Any person who wishes to submit written data, views or arguments concerning the proposed amendment may do so by filing them with Deputy Administrator, Veterinary Services, Animal and Plant Health Inspection Service, U.S. Department of Agriculture, Hyattsville, Maryland 20782 before August 12, 1974.

All written submissions made pursuant to this notice will be made available for public inspection at the Federal Building, 6505 Belcrest Road, Room 870, Hyattsville, Maryland 20782, during regular hours of business (8 a.m. to 4:30 p.m., Monday to Friday, except holidays) in a manner convenient to the public business (7 CFR 1.27(b)).

Comments submitted should bear a reference to the date and page number of this issue in the FEDERAL REGISTER.

Done at Washington, D.C., this 7th day of MAY 1974.

PIERRE A. CHALOUX,
Acting Deputy Administrator, Veterinary Services, Animal and Plant Health Inspection Service.

[FR Doc.74-10882 Filed 5-9-74;8:45 am]

DEPARTMENT OF LABOR

Occupational Safety and Health Administration

[29 CFR Part 1910]

[Docket OSH-36]

VINYL CHLORIDE

Proposed Standard

1. *Background.* Vinyl chloride (chloroethene) Chemical Abstracts Service Registry No. 75015, is a synthetic chemical made by oxychlorination of ethylene or by hydrochlorination of acetylene. It is the parent compound of a series of thermoplastic resin polymers and copolymers which are widely used for containers, wrapping film, electrical insulation, pipe, conduit, and a variety of other products. Vinyl chloride has been made commercially in this country since 1939 and present production is in excess of seven billion pounds per year.

Vinyl chloride (VC) is a gas at ambient temperature and pressure and is a chlorinated hydrocarbon which has moderate liver toxicity. The previous standard set a ceiling value of 500 parts per million (ppm) (29 CFR 1910.93, Table G-1).

On January 22, 1974, the Occupational Safety and Health Administration (OSHA) was informed by the National Institute for Occupational Safety and Health (NIOSH) that the B. F. Goodrich Chemical Company reported that deaths of several of its employees from a rare liver cancer (angiosarcoma) may have been occupationally related. As a result of this notification and after consultation with the National Institute for Occupational Safety and Health (NIOSH), and a joint inspection of the plant by OSHA, NIOSH, and the Kentucky Department of Labor, a fact-finding hearing on possible hazards involved with the manufacture and use of VC was announced on January 30, 1974 (39 FR 3874) and held on February 15, 1974.

2. *Carcinogenicity of VC.* Information produced at this hearing demonstrated that exposure of laboratory animals (mostly Sprague-Dawley rats) to VC by inhalation at and below the then current OSHA standard of 500 ppm induced tumors, including angiosarcomas of the liver. Professor Cesare Maltoni, of the Instituto di Oncologia, Bologna, Italy, reported on a series of experiments on the effect of exposure of rats, mice, and hamsters to VC at concentrations of 10,000; 6,000; 3,500; 500; 250; and 50 ppm for varying periods of time (TR-43-63). Some of the experiments have been concluded, and others are still ongoing. The experimental results reported were that tumors have been observed in groups of animals exposed to VC at concentrations as low as 250 ppm. No tumors were observed in the group of animals exposed to VC at a concentration of 50 ppm. It also appears that the total number of tumors, as well as the numbers of angiosarcomas of the liver, decreased as the concentrations of VC were reduced to 250 ppm. Another experiment by Professor Maltoni was reported underway involving the exposure of 300 animals to VC at concentrations of 50 ppm, in order to assess in a more definitive way whether that level of exposure produces tumors in animals. Data reported by Torkelson, Oyen and Rowe (American Industrial Hygiene Association J 22: 254-261 (1961)) indicate that exposure to VC at concentrations of 50 ppm failed to induce tumors in rats, hamsters, rabbits, and dogs.

The employees of the B. F. Goodrich Chemical Company who died from angiosarcoma of the liver had an average exposure of approximately 19 years to vinyl chloride, at unknown concentrations, and variable exposures to other volatile chemicals. (TR 83). Some employees of Union Carbide, Firestone Tire and Rubber, and Goodyear were also reported in post-hearing comments to have had exposure to vinyl chloride and to have died from angiosarcoma of the liver. Finally, autopsies of four deceased employees revealed their liver angiosarcoma tumors were histologically indistinguishable from the angiosarcoma tumors observed in Professor Maltoni's experimental animals.

3. *The Emergency Temporary Standard.* On the basis of all information available at that time, and the fact that employees were being exposed at levels around the experimentally observed effect level of 250 ppm, an Emergency Temporary Standard (ETS) was promulgated on April 5, 1974 (39 FR 12342) as 29 CFR 1910.93q. This standard reduced the level from a ceiling of 500 ppm to 50 ppm ceiling. It was expressly recognized that this standard limiting exposures to a 50 ppm level was intended to be a tentative, interim standard, to be in effect no longer than six months, during which time the whole question of possible safe exposure to VC would be reconsidered more fully and in the light of more information, especially results of experiments which were known to be underway at that time.

4. *Additional information.* On April 15, 1974, information and data were presented to representatives of OSHA, NIOSH and the EPA by the Industrial Bio-Test Laboratories, Northbrook, Illinois, concerning results of animal exposure studies with VC, sponsored by the Manufacturing Chemists Association (MCA). Although only preliminary in nature, these results revealed that 2 out of 200 mice exposed to VC concentrations of 50 ppm for 7 hours a day, five days a week, for approximately 7 months, developed angiosarcomas of the liver.

