NIOSH

CRITERIA FOR A RECOMMENDED STANDARD....

OCCUPATIONAL EXPOSURE TO

VINYL ACETATE

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

criteria for a recommended standard....

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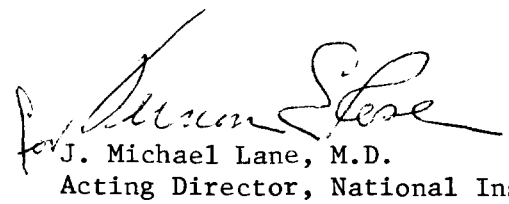
PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and provide for the safety of workers occupationally exposed to an ever-increasing number of potential hazards. The National Institute for Occupational Safety and Health (NIOSH) evaluates all available research data and criteria and recommends standards for occupational exposure. The Secretary of Labor will weigh these recommendations along with other considerations, such as feasibility and means of implementation, in promulgating regulatory standards.

NIOSH will periodically review the recommended standards to ensure continuing protection of workers and will make successive reports as new research and epidemiologic studies are completed and as sampling and analytical methods are developed.

The contributions to this document on vinyl acetate by NIOSH staff, other Federal agencies or departments, the review consultants, the reviewers selected by the Society of the Plastics Industry, Inc., the American Academy of Occupational Medicine, the American Academy of Industrial Hygiene, and Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, are gratefully acknowledged.

The views and conclusions expressed in this document, together with the recommendations for a standard, are those of NIOSH. They are not necessarily those of the consultants, the reviewers selected by professional societies, or other Federal agencies. However, all comments, whether or not incorporated, have been sent with the criteria document to the Occupational Safety and Health Administration for consideration in setting the standard. The review consultants and the Federal agencies which received the document for review appear on pages v and vi.



for J. Michael Lane, M.D.
Acting Director, National Institute
for Occupational Safety and Health

The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for the development of the criteria and recommended standard for vinyl acetate. Alfred N. Milbert, Ph.D., and Jerry LR Chandler, Ph.D., of this Division served as criteria managers. SRI International developed the basic information for consideration by NIOSH staff and consultants under contract CDC-99-74-31.

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I. RECOMMENDATIONS FOR A VINYL ACETATE STANDARD

NIOSH recommends that employee exposure to vinyl acetate in the workplace be controlled by adherence to the following sections. The recommended standard is designed to protect the health and provide for the safety of employees for up to a 10-hour workshift, 40-hour workweek, over a working lifetime. Compliance with all sections of the standard should prevent adverse effects of vinyl acetate on the health of workers and provide for their safety. Sufficient technology exists to permit compliance with the recommended standard. Although NIOSH considers the workplace environmental limit to be a safe level based on current information, the employer should regard it as the upper boundary of exposure and make every effort to maintain exposures as low as possible. The standard will be subject to review and revision as necessary.

Vinyl acetate, $CH_3COOCH=CH_2$, is a liquid at room temperature and is easily vaporized. Synonyms for vinyl acetate include: acetic acid, vinyl ester; acetic acid, ethenyl ester; vinyl A monomer; ethenyl ethanoate; and Vy Ac. "Occupational exposure to vinyl acetate" is defined as exposure to airborne vinyl acetate at concentrations above one-half the recommended ceiling limit. Exposure to airborne vinyl acetate at concentrations at or below one-half the recommended ceiling limit will require adherence to the following Sections only: Sections 1(b), 2(a,c,d), 3, 4, 5, 6, 7, and 8(a,c).

The recommended standard is based on data indicating that vinyl acetate vapor at concentrations below 250 mg/cu m is a primary irritant to the upper respiratory tract and eyes, and that the liquid may irritate skin to the point of vesiculation. The irritations reported have all been reversible, and there are no known residual systemic effects.

Section 1 - Environmental (Workplace Air)

(a) Concentrations

Exposure to vinyl acetate in the workplace shall be controlled so that employees are not exposed at concentrations greater than 15 milligrams per cubic meter of air, or 4 parts per million parts of air, measured as a ceiling concentration in samples collected during any 15-minute period.

(b) Sampling and Analysis

Workroom air samples shall be collected and analyzed as described in Appendix I, or by any other methods at least equivalent in accuracy, precision, and sensitivity.

Section 2 - Medical

Medical surveillance shall be made available as outlined below to all employees subject to occupational exposure to vinyl acetate.

(a) Preplacement examinations shall include at least:

(1) Comprehensive medical and work histories, with special emphasis directed to evidence of any preexisting eye, respiratory, or skin disorders.

(2) Physical examination giving particular attention to the upper respiratory tract, eyes, and skin.

(3) A judgment of the employee's ability to use positive pressure air-supplied respirators.

(b) Periodic examinations shall be made available at least annually, except as otherwise determined by the responsible physician, and shall include:

(1) Interim medical and work histories.