The Industrial Bio-Test Lab data indicate that exposure to VC at 50 ppm may well constitute a serious health hazard to employees. Also, the question of a safe level of exposure for humans cannot be determined at this time, and may continue as a matter for scientific deliberation for many years. We therefore conclude that it is now necessary to propose to change the 50 ppm level established in the ETS to as low a level as can be detected using methodologies outlined in this proposal.

5. *The proposed permanent standard.* The requirements for a complete standard under section 6(b) of the Occupational Safety and Health Act of 1970 are much more comprehensive than the provisions of the ETS promulgated on April 5. The following proposals are responsive to the additional information on the carcinogenicity of VC, and the requirements of the Act.

A. *Level of exposure.* The proposed standard for employee exposure is set at no detectable level, as determined by a sampling and analytical method capable of detecting vinyl chloride at concentrations of 1 ppm with an accuracy of 1 ppm or 50 percent. Although more sensitive methods may be available now or in the future, the methodological sensitivity proposed appears to be the most feasible and generally available. A method of 1 ppm sensitivity has been recommended to OSHA by NIOSH. To minimize the number of persons at risk, a requirement would be established for regulating areas where vinyl chloride is manufactured, reacted, stored, handled, released, reworked, or used, including operations with polyvinyl chloride containing detectable levels of vinyl chloride. Access to the areas would be limited to authorized employees.

B. *Monitoring.* A program of monitoring would be required to establish whether there are detectable levels in regulated areas and to permit determination of employee exposures on an individual basis. Provision would also be

made for an opportunity to observe monitoring by employees or their designated representatives, as required by section 8(c)(3) of the Act.

C. Control methods. Where detectable levels of VC are monitored, two programs would be triggered: an engineering and work practice program to reduce levels below detectability; and while this is on-going, a respiratory protection program for employees in the regulated area.

Engineering controls and work practices are favored methods of compliance because they tend to avoid contamination of the ambient air in the workplace. Accordingly, it is proposed to require the institution of engineering controls and of workpractice methods as soon as feasible, and to require the use of respirators pending the institution of such controls, to supplement such controls where they are insufficient to reduce concentrations of vinyl chloride below the detectable level, in specified work situations, and in cases of emergency. The proposal for continuous flow and pressure demand types of respirators is based on the recommendations of NIOSH, which has observed leakage through chemical cartridge respirators at high concentrations of VC.

A requirement would also be established for the provision and use of protective clothing for employees in the regulated areas. The protective clothing would minimize skin contact with VC vapor, and would provide some measure of protection from splash of liquid in the event of a spill or rupture of equipment. Food, beverages, and like products would be prohibited in the regulated area.

Written operational and emergency plans would be required, along with employee training in routine and emergency duties. Specific requirements would be established for emergency actions and for routine maintenance and decontamination operations, including vessel entry, which are known to present particular hazards.

The purposes of operational and emergency plans and training are to apprise employees of the hazards to which they may be exposed, of the precautions they must take to avoid such hazards, and to rehearse employees in the procedures they must follow in emergencies.

D. Medical surveillance. Comprehensive requirements for employee medical examinations are proposed, including necessary tests. Some additional guidance is included for the convenience of physicians. The proposed requirements have been recommended to OSHA by NIOSH as reasonably appropriate to detect liver dysfunction which may be indicative of, or predisposing to, the development of liver angiosarcomas.

E. Records and reports. Records of monitoring, medical examinations, and entry to regulated areas are proposed, with provision for access by appropriate OSHA and NIOSH officials. Specific provisions for employee access to monitoring records are included, as well as the requirement to furnish a copy of a medical record to an employee's physician on the employee's request. Establishments conducting VC operations would be required to identify themselves to OSHA, and to report incidents (accidents) resulting in the release of vinyl chloride.

Accordingly, pursuant to sections 6(b), 6(e), and 8(c) of the Occupational Safety and Health Act of 1970 (84 Stat. 1593, 1596, 1599; 29 U.S.C. 655, 657), Secretary of Labor's Order No. 12–71 (36 FR 8754) and 29 CFR Part 1911, it is hereby proposed to amend 29 CFR Part 1910 by revising § 1910.93q as set forth below.

Written data, views, and arguments concerning the proposals may be mailed to the Docket Officer, Docket OSH–36, Room 230, 1726 M Street, N.W., Occupational Safety and Health Administration, Washington, D.C. 20210, postmarked not later than June 10, 1974.

Pursuant to 29 CFR 1911.11 (b) and (c), interested persons may file objections to the proposals, requesting an informal hearing with respect thereto, in accordance with the following conditions:

(1) The objections must include the name and address of the objector;

(2) The objections must be postmarked on or before June 10, 1974;

(3) The objections must specify the provisions of the proposed rule to which objection is taken, and must state the grounds therefor;

(4) Each objection must be separately stated and numbered; and

(5) The objections must be accompanied by a summary of the evidence proposed to be adduced at the requested hearing.

As revised, § 1910.93q would read as follows:

§ 1910.93q Vinyl Chloride.

(a) *Scope and application.* (1) This section applies to any area or operation in which vinyl chloride (chloroethene), Chemical Abstracts Service Registry No. 75015, is manufactured, reacted, released, repackaged, stored, or used, including areas and operations involving polyvinyl chloride where detectable levels of vinyl chloride are released.

(2) *This section does not apply to the* handling or use of fabricated products made entirely or in part of polyvinyl chloride.

(b) *Definitions.* (1) "Assistant Secretary" means the Assistant Secretary of Labor for Occupational Safety and Health, U.S. Department of Labor or his designee.

(2) "Authorized employee" means an employee whose duties require him to be in the regulated area and who has been specifically assigned by the employer; and any employee who enters such an area as a designated representative of employees to exercise an opportunity to observe monitoring and measuring of vinyl chloride.

(3) "Closed container" means any container which prevents the release of vinyl chloride to the environment.

(4) "Contaminated" means capable of releasing a detectable level of vinyl chloride.

(5) "Decontamination" means reduction of vinyl chloride concentrations to less than detectable levels.

(6) "Detectable level" means an airborne concentration of vinyl chloride measurable by a sampling and analytical method capable of measuring concentrations of 1 ppm, with an accuracy of 1 ppm±50 percent.

(7) "Director" means the Director, National Institute for Occupational Safety and Health, or any person directed by him or the Secretary of Health, Education, and Welfare to act for the Director.

(8) "Emergency" means an unforseen circumstance or set of circumstances, resulting in the release of vinyl chloride into areas occupied by employees.

(9) "Exposure" means actual contact with vinyl chloride when unprotected by required personal protective equipment and clothing.

(10) "Fabricated product" means a finished product or part of such product, made of polyvinyl chloride, entirely or in part, including semifinished products such as film, sheet, block, bar, or extrusion stock.

(11) "OSHA Area Director" means the Director for the Occupational Safety and Health Administration Area Office having jurisdiction over the geographic area in which the establishment is located.

(12) "Polyvinyl chloride" means polyvinyl chloride homopolymer or copolymer before such is converted to a fabricated product.

(13) "Protective clothing" means clothing protective against vinyl chloride.

(14) "Vinyl chloride" means vinyl chloride monomer.

(15) "Waste resin" means any resin or other reaction products removed in the cleaning of equipment, such as vessels and piping.

(c) *Reference.* College of American Pathologists, 230 N. Michigan Ave., Chicago, Illinois 60601.

(d) *Regulated areas.* (1) A regulated area shall be established where (i) vinyl chloride is manufactured, reacted, released, repackaged, stored, or used; or (ii) polyvinyl chloride capable of releasing detectable levels of vinyl chloride is manufactured, reacted, released, repackaged, stored, or used.

(2) Access to regulated areas shall be limited to authorized employees.

(3) A daily roster of employees entering regulated areas shall be made and maintained. The rosters, or summaries thereof, shall be kept for at least 20 years.

(e) *Monitoring.* (1) Every regulated area shall be monitored for detectable levels of vinyl chloride.

(2) The monitoring shall assure that any exposure may be determined for each authorized employee with a confidence level of 95 percent.

(3) Employees or their designated representatives shall be afforded an opportunity to observe monitoring and measuring required by this paragraph.

(4) Where exercise of an opportunity requires entry to an area where the use

of protective clothing, equipm facilities, or procedures is required, such clothing, equipment, facilities, and procedures shall be provided to all persons entitled to exercise the opportunity, at no cost to any of them.

(ii) Persons exercising the opportunity shall be instructed regarding:

(A) The toxicity and fire hazard of vinyl chloride; and

(B) The protective steps and measures necessary for their protection.

(iii) Observers shall be permitted, without interference to the persons performing the monitoring and measuring, to:

(A) Observe all steps and procedures related to the collecting, processing, and evaluation of particular monitoring and measurement samples;

(B) Record quantities and results obtained;

(C) Observe the condition of monitoring and measuring equipment;

(D) Receive a demonstration of the calibration and function tests of the monitoring and measuring equipment performed on site; and

(E) Examine instructions and documents related to the procedures and equipment for monitoring and measuring.

(4) Accurate and complete records of all required monitoring shall be made and maintained for not less than 20 years. Such a record shall (i) state the date of such monitoring and the levels determined; and (ii) identify the instruments and methods used.

(f) *Engineering controls and workpractice methods.* (1) Where detectable levels of vinyl chloride are measured, immediate protection shall be provided against exposure to vinyl chloride by the use of engineering controls, workpractice methods, and respirators as follows:

(i) Feasible engineering controls and workpractice methods shall immediately be used to reduce airborne concentrations of vinyl chloride below the detectable level;

(ii) Wherever feasible engineering controls and workpractice methods which can be instituted immediately are not sufficient to reduce concentrations of vinyl chloride below the detectable level, they shall nonetheless be used to reduce the concentrations to the lowest practicable level, and shall be supplemented by means of respirators in accordance with paragraph (g) of this section;

(iii) Wherever no feasible engineering control or workpractice method can be instituted immediately, immediate respiratory protection shall be provided in accordance with paragraph (g) of this section; and

(iv) In any case covered by paragraph (f)(1) (ii) or (iii) of this section, the employer shall also undertake as soon as practicable a program to reduce airborne concentrations of vinyl chloride below the detectable level, or to the greatest extent feasible, solely by means of engineering controls and workpractice methods and as soon as feasible.

(2) There shall be tests made for process or equipment leaks and for emission of vinyl chloride which may result from workpractices. The frequency of these tests shall be such as to insure the integrity of equipment and adherence to proper workpractices.

(g) *Respiratory protection.* (1) A respiratory protection program in accordance with § 1910.134 shall be established and implemented where respirators are required to be used by this section.

(2) Respirators shall be used only in cases of emergency and where required by any other provision of this section. Respirators may not be used in lieu of feasible engineering controls or workpractice methods.