(2) Physical examination as outlined in paragraph (a)(2) of this section.

(c) Applicants or employees found during examinations to have medical conditions that could be directly or indirectly aggravated by exposure to vinyl acetate, eg, chronic irritation of the respiratory tract, chronic inflammatory conditions of the skin, or chronic eye irritation, shall be counseled on the increased risk of impairment of their health from working with the compound.

(d) Pertinent medical records for all employees subject to exposure to vinyl acetate in the workplace shall be retained for at least 30 years after termination of employment. Records of environmental exposures applicable to an employee shall be included in that employee's medical records. These records shall be made available to the designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

Section 3 - Labeling and Posting

All labels and warning signs shall be printed both in English and in the predominant language of non-English-reading workers. Employees unable to read the labels and signs provided shall receive information regarding hazardous

areas and shall be informed of the instructions printed on labels and signs.

(a) Labeling

Each container of vinyl acetate shall carry, in a readily visible location, a label which bears the trade name of the product, if appropriate, and information on its known effects on human health. The name and pertinent information shall be arranged as in the example below.

VINYL ACETATE
(Trade Name)

DANGER! EXTREMELY FLAMMABLE
MAY POLYMERIZE VIOLENTLY IF HEATED
MAY CAUSE SKIN AND EYE IRRITATION

Keep away from heat, sparks, and open flame.
Keep container closed when not in use.
Use only with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.
Avoid prolonged or repeated contact with skin.
Ground metal containers when emptying or filling.

FIRST AID: In case of contact of liquid with eyes or skin, flush with copious amounts of water. Wash clothing before reuse.

SPILL OR LEAK: Contain the product within an area and flush with water spray. Vinyl acetate will float on water and create a fire hazard.

FIREFIGHTING: In case of fire, use foam, dry chemical, carbon dioxide, or water spray.

(b) Posting

(1) The following warning sign shall be posted in readily visible locations at or near all entrances to areas where vinyl acetate is manufactured, used, or stored.

VINYL ACETATE

DANGER! EXTREMELY FLAMMABLE
MAY POLYMERIZE VIOLENTLY IF HEATED
MAY CAUSE SKIN AND EYE IRRITATION

Keep away from heat, sparks, and open flame.
Use only with adequate ventilation.
Avoid prolonged or repeated breathing of vapor.

(2) If the use of respirators is permissible in accordance with Section 4 (c), the following statement shall be displayed in addition to the sign required in Section 3(b):

RESPIRATORY PROTECTION REQUIRED IN THIS AREA

Section 4 - Personal Protective Clothing and Equipment

Engineering controls shall be used when needed to keep concentrations of airborne vinyl acetate at or below the recommended ceiling limit and to minimize skin and eye contact. In addition, protective equipment and clothing shall be provided to employees when necessary.

(a) Eye Protection

Employers shall provide chemical safety goggles or face shields (8-inch minimum) with goggles and shall ensure that employees wear this protective equipment during any operation in which there is the likelihood of exposure to liquid vinyl acetate. Eye protective devices shall be selected, used, and maintained in accordance with 29 CFR 1910.133.

(b) Protective Clothing

Employees shall wear appropriate protective clothing, including gloves, aprons, suits, and boots, when needed, to prevent skin contact with liquid vinyl acetate.

(c) Respiratory Protection

(1) The use of respirators to achieve compliance with the recommended exposure limit is permitted only:

(A) During the time required to install or test the necessary engineering controls.

(B) During performance of nonroutine maintenance or repair activities, during work in confined spaces, or during emergencies when the concentration of airborne vinyl acetate may exceed the recommended environmental limit.

(2) When use of a respirator is permitted, it shall be selected and used in accordance with the following requirements:

(A) Employers shall establish and enforce respiratory protective programs meeting the requirements of 29 CFR 1910.134.

(B) Employers shall provide respirators in accordance with Table I-1 and shall ensure that employees use the respirators provided when necessary. The respiratory protective devices provided in conformance with Table I-1 shall be those approved by NIOSH and the Mine Safety and Health Administration as specified under 30 CFR 11.

(C) Respirators specified for use in higher concentrations of airborne vinyl acetate may be used in atmospheres of lower concentrations.

(D) Employers shall ensure that respirators are adequately cleaned and maintained and that employees are instructed and drilled at least annually in the proper use and testing for leakage of respirators assigned to them.

(E) Respirators shall be easily accessible, and employees shall be informed of their locations.

Section 5 - Informing Employees of Hazards from Vinyl Acetate

(a) All new and present employees working in areas where occupational exposure to vinyl acetate may reasonably be expected to occur shall be informed of the hazards of such employment, relevant symptoms of overexposure, appropriate emergency procedures, and conditions and precautions for the safe use and handling of vinyl acetate, including the information prescribed in paragraph (b) of this section. Employees shall be advised of the availability of this information.