(3) Respirators or combinations of respirators for protection against vinyl chloride shall be selected from among the following:

(i) A positive pressure full facepiece self-contained breathing apparatus;

(ii) A pressure-demand full facepiece self-contained breathing apparatus operating in the pressure-demand mode;

(iii) A combination type "C" pressure-demand full facepiece respirator operating in the pressure-demand mode and a pressure-demand self-contained breathing apparatus operating in the pressure-demand mode; or

(iv) A combination type "C" continuous flow respirator and a pressure-demand self-contained breathing apparatus operating in the pressure-demand mode.

(h) *Protective clothing.* (1) Employees entering regulated areas shall be provided full-body protective clothing, footwear or shoe covers, and gloves, at no cost to them, and required to wear it while in the regulated area.

(2) Where polyvinyl chloride powder containing detectable levels of vinyl chloride is handled, employees shall also be:

(i) Provided and required to wear headcoverings;

(ii) Required to remove all protective clothing at each exit from the regulated area; and

(iii) Required to shower after the last exit of the day.

(3) Clean protective clothing shall be provided whenever contaminated or soiled, but not less frequently than weekly. Contaminated clothing shall be decontaminated before reuse by removal for laundering or disposal.

(i) *Hygiene facilities and practices.* (1) Where employees are required by this section to wear protective clothing and equipment, change rooms shall be provided in accordance with § 1910.141(e).

(2) Where employees are required by this section to shower, shower facilities shall be provided in accordance with § 1910.141(d)(3).

(3) Storage or consumption of food or beverages, storage or use of smoking or non-food chewing products, and the storage or application of cosmetics are prohibited in regulated areas.

(j) *Emergency situations.* (1) A written operational plan for emergency situations shall be developed for each regulated area.

(2) In the event of an emergency, appropriate portions of the plan shall be put into operation.

(i) Hazardous conditions created by the emergency shall be eliminated and the affected area shall be decontaminated prior to the resumption of normal operations.

(ii) Special medical surveillance by a physician shall be instituted within 24-hours for employees present in the affected area at the time of the emergency.

(iii) Where an employee has a known contact with liquid vinyl chloride such employee shall be required to shower as soon as possible, unless contraindicated by physical injuries.

(iv) An incident report on the emergency shall be reported as required in paragraph (q)(2) of this section.

(3) Each authorized employee shall be trained in a program relating to the hazards of vinyl chloride and the precautions for safe use.

(i) The program shall include:

(A) The nature of the fire hazard, and the necessary protective steps;

(B) The nature of the toxic hazard, including local and systemic effects, acute and chronic effects including specifically the carcinogenic hazard;

(C) The specific nature of operations which could result in exposure to vinyl chloride, and necessary protective steps;

(D) The purpose for and application of the medical surveillance program;

(E) The purpose for and application of decontamination practices;

(F) The purpose for and significance of emergency practices and procedures;

(G) The employee's specific role under normal operating or emergency conditions;

(H) Specific information to aid the employee in recognition and evaluation of conditions and situations which may result in the release of vinyl chloride;

(I) The purpose for and application of specific first aid procedures and practices;

(J) A review of this standard at the employee's first training and indoctrination program and annually thereafter.

(ii) All materials relating to the program shall be provided upon request to authorized representatives of the Assistant Secretary and the Director.

(k) *Signs and labels.* (1) Entrances to regulated areas shall be posted with signs bearing the legend:

CANCER-SUSPECT AGENT AREA
AUTHORIZED PERSONNEL ONLY

(2) Areas containing operations covered in paragraph (k)(1)(4) of this section shall be posted with signs bearing the legend:

CANCER-SUSPECT AGENT IN THIS AREA
FULL IMPERVIOUS AIR-SUPPLIED EQUIPMENT REQUIRED
AUTHORIZED PERSONNEL ONLY

(3) Containers of waste or other materials contaminated with vinyl chloride shall be labeled:

VINYL CHLORIDE CONTAMINATED MATERIAL
CANCER-SUSPECT AGENT
DISPOSE OF OR DECONTAMINATE USING AUTHORIZED PRECEDURES

(4) Containers of polyvinyl chloride containing detectable levels of vinyl chloride shall be labeled:

POLYVINYL CHLORIDE
CONTAINS VINYL CHLORIDE
VINYL CHLORIDE IS A CANCER-SUSPECT AGENT
ABSORBED BY BREATHING AND THROUGH SKIN

(5) Containers of vinyl chloride shall be labeled:

VINYL CHLORIDE
DANGER
EXTREMELY FLAMMABLE GAS UNDER PRESSURE
MAY POLYMERIZE WITH EXPLOSIVE FORCE
POISON
CANCER SUSPECT AGENT AND ANESTHETIC
ABSORBED BY BREATHING AND THROUGH SKIN

(6) No statement shall appear on or near any required sign, label or instruction, which contradicts or detracts from the effect of any required warning, information or instruction.

(l) *Maintenance and decontamination.* (1) Emphasis shall be placed upon immediate clean up of spills, periodic inspection, prompt repair of equipment and leaks, and proper handling, storage and disposal or decontamination of materials to prevent airborne contamination and accidental skin contact with vinyl chloride. Waste materials, equipment, and other sources of vinyl chloride in closed containers, may not be placed in areas of excessive temperature or sunlight since build-up of internal pressure may result in rupture of the container, fire or explosion.

(2) Waste resins or other materials contaminated with vinyl chloride shall be placed in closed containers pending disposal or decontamination.

(3) Appropriate procedures shall be developed and implemented for the decontamination or disposal of all such waste material.

(4) In maintenance or repair operations on contaminated—systems or equipment, including vessel entry, employees engaged in such operations shall be (i) provided with and required to wear and use a whole-body air-supplied suit impervious to vinyl chloride, and a respirator in accordance with paragraph (g) of this section; and (ii) required to shower after removing protective equipment.

(5) Protective clothing and equipment shall be clean and dry for each use.

(6) When vessels or piping systems are opened local exhaust ventilation shall be provided to remove the escaping vapor from all occupied areas.

(7) (i) Vessels to be entered shall first be ventilated and monitored so that the concentration of vinyl chloride is reduced to a level within the protection factor capability of the protective equipment.

(ii) When vessels are to be entered, all piping to such vessel shall be:

(A) Opened, blanked and tagged; or

(B) Where welded piping is in use, not less than 3 valves in series, which isolate the vessel from any other connection to such line, must be closed and secured.

(iii) No employee shall enter a vessel, except when another employee properly trained and equipped for entry is present and is observing the employee in the vessel. The observer shall have means for signalling for help in the event the employee experiences problems. Under such conditions, the observer shall signal for help, and shall not enter to assist the employee until another person is present to observe.

(m) *Transportation loading and unloading.* (1) Facilities for the loading and unloading of vinyl chloride to and from containers shall have each transfer line and vapor-equalizing line equipped with vent connections, and shall have an inert gas purging system. Vent and purge effluent shall be returned to a process stream or flared in a safe location.

(2) Procedures shall be developed and implemented for the transfer of vinyl chloride. Written copies of such procedures shall be provided employees engaged in such operations, and such employees shall be fully trained and rehearsed in all procedures.

(3) Employees engaged in transfer operations shall be provided with and required to wear respirators in accordance with paragraph (g) of this section.

(n) *Polymer handling operations.* (1) Containers of polyvinyl chloride releasing detectable levels of vinyl chloride shall be opened and transferred only under local exhaust ventilation which reduces the concentration of vinyl chloride below the detectable level.

(2) Hot operations, such as but not limited to milling, calendering and extruding, which release detectable levels of vinyl chloride, shall be carried on only under local exhaust ventilation which reduces the concentration of vinyl chloride below the detectable level.

(o) *Medical surveillance.* Not later than _____ 1974, a program of medical surveillance shall be instituted, and shall provide each authorized employee with an opportunity for examinations in accordance with this paragraph. All medical examinations and procedures shall be performed by or under the supervision of a licensed Doctor of Medicine (MD) or Doctor of Osteopathy (DO). All medical examinations and tests shall be provided without cost to the employee.

(1) At the time of initial employment, or upon institution of screening, a physical examination shall be performed with specific attention to detecting enlargement of liver or spleen by abdominal palpation.

(2) At the time of initial employment or upon institution of screening, and annually thereafter, a medical history checklist shall be completed by the employee. This list shall include questions concerning:

(i) Alcohol intake;

(ii) Past history of hepatitis;

(iii) Past exposure to potential hepatotoxic agents, including drugs and chemicals;

(iv) Past history of blood transfusions; and

(v) Past history of hospitalizations.

(3) At the time of initial employment, or upon institution of screening, a serum specimen shall be obtained for screening with respect to the following bio-chemical determinations of liver function:

(i) Total bilirubin;

(ii) Alkaline phosphatase;

(iii) Serum glutamic oxaloacetic transaminase (SGOT);

(iv) Serum glutamic pyruvic transaminase (SGPT); and

(v) Gamma glutamyl transpeptidase (GGTP).

(4) Additional tests that may optionally be considered for use in screening include:

(i) Lactic dehydrogenase;

(ii) Serum protein determinations;

(iii) Serum protein electrophoresis; and

(iv) Platelet count.

(5) Laboratory analyses for all biological specimens included in medical examinations shall be performed in laboratories accredited by the College of American Pathologists or licensed under 13 CFR Part 74.

(6) If the results of screening required in paragraph (o) (3) of this section are normal, screening shall be repeated:

(i) Every six months for employees who have been employed in vinyl chloride related operations for 10 years or more; and

(ii) Annually for all other employees entering regulated areas.

(7) If one or more liver function tests performed are abnormal, serum testing shall be repeated as soon as possible, preferably within two to four weeks. If no abnormalities are present upon rescreening, serum testing shall be repeated in three months.

(8) If abnormalities persist upon rescreening, the employee shall be withdrawn from areas where contact with vinyl chloride is possible, and an individualized medical workshop shall be instituted. Suggested as initial steps are a complete physical examination and various special procedures such as hepatitis B antigen determination and liver scanning. If liver function abnormalities are determined to be unrelated to liver disease, the employee may be permitted to return to vinyl chloride-related employment, subject to individual medical evaluation.

(9) A complete and accurate record of the results of medical examinations shall be made and maintained for the duration of employment plus five years, or for 20 years, whichever is longer.

(p) *Records.* (1) Records of monitoring and measuring, medical records, and regulated area entry rosters and summaries, shall be made available for examination and copying upon request to authorized representatives of the Assistant Secretary and the Director.

(2) In the event that the employer ceases to do business and there is no successor to receive and retain his records for the prescribed period, these records shall be transmitted by registered mail to the Director, and each employee individually notified in writing of this transfer.

(3) Employees and their designated representatives shall be provided access to examine and copy records of monitoring and measuring.

(4) Former employees shall be provided acces to examine and copy records reflecting their own exposures.

(5) Upon written request of any employee, a copy of the medical record of such employee shall be furnished to a physician designated by the employee in such request.