(b) Employers shall institute a continuing education program, conducted by persons qualified by experience or training, to ensure that all employees have current knowledge of job hazards, proper maintenance, and cleanup methods. The instructional program shall include oral and written descriptions of the general nature of the environmental and medical surveillance procedures and of the advantages to the employee of participating in these surveillance procedures.

(c) Required information shall be recorded on the "Material Safety Data Sheet" shown in Appendix II or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

TABLE I-1

RESPIRATOR SELECTION GUIDE FOR VINYL ACETATE

Concentration	Respirator Type Approved under Provisions of 30 CFR 11
Less than or equal to 140 mg/cu m	Type C supplied-air respirator with half-mask facepiece operated in pressure-demand mode
Less than or equal to 1,400 mg/cu m	(1) Gas mask with full facepiece and chin-type organic vapor canister (maximum service life, 2 hr) (2) Gas mask with full facepiece and chest- or back-mounted organic vapor canister (3) Type C supplied-air respirator with full facepiece operated in positive pressure mode (4) Self-contained breathing apparatus with full facepiece operated in positive pressure mode
Less than or equal to 14,000 mg/cu m	(1) Type C supplied-air respirator with half-mask or full facepiece operated in continuous-flow, pressure-demand, or other positive pressure mode (2) Type C supplied-air respirator with hood, helmet, or suit operated in continuous-flow mode
Greater than 14,000 mg/cu m	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode (2) Combination Type C supplied-air respirator with full facepiece operated in pressure-demand mode and with auxiliary self-contained air supply
Emergency (entry into area of unknown concentration)	Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode

Section 6 - Work Practices

(a) Engineering Controls

All electrical equipment shall meet the requirements of 29 CFR 1910 for hazardous locations. Ventilation systems, if used, shall be designed to prevent the accumulation or recirculation of vinyl acetate in the workplace environment and to effectively maintain safe levels of vinyl acetate in the breathing zones of employees. Exhaust ventilation systems discharging to outside air shall conform with applicable local, state, and Federal air pollution regulations and shall not constitute a hazard to employees or to the general population. Ventilation systems shall be regularly maintained and cleaned to ensure effectiveness, which shall be verified by at least annual airflow measurements. Results of such airflow measurements shall be recorded and such records kept for at least 1 year.

(b) Confined Spaces

(1) Entry into confined spaces, such as tanks, pits, and process vessels, shall be controlled by a permit system. Permits shall be signed by an authorized employer representative and shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate and that precautions have been taken to ensure that prescribed procedures will be followed.

(2) Confined spaces that have contained vinyl acetate shall be cleaned with water, purged with air, thoroughly ventilated, inspected, and tested for oxygen deficiency and for the presence of vinyl acetate and any other known or suspected contaminants. Every effort shall be made to prevent inadvertent release of vinyl acetate into confined spaces in which work is in progress. Vinyl acetate supply lines shall be disconnected or blocked off before and while such work is in progress.

(3) If the concentration of vinyl acetate in the confined space exceeds the recommended environmental limit, respiratory protective equipment is required for entry.

(4) No employee shall enter any confined space that does not have an entryway large enough to admit an employee wearing safety harness, lifeline, and appropriate respiratory equipment as specified in Section 4(c).

(5) Confined spaces shall be ventilated while work is in progress to keep the concentration of vinyl acetate at or below the recommended limit, to keep the concentration of other contaminants below dangerous levels, and to prevent oxygen deficiency.

(6) Anyone entering a confined space shall be kept under observation from the outside by another properly trained and protected worker. An additional supplied-air or self-contained breathing apparatus with safety harness and lifeline shall be located outside the confined space for emergency use. The person entering the confined space shall maintain continuous communication with the standby worker.

(c) Emergency Procedures

Emergency plans and procedures shall be developed for all work areas where there is a potential for exposure to vinyl acetate. They shall include those specified below and any others considered appropriate for a specific operation or process. Employees shall be instructed in the effective implementation of these plans and procedures.

(1) Plans shall be developed for obtaining emergency medical care and for the transportation of injured workers. A sufficient number of employees shall be trained in first aid so that assistance is available immediately when necessary.

(2) Spills of vinyl acetate shall be cleaned up immediately. Spill areas shall be posted and secured. All sources of ignition shall be eliminated. Only authorized personnel, adequately protected and properly trained, shall be permitted to enter the area to shut off sources of vinyl acetate. If sufficient drainage to suitable collection basins is available, the spilled liquid can be hosed away with large quantities of water. A water spray can be used to knock down vapors. Because vinyl acetate floats on water, spills shall not be allowed to enter public sewers or drains in amounts that could result in explosion or fire hazards.

(3) The collected runoff shall be either recovered or destroyed by chemical degradation or burning, in accordance with applicable Federal, state, and local regulations. If a vacuum system is used to remove spilled vinyl acetate, there shall be no sources of ignition in the vicinity and appropriate flashback-prevention devices shall be provided and maintained in proper operating condition.

(d) Storage

Vinyl acetate shall be stored at temperatures less than 100 F (37.8 C) in well-ventilated areas and kept away from ignition sources such as heat and direct sunlight. No heating apparatus capable of exceeding 80% of the autoignition temperature of vinyl acetate (427 C) shall be used in vinyl acetate storage areas. The Federal standard for the storage and handling of flammable liquids is contained in 29 CFR 1910.106. The storage of vinyl

acetate in glass containers should be avoided. Vinyl acetate shall not be stored in the same areas as oxidizing agents or other incompatible chemicals. Containers of vinyl acetate shall be kept tightly closed when not in use and shall be stored so as to minimize accidental ruptures and spills.

(e) Handling and General Work Practices

(1) Before maintenance work is undertaken on equipment or systems, sources of vinyl acetate shall be disconnected and blocked off.

(2) Employees who experience skin contact with liquid vinyl acetate shall wash or shower to remove vinyl acetate from the skin. Contaminated clothing shall be removed and either cleaned before reuse or discarded. Uncleaned, contaminated clothing shall be stored in a container that is impervious to vinyl acetate. Personnel who clean contaminated clothing shall be informed of the hazards involved and be provided with guidelines on how to handle such clothing safely.

(3) Smoking and the carrying of matches, lighters, or other instruments of ignition shall be prohibited in all vinyl acetate work areas.

(4) Waste material contaminated with vinyl acetate shall be disposed of in ways that pose no hazard to employees. Disposal methods must conform with applicable local, state, and Federal regulations and must not constitute a hazard to the surrounding population or to the environment.

Section 7 - Sanitation

(a) The preparation, storage, dispensing (including vending machines), or consumption of food shall be prohibited in vinyl acetate work areas.

(b) Employees who handle vinyl acetate or equipment contaminated with vinyl acetate shall be instructed to wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

Section 8 - Monitoring and Recordkeeping Requirements

(a) Industrial Hygiene Surveys

Employers shall determine by industrial hygiene survey whether there is exposure to airborne vinyl acetate at concentrations greater than one-half the recommended ceiling limit. Records of these surveys, including the basis for any conclusion that concentrations of airborne vinyl acetate are at or below

one-half the recommended limit, shall be kept. Surveys shall be repeated at least annually and as soon as possible after any process change likely to result in increased concentrations of airborne vinyl acetate in the workplace. If it is determined that concentrations of airborne vinyl acetate are above one-half of the recommended ceiling limit, the following requirements shall apply:

(b) Personal Monitoring

(1) A program of personal monitoring shall be instituted to identify and measure, or permit calculation of, the exposure of each employee subject to exposure to vinyl acetate. Source and area monitoring may be used to supplement personal monitoring.

(2) In all personal monitoring, samples representative of the exposure to vinyl acetate in the breathing zone of the employee shall be collected. Procedures for sampling and analysis shall be in accordance with Section 1(b).

(3) For each determination of an occupational exposure concentration, a sufficient number of samples shall be collected to characterize employees' exposures during each workshift. Variations in work and production schedules and in employee locations and job functions shall be considered when deciding upon collection schedules.

(4) Each operation in each work area shall be sampled at least once every 6 months or as otherwise indicated by a professional industrial hygienist. If an employee is found to be exposed to vinyl acetate at concentrations above the recommended ceiling limit, control measures shall be initiated, the employee shall be notified of the exposure and of the control measures being implemented, and the exposure of the employee shall be measured at least once every week. Such monitoring shall continue until two consecutive determinations, at least 1 week apart, indicate that the employee's exposure is no longer in excess of the recommended limit. At that point, semiannual monitoring may be resumed. If such monitoring indicates that the employee's exposure no longer exceeds one-half of the recommended ceiling limit, personal monitoring may be discontinued.

(c) Recordkeeping

Records of environmental monitoring for each employee shall be retained for at least 30 years after the individual's employment has ended. These records shall include the name of the employee being monitored, duties performed and job locations within the worksite, dates and times of measurements, sampling and analytical methods used, number, duration, and

results of samples taken, concentrations of airborne vinyl acetate estimated from these samples, and the type of personal protection used, if any. Employees shall be able to obtain information on their own environmental exposures. These records shall be made available upon request to designated representatives of the Secretary of Labor, of the Secretary of Health, Education, and Welfare, and of the employee or former employee.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon that were prepared to meet the need for preventing impairment of health resulting from workplace exposure to vinyl acetate. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe exposure levels...at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

After reviewing data and consulting with others, NIOSH formalized a system for the development of criteria on which standards can be established to protect the health and to provide for the safety of employees exposed to hazardous chemical and physical agents. The criteria and recommended standard should enable management and labor to develop better engineering controls resulting in more healthful work environments. Simple compliance with the recommended standard should not be the final goal.