(q) *Reports.* (1) Not later than _____ the following information shall be reported to the OSHA Area Director. Any change in such information shall be reported to the OSHA Area Director within 15 days of such change.

(i) The address and location of each establishment which has one or more regulated areas; and

(ii) The number of employees in each regulated area during normal operations, including maintenance.

(2) Incidents which result in the release of vinyl chloride into any area where employees may be exposed shall be reported in accordance with this paragraph.

(i) A report of the occurrence of the incident and the facts obtainable at that time including a report on any medical treatment of affected employees shall be made within 24 hours to the OSHA Area Director.

(ii) A written report shall be filed with the OSHA Area Director within 15 calendar days thereafter and shall include:

(A) A specification of the amount of material released;

(B) A description of the area involved and the extent of known and potential employee exposure and area affected;

(C) A report on any medical treatment of affected employees and any medical surveillance program implemented; and

(D) An analysis of the circumstances of the incident, and measures taken or to be taken, with specific completion dates, to avoid further similar releases.

(3) Upon completion of any monitoring and measuring which discloses that any employee has actually been exposed to detectable levels of vinyl chloride, each such employee shall be individually notified in writing. The notice shall:

(i) Be delivered not later than 10 working days after completion of the monitoring and measuring;

(ii) State the actual exposure in terms of concentration and time; and

(iii) State the steps which have been taken, are being taken, and will be taken, with specific completion dates, to terminate the exposure and prevent a recurrence.

(Secs. 6(b), 6(c), and 8(c), 84 Stat. 1593, 1596, 1599 (29 U.S.C. 655, 657); Secretary of Labor's Order No. 12-71 (36 FR 8754))

Signed at Washington, D.C. this 6th day of May, 1974.

JOHN STENDER,
Assistant Secretary of Labor.

[FR Doc.74-10748 Filed 5-9-74;8:45 am]

DEPARTMENT OF TRANSPORTATION

Federal Aviation Administration

[14 CFR Part 25]

[Docket No. 13606; Notice 74-19]

TRANSPORT CATEGORY AIRPLANES

Type A Passenger Emergency Exit Capacity

The FAA is considering rule making to revise the passenger seating configuration limit that is applicable to Type A exits on transport category airplanes. Sections 25.807(c) (2) and (3) of the Federal Aviation Regulations (FARs) currently provide that for each pair of Type A exits (consisting of one on each side of the fuselage) the airplane may have a maximum passenger seating configuration of 100.

This advance notice of proposed rule making is being issued in accordance with the FAA's policy for early institution of public proceedings in actions related to rule making. An "advance" notice is issued to invite early public participation in the identification and selection of a course or alternate courses of action with respect to a particular rule making problem.

Interested persons are invited to participate in the rule making by submitting such written data, views, or arguments as they may desire. Communications should identify the regulatory docket or notice number and be submitted in duplicate to: Federal Aviation Administration, Office of the Chief Counsel, Attention: Rules Docket, AGC-24, 800 Independence Avenue, SW., Washington, D.C. 20591. Communications should be received on or before July 9, 1974, to assure proper consideration. All comments submitted will be available, both before and after the closing date for comments, for examination by interested persons.

The regulatory provisions relating to Type A exits that are contained in § 25.807 of the Federal Aviation Regulations were adopted by Amendment 25-15, effective October 24, 1967. That amendment also established the provision, in § 25.803(c), that manufacturers show by demonstration that the maximum seating capacity of an airplane having a capacity of more than 44 passengers can be evacuated to the ground within 90 seconds, under conditions prescribed in the regulation. As discussed in the preamble to Amendment 25-15, the allowable passenger seating limit of 100 that was established for each pair of Type A exits was less than the evacuation capacity that had been demonstrated by test. As a result of receiving data and information tending to indicate that some of the considerations leading to the conservative limitation may no l be applicable, the FAA has institu regulatory study project to reeva the limitation. The study will includ factors originally considered in e lishing the limitation as well as any factors found to be pertinent. T factors originally considered include tinent evacuation tests and demon tions, exterior slides, the number, tion, and size of aisles and passage and evacuation system reliability.

Data available to the FAA on in- ice evacuations, slide deployments, evacuation demonstrations indicate more than 100 passengers have evacuated through a Type A exit w 90 seconds. The data further ind that Type A exit systems may higher in-service reliability than wa ticipated at the time the limitation established in the regulations. How the FAA believes it is important t view all relevant data on safety and considerations that may be applica any proposed change in the Type A passenger seating limitation. To this the FAA solicits data, views, and a ments from all interested persons o questions set forth below. Data supp ing an answer should be submitte identified sufficiently that the FAA obtain or develop it.

1. Do the data available on evacu tests and in-service incidents that r to the evacuation capacity of Ty exits under emergency conditions i cate that the 100 passenger limita may safely be increased?

2. What reliability has been den strated for Type A exit systems by s ice experience and tests?

3. What relationships may be es lished between reliability and passe emergency evacuation capability of T A exits?

4. How would the emergency eva tion capability of Type A exits be fected by specific increases in passe seating capacity and by specific pas ger seating configuration considerati

5. If there are other factors should be considered, how should the evant data be related to the emerg evacuation capability of Type A e

6. If the commentator recomm specific passenger capacities for con eration, what economic and safety b fits or penalties would be associated them?

Issued in Washington, D.C., on Ma 1974.