These criteria for a standard for vinyl acetate are part of a continuing series of criteria developed by NIOSH. The proposed standard applies to workplace exposure arising from the processing, manufacture, use, storage, and handling of vinyl acetate. The standard was not designed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted. It is intended to (1) protect against impairment of health by vinyl acetate, (2) be measurable by techniques that are valid, reproducible, and available to industry and government agencies, and (3) be attainable with existing technology.

During the development of the recommended standard for occupational exposure to vinyl acetate, it became apparent that there are deficiencies in available information on (1) effects on humans and animals exposed to vinyl acetate at low levels for extended periods, (2) possible carcinogenic, mutagenic, teratogenic, or reproductive effects of vinyl acetate on animals and humans, (3) the utility of the electroencephalograph in estimating the toxic potential of vinyl acetate, and (4) sensitive analytical methods and direct-reading monitoring devices for airborne vinyl acetate.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Vinyl acetate, molecular formula CH3COOCH=CH2, is a colorless flammable liquid at room temperature. It has a vapor pressure of 100 mmHg at 21.5 C [1] and a boiling point of 72.7 C. Its odor is at first pleasant but quickly becomes sharp and irritating [2]. The threshold of odor detection for vinyl acetate has been reported to be as low as 1 mg/cu m (0.284 ppm) [3]. Olfactory fatigue has occurred at 19.5 ppm (68.3 mg/cu m) [4]. Some salient physical and chemical properties of vinyl acetate are listed in Table XI-1 [1,2,5-9]. Vinyl acetate is produced by a vapor-phase reaction between ethylene and acetic acid in the presence of a palladium catalyst or between acetylene and acetic acid in the presence of a zinc acetate catalyst [7]. In the United States, 1,481 and 1,606 million pounds of vinyl acetate were produced in 1976 and 1977, respectively [10,11].

Vinyl acetate is used primarily in polymerization processes, eg, to produce polyvinyl acetate, polyvinyl alcohol, and vinyl chloride-vinyl acetate copolymer [2]. The polymers, usually made as emulsions, suspensions, solutions, or resins, are used to prepare adhesives, paints, paper coatings, and textile finishes [7]. Low-molecular-weight polyvinyl acetate is used as a chewing gum base [12]. Vinyl acetate is extremely flammable and forms explosive mixtures at from 2.6 to 13.4% by volume in air [5].

Occupational exposure to vinyl acetate may occur in any work involving the production, storage, transport, or use of the chemical. Occupations with potential exposure to vinyl acetate are listed in Table XI-2 [2,5,8].

NIOSH estimates that approximately 70,000 workers are potentially exposed to vinyl acetate in the United States.

Historical Reports

The earliest report of vinyl acetate seems to have appeared in 1912 [2]. At that time, it was a minor byproduct formed when acetylene and acetic acid were reacted to produce ethylidene diacetate. During World War I, vinyl acetate was prepared and polymerized in Germany [13]. In the late 1920's, vinyl acetate production was commercialized; acetylene and acetic acid were reacted in the liquid phase using such catalysts as mercuric oxide [13].

The toxicity of vinyl acetate was evaluated in 1949 as part of a range-finding study of 96 chemicals by Carpenter et al [14]. Sherman rats were exposed to the test substances for 4 hours to determine the nominal concentrations necessary to kill two to four of six exposed animals within 14

days. For vinyl acetate, this concentration was 4,000 ppm (14,000 mg/cu m), causing the authors to classify it as a "moderate hazard."

Before 1970, few industrial exposure studies had been conducted on vinyl compounds other than vinyl chloride. Research on the biologic effects of vinyl acetate and other vinyl compounds was accelerated after the carcinogenic hazard of vinyl chloride exposure became recognized.

Effects on Humans

Much of the information on short-term effects of vinyl acetate on humans has come from controlled experimental exposures of volunteers and from one short-term study at a vinyl acetate production plant.

Gofmekler [3] tested vinyl acetate on volunteers to determine threshold concentrations for olfactory perception, changes in light sensitivity of the eye, and ability to produce a conditioned-response change in the electrical activity of the brain. Vinyl acetate concentrations were determined by a colorimetric method reported to have a sensitivity of 0.025 μg/ml of sample.

Odor determinations were made by 77 subjects, ranging from 20 to 65 years old [3]. Each test concentration was administered for 2-3 hours and was repeated at an average interval of 3-5 days with each person during a 2-month period.

Light sensitivity was determined in 15 persons over a 3.5-month period [3]. Subjects were placed in a dark room free of noise and other extraneous stimuli. After their eyes became dark adapted, their ability to perceive a light stimulus from an ADM adaptometer was measured. After 5-7 days of exposure to air to establish baseline data on light sensitivity, subjects were exposed to vinyl acetate at least three times at each concentration tested. Only those concentrations that produced a change in light sensitivity at least twice the mean error of the baseline values were considered effective.

To determine the concentration of vinyl acetate that could produce a conditioned response, two subjects inhaled vinyl acetate while their brain electrical activity was recorded on an electroencephalograph (EEG) [3]. After 10-15 seconds of exposure, the vinyl acetate stimulus was reinforced by light, which caused a desynchronization in the EEG. Through association with the light (unconditioned stimulus), addition of vinyl acetate to the inspired air could become a conditioned stimulus, producing EEG desynchronization before the light was presented [15]. Vinyl acetate exposures were conducted once a day at gradually decreasing concentrations to determine the lowest concentration that could produce this conditioned change in brain electrical activity.

Gofmekler [3] found that the minimum perceptible concentration of vinyl acetate in odor detection tests was 1.0 mg/cu m (0.3 ppm), while 0.7 mg/cu m (0.2 ppm) was the maximum imperceptible concentration. The minimum active and maximum inactive concentrations for affecting light sensitivity of the eye were 0.77 and 0.60 mg/cu m (0.22 and 0.17 ppm), respectively. For production of a conditioned change in brain electrical activity, the minimum active concentration was 0.32 mg/cu m (0.09 ppm) and the maximum inactive concentration was 0.21 mg/cu m (0.06 ppm); apparently, vinyl acetate at these concentrations did not produce any observable unconditioned change in EEG patterns. The author concluded that the maximum acceptable concentration for occupational exposure to vinyl acetate should be 0.20 mg/cu m (0.06 ppm). However, this study presented no evidence that adverse effects resulted from exposure to vinyl acetate at the low concentrations that produced positive responses in these tests.

In 1968, investigators [4] at the Mellon Institute described olfactory perception findings in nine volunteers exposed to vinyl acetate vapor at various concentrations for 2-minute periods. Each concentration was tested twice, and the concentrations were measured by gas chromatography; no other experimental details were provided. The lowest concentration at which all subjects could detect an odor was 1.3 ppm (4.6 mg/cu m), and the highest concentration at which all subjects (with one questionable exception) could not detect an odor was 0.6 ppm (2.1 mg/cu m).

The investigators then determined the reactions of four volunteers exposed to vinyl acetate at higher concentrations for longer periods [4]. In experiments conducted on 4 consecutive days, from one to four of the subjects inhaled air containing vinyl acetate at various concentrations ranging from 19.5 to 71.5 ppm (68.3-250.3 mg/cu m) for 0.5-4 hours in a test chamber. Exposure information and the effects reported by each subject are shown in Table III-1. All subjects agreed that they could not work for 8 hours at the highest concentration tested, 71.5 ppm. Although all subjects developed olfactory fatigue, the investigators noted that they returned to the chamber within 10 minutes after each test and reported that the odor was as strong as it had been at the beginning of the test, indicating rapid recovery from olfactory fatigue.

This report [4] indicates that vinyl acetate can irritate the mucous membranes of the throat at concentrations as low as 19.5 ppm (68.3 mg/cu m) and can produce eye irritation at 71.5 ppm (250.3 mg/cu m). It also shows a wide variation in individual sensitivity; only one (B) of three subjects reported throat irritation at 19.5 ppm and another (C) did not report throat irritation at any concentration, although he did experience throat "dryness" at 71.5 ppm.

In 1969, EI du Pont de Nemours and Company conducted an industrial hygiene survey of the vinyl acetate production area at its Niagara Falls plant [16]. Air was sampled from the breathing zones of the workers with a midget impinger

TABLE III-1

EFFECTS OF SHORT-TERM EXPOSURE OF FOUR VOLUNTEERS TO VINYL ACETATE VAPOR

Concentration (ppm)	Concentration (mg/cu m)	Duration (hr)	Subject and Effects
19.5	68.3	4	A - Complete olfactory fatigue in 71 min; no irritative effects B - Complete olfactory fatigue in 3 min*; slight, persistent throat irritation starting at 1 min C - Complete olfactory fatigue in 116 min; no irritative effects
22.9	80.2	4	A - Complete olfactory fatigue in 92 min; no irritative effects
34.2	119.7	2	A - Olfactory fatigue, never complete; transient nose and throat irritation B - Olfactory fatigue, never complete; throat irritation, no worse than in preceding experiment C - Complete olfactory fatigue in 40 min; no irritative effects
71.5**	250.3	0.5	A - Strong odor; olfactory fatigue, never complete; slight throat irritation at 13 min, lasting 20 min after exposure; transient eye irritation at 20 min B - Nearly complete olfactory fatigue; slight, persistent throat irritation at 4 min, lasting 30 min after exposure C - Strong odor; olfactory fatigue, never complete; reddening of sclera at 10 min, lasting 1 hr after exposure; dryness of throat at 20 min, lasting 2 hr after exposure D - Sharp odor; olfactory fatigue, never complete; slight eye and throat irritation at 1 min, lasting until end of exposure

*Considered questionable by the author
**Consensus: "We could not work at this concentration for 8 hours."