C. R. MELUGIN, JR.,
Acting Director,
Flight Standards Servic

[FR Doc.74-10787 Filed 5-9-74;8:45 am]

[14 CFR Part 39]

[Docket No. 74-NW-4-AD]

AIRWORTHINESS DIRECTIVES

Boeing Model 737-100/200 Series Airplanes

The Federal Aviation Administrat is considering amending Part 39 of

The vinyl chloride fight is on

Chemical companies are filing objections to the Occupational Safety and Health Administration's proposed permanent exposure standards for vinyl chloride (*CW, May 15, p. 25*). But despite the outlook for prolonged hearings and accumulated data from many studies, OSHA is still hoping to adopt the standards, which call for "no detectable level" of VCM, by October.

Calling the proposed standards "impractical," "unachievable" and "a disaster for the industry," producers of vinyl chloride and polyvinyl chloride are basing objections on three main points. These are, they allege, the unavailability of manufacturing technology to eliminate VCM completely, the economic impact on the industry (they contend that plants will be closed, jobs and markets lost) and lack of data to support the new rules.

But industry chances of changing the standards appear to be getting worse, if last week's New York Academy of Sciences meeting on toxicity of VCM and PVC is any indication. Charges of blood, liver and respiratory abnormalities resulting from exposure to vinyl chloride were added to the known cases of angiosarcoma.

Standard Setting: The new standards proposed by OSHA define "no detectable exposure level" as being determined by devices capable of detecting concentrations of 1 ppm. with an accuracy of 1 ppm., plus or minus 50%. "That's going to be tough to achieve," says Daniel Boyd, director of the agency's standards development office.

But Boyd observes that a combination of engineering controls, work practice methods and respirators could be used in complying with the rules. The standards would put plants in three categories: those at which "feasible engineering controls" would be used to reduce exposure below detectable levels, those at which respirators would supplement work practice and engineering changes, and those at which respirators alone would be used because "no feasible engineering control or work practice method can be instituted immediately."

But industry is saying that these categories are not practical. Reason: there is no technology available to completely eliminate exposure, so there has to be reliance on respirator systems. And these, industry adds, are dangerous and won't work. "Maybe we can build a new plant to approach the proposed standards," says Harry Connors, general manager of Diamond Shamrock's plastics division, "but we can't adapt existing plants to it."

More Studies: What choice is left to industry? The answer could come from a series of economic impact studies that are being undertaken.

One will be done by OSHA, although a contractor to do the work has not yet been hired. The Society of the Plastics Industry has hired Arthur D. Little to study the economic impact of the new regulations. That study could be ready within two months.

In formulating its VCM rules, OSHA relied heavily on evidence of development of angiosarcoma in mice at 50-ppm. exposure during tests sponsored by the Manufacturing Chemists Assn. at Industrial Biotest Labs. And now those labs and those of Cesare Maltoni, in Bologna, Italy, are going to run further tests on mice at 25, 10 and 5 ppm. But the industry contends that much of this data doesn't relate to human exposure. Connors cites cases of 17 workers at Diamond Shamrock's Deer Park, Tex., plant who have had 20 years' exposure, he says, without damage.

Also under investigation is emissions of vinyl chloride from manufacturing plants. The Environmental Protection Agency maintains that there are 6% VCM losses from PVC plants and concentrations of 1-2 ppm. in air outside plants. Several PVC makers have been installing ventilation systems as protection for workers. Closing this outlet for air pollution reasons will prove an added hardship for the already-hard-pressed makers of VCM and PVC.

And if limits are put on the amount of unreacted VCM on PVC resins, as is being considered by EPA, the industry may find it has "nowhere to go," as one company spokesman put it.

Dart takes the plunge

Improved market conditions have triggered one polypropylene expansion, and more may be in the works.

Dart Industries, which had been considering expansion for some time (*CW, Apr. 11, '73, p. 15*), said last week it will build a 150-million-lbs./year polypropylene plant near Houston in a joint venture with El Paso Products, a subsidiary of El Paso Natural Gas. Startup is expected in '76; cost was not disclosed.

The partnership already operates a 130-million-lbs./year polypropylene plant in Odessa, Tex. That unit will be debottlenecked to up capacity by 10 million lbs./year, according to Dart's chemical group president, Ralph M. Knight.

Knight said the decision to build a new plant was based on forecasts that U.S. polypropylene demand will double, to about 6 billion lbs./year, by '80. Recent increases in prices of the material, he adds, should offset higher costs.

Site for the new plant will be 550 acres in Bayport, Tex., recently acquired by the partnership from Friendswood Development. Knight said the site was chosen because it is close to other petrochemical complexes and to shipping facilities.

Polypropylene is tight, although not as scarce as some other resins. Prices are firm, and industry observers say additional capacity is needed, since only Hercules and Amoco Chemicals have major U.S. expansions now in the works.

Shortages won't vanish

Shortages of vital feedstocks will be a major and long-lasting problem for the plastics industry, Amoco Chemicals' environmental coordinator, Victor A. Denslow, said last week at the annual technical conference of the Society of Plastics Engineers in San Francisco. The shortages, he predicted, will last at least three years, perhaps 10.

Denslow maintains that new feedstock capacity has been discouraged by low rates of return on investment ("3-5% in recent years, sometimes almost zero").

In addition, he says, environmental considerations have limited the availability of energy and feedstocks. He cites these examples: nuclear plants, which could free hydrocarbons for chemical use, have been held up; the Alaska pipeline has also been delayed; Santa Barbara channel oil has not been available; and sulfur and strip-mining restrictions have cut the availability of coal.