Adapted from reference 4

containing 10 cc of dimethylformamide as the absorbent, and the solution was analyzed by gas chromatography. Samples were collected in both summer and winter. Time-weighted average (TWA) concentrations ranged from 0.4 to 4.9 ppm (1.4-17.2 mg/cu m), with no seasonal variation detected. When workers were questioned about eye or upper respiratory tract irritation experiences, there were no affirmative responses. The only irritation reported was that which had resulted from high concentrations of airborne vinyl acetate during "spills." No spills or leaks occurred during the survey, so that vinyl acetate concentrations capable of producing irritation could not be determined.

According to a Union Carbide Corporation publication [17], plant experience indicated that some persons might react to dermal contact with vinyl acetate with blister formation, particularly on the thin skin of the finger web and the underside of the wrist, and that continued contact, such as that afforded by clothing wet with vinyl acetate, might result in severe irritation or blistering of the skin [17].

Epidemiologic Studies

The only available epidemiologic data on vinyl acetate resulted from a cross-sectional study. In 1969, Deese and Joyner [18] described the effects of long-term exposure of chemical operators to vinyl acetate in three production units of a Gulf Coast chemical plant. The study population consisted of 21 volunteers of the 26 operators then assigned to a vinyl acetate complex. The men ranged in age from 26 to 61 years (average 45.3 years) and had been employed in the vinyl acetate complex for an average of 15.2 years; 3 had been employed for less than 2 years, 12 for 2-20 years, and 6 for over 20 years. The control group, 21 operators from other production units not involved with vinyl acetate, was selected from participants in the company's multiphasic screening program, which included complete physical examinations, chest x-rays films, spirometry, electrocardiograms (ECG's), and analyses of blood and urine. The controls were closely matched in age with the vinyl acetate workers. Medical records were reviewed for the previous 5 years for all participants in the study, and the results of their most recent medical examinations were compared. The 21 exposed workers also answered a supplementary questionnaire designed to elicit their personal opinions regarding effects of exposure to vinyl acetate.

To characterize employee exposure to vinyl acetate, the authors collected 40 air samples at 3-6 sites in each of 3 production units during 2 sampling periods 1 month apart [18]. Both 10-minute and 2-hour samples were collected in order to characterize average exposure and excursions. Samples were analyzed for vinyl acetate by gas chromatography, and TWA exposures were calculated for the operators in each unit.

Results of these analyses showed vinyl acetate concentrations ranging from undetectable to 49.3 ppm (173 mg/cu m), with a mean of 8.6 ppm (30 mg/cu m);

83% of the samples showed concentrations of less than 10 ppm (35 mg/cu m) [18]. TWA exposures for operators in the three process units were 8.2, 7.7, and 5.2 ppm (29, 27, and 18 mg/cu m). The authors assumed that these values were representative of the long-term exposure of workers in the study, since operating conditions, processes, and equipment in the plant had been unchanged for more than 5 years. They noted, however, that these values did not reflect high exposures that might occur during nonroutine operations. Vinyl acetate concentrations of 123.3-326.5 ppm (432-1,143 mg/cu m) were measured during one such operation, the opening of a hopper door to remove material, which required about 3 minutes to complete and was carried out an average of twice a day. The lowest concentrations of vinyl acetate, below 0.8 ppm (2.8 mg/cu m), were found in an "acoustically designed" control room equipped with a positive pressure ventilating system; the mean concentration inside each control room was lower than that of the general plant environs.

No major differences were found between the group exposed to vinyl acetate and the controls [18]. A comparison of results of their most recent medical examinations showed some differences in mean blood chemistry values, but all mean values were within normal limits. The numbers of individual abnormalities in blood chemistry were similar in the two groups (12 in the vinyl acetate group and 9 in controls). Medical records for the two groups showed that the numbers of days lost due to illness during the last 5 years did not differ significantly; however, the number of episodes of absence was almost twice as high in the control group as in the exposed group. Vinyl acetate workers lost more time due to respiratory illness, but the authors attributed this excess to one worker with a recurrent upper respiratory infection; similarly, excess absenteeism from gastrointestinal illness in the exposed group was attributable to a single individual with an inflamed gall bladder.

In responses to the questionnaire, 13 of 21 vinyl acetate workers (61%) said they had never been bothered by vinyl acetate, 15 (71%) said it did not irritate their eyes, nose, or throat, and 18 (86%) reported no dermatitis [18]. Two were "bothered" by the odor, and three specifically mentioned eye irritation. Two workers reported upper respiratory tract irritation, specifically associated in one case with unplugging the hoppers, and one reported "a hurting in the chest" from breathing vinyl acetate at high concentrations. Skin effects noted by the workers included dryness of hands and irritation between the fingers; two workers reported that they had experienced skin rashes. The authors reported that there was no positive relationship between length of employment and responses to the questionnaire.

During air sampling, five subjects, including Deese and a laboratory analyst and one operator from each production unit, were asked to record the degrees of odor detection and irritation of the eyes and of the upper respiratory tract that they experienced [18]. Data from 12 sampling operations were reported; 1 sample contained vinyl acetate at a concentration of 21.6 ppm (75.6 mg/cu m) and the remainder ranged between 0.4 and 9.9 ppm (1.4-34.7 mg/cu m).

Three of three subjects exposed at 0.4 ppm (1.4 mg/cu m) reported detecting a slight odor of vinyl acetate [18]. One of three subjects exposed at 7.6 ppm (26.6 mg/cu m) was unable to detect an odor, but all subjects detected the odor at higher concentrations; at 21.6 ppm (75.6 mg/cu m), all three exposed subjects agreed that the odor was marked. The authors noted that the three operators tended to be less sensitive to the odor of vinyl acetate than the two persons, one of whom was Deese, who had not been chronically exposed to odors of various chemicals.

Although Deese experienced slight eye irritation at 5.7 and 6.8 ppm (20.0 and 23.8 mg/cu m), no other eye irritation was reported at concentrations below 10 ppm (35 mg/cu m) [18]. However, all three subjects exposed at 21.6 ppm (75.6 mg/cu m) agreed that the eye irritation they experienced would be intolerable over a prolonged period. All three subjects also reported either hoarseness or cough at 21.6 ppm, but only Deese had upper respiratory tract irritation at lower concentrations, experiencing hoarseness at 4.2 and 5.7 ppm (14.7 and 20.0 mg/cu m).

The authors [18] concluded that long-term exposure to vinyl acetate at concentrations of 5-10 ppm (18-35 mg/cu m) produced no serious chronic effects. They noted that some subjects might be sensitive at concentrations of about 6 ppm (21 mg/cu m), but that concentrations up to 10 ppm (35 mg/cu m) were unlikely to produce irritation of the eyes or respiratory tract in most workers; however, concentrations above 20 ppm (70 mg/cu m) appeared to produce irritation in most persons. The authors also concluded that liquid vinyl acetate was not a serious skin or eye injurant provided prompt washing was carried out. Since this study was limited to a cross-sectional population of 21 of 26 vinyl acetate operators, no general conclusions can be drawn with respect to mortality or other chronic effects in human populations occupationally exposed to vinyl acetate.

No long-term (over 20 years) epidemiologic studies on vinyl acetate were found in the literature.

Animal Toxicity

In 1968, the Mellon Institute, in an unpublished report [4], summarized the responses of rats, guinea pigs, mice, rabbits, and beagles to inhalation of various concentrations of vinyl acetate for 4 hours in a chamber monitored by gas chromatography. Exposure concentrations or ranges were not fully reported. The 4-hour LC50's for six male rats, six female rats, six male guinea pigs, six male mice, and four male rabbits were 3,987, 3,987, 6,215, 1,546, and 2,511 ppm (13,955, 13,955, 21,753, 5,411, and 8,789 mg/cu m), respectively; no information was given on sublethal effects on any of these species. The one male dog exposed to vinyl acetate at 3,825 ppm (13,388 mg/cu m) for 4 hours survived. The highest concentration at which no

observable adverse effect was seen in a dog was 106 ppm (371 mg/cu m); exposure at 240 ppm (840 mg/cu m) caused some blinking and reddening of the sclera.

In a similar investigation sponsored by the Union Carbide Corporation [17], three groups of rats were exposed to vinyl acetate at 1,000, 4,000, or 8,000 ppm (3,500, 14,000, or 28,000 mg/cu m) for 4, 2, and 2 hours, respectively. All rats survived the exposure at 1,000 ppm, three of six rats died "in two hours" at 4,000 ppm, and all of the rats exposed at 8,000 ppm died "in two hours." No sublethal effects were described. The authors also reported that the oral LD50 of vinyl acetate in rats was 2.92 g/kg and that the percutaneous LD50 (covered, 24-hour contact) in rabbits was greater than 5 ml/kg. In addition, they found that "undiluted" vinyl acetate caused no reaction on the rabbit abdomen, but that 0.5 ml applied to the rabbit eye caused severe irritation or mild burns. The test material contained hydroquinone as an inhibitor, but in concentrations that the authors thought