All these factors, Denslow notes, will result in reduced availability of plastics and higher prices. "We can't yet assess the effect of higher prices on demand for plastics," he adds, but he says that it will probably lead to a drop in demand.

Conference leader John J. Haher, general sales manager for Borg-Warner Chemicals, emphasized that "the plastics industry must prove to the oil companies that plastics represent a favorable return on investment to their refineries."

To get a share of available crude oil, he added, plastic producers will have to pay much higher prices.

Taxes undermine mining

Texasgulf last week dramatized the growing concern of chemical process companies about tax measures now being considered in Ontario and elsewhere in Canada. The company said it postponed indefinitely its planned $95-million mine expansion at Kidd Creek, Ont., citing tax uncertainties. The mine expansion would up copper-silver-lead-zinc ore production to 5 million tons/year from 3.6 million.

The Ontario proposals pending in the legislature could tax "new" mine production by large firms, such as Texasgulf, at rates as high as 77%, according to mining sources. Texasgulf, however, has said that it believes the new proposals also will contain some offsetting incentives, especially regarding processing and exploration. Meanwhile, federal tax proposals that would increase levies on mineral profits to 50% also are pending but their future may depend largely on the outcome of the new Canadian elections now set for July 8.

The Ontario proposals followed disclosures by both British Columbia and Manitoba that they want a bigger tax bite. One mining company calculates that the combined effects of the British Columbia and federal taxes could be a 104% assessment against its income.

Falconbridge Nickel Mines comments that it will be re-evaluating expansion plans in the Sudbury area. Hudson Bay Mining and Smelting President H.A. McKenzie says the company's Stikine copper project in northwestern British Columbia is "in jeopardy."

But International Nickel Chairman L. Edward Grubb asserts: "We cannot help but believe that as the long-range impact of the various tax programs becomes clearer, modifications will be made."

Chlorine demand shifts

After '75, the inorganic chemical industry will move up behind organics to become the second-biggest consumer of chlorine. That was the prediction of Allied Chemical's H.W. Schultze at the Chlorine Institute's bicentennial symposium in San Francisco last week.

Next year, said Schultze, total chlorine demand will reach about 12 million net tons. The breakdown by industry, he added, will be organic chemicals, 8.43 million tons; pulp and paper, 1.42 million tons; inorganic chemicals, 1.15 million tons; water treatment, 527,000 tons; miscellaneous uses, 471,000 tons.

Schultze asserted that the growth of chlorinated hydrocarbons (especially vinyl chloride, chloromethanes and propylene chlorohydrin intermediates) will have the biggest impact on the growth of chlorine demand. He cautioned, however, that feedstock shortages and environmental problems in manufacture, use and disposal of chlorinated hydrocarbons could curtail that growth.

In inorganics, said Schultze, the increase in titanium dioxide production via the chloride route also should boost chlorine demand.

One industry that Schultze said would reduce its demand for chlorine is pulp and paper. Reason: recent success of the oxygen bleaching technique in paper production could substantially cut back chlorine use in bleaching.

Schultze forecast a growth rate of 6% for chlorine in the U.S. and 7-8% worldwide during the next 10 years. The faster foreign rate, he said, is a result of more rapid gains abroad by organic chemicals, particularly plastics.

Schultze stated that demand will not increase as fast for caustic soda, caustic potash, metallic sodium, potassium nitrate, magnesium and other by-products of chlorine manufacture as for chlorine.

How now, biphenyl cow?

About 1,000 Michigan dairy cows were quarantined last week after a 10-month investigation by federal and state agencies tied a drop in milk production to feed tainted by a fire-retardant chemical.

The investigation disclosed that the affected cows, producing both consumer- and industrial-grade milk, were given feed contaminated with brominated biphenyl, a flameproofing material for roofing and textiles. The chemical was accidentally blended with magnesium oxide, a milk production booster, in special feed mixes prepared by Michigan Farm Bureau Services (Lansing).

The probe found that the fire retardant and magnesium oxide were packaged in similar brown bags by the manufacturer, Michigan Chemical (St. Louis, Mich.).

Michigan officials say the tainted milk may have been distributed, but add that there is little health threat to consumers because in the packaging process it was greatly diluted with milk from unaffected herds.

Health authorities are uncertain of the effect of brominated biphenyl on humans, but state officials say the level of the chemical in the milk was "considerably" higher than is permitted under federal regulations.

GCA'S COLE: Powder coatings sales will jump, but fall short of earlier forecasts.

Coated with uncertainty

Sales of powder coating materials and application equipment will pick up significantly during the rest of the decade—but perhaps not as quickly as had been expected. That was the forecast of GCA Associates President Gordon E. Cole, Jr., at a powder coatings conference sponsored by New York University in New York last week.

Because of the uncertainties about automotive and glass bottle developments, Cole said, GCA's earlier sales forecast of 250 million lbs. of powder coating materials in '80 probably will not be reached until '82 or '83. In '74, he predicted, sales of the material will amount to 40 million lbs.

Large automatic coating installations will grow in popularity, Cole said, because they save on energy and raw materials. On the other hand, the use of powder coating for automobile tops will be "deferred," he said, because manufacturers are busy converting to the production of compact cars, lack the extra capital needed to develop new coating equipment for car tops.

Cole also stated that it is not certain when there will be large-volume powder coating of glass bottles for carbonated beverages. He said much will depend on the actions of soft-drink producers and on consumer protection legislation.

The biggest '73 powder coatings markets, said Cole, included piping; electrical, fire and marine equipment; appliances and wire goods; metal furniture. Epoxy, vinyl and polyester coatings went into these applications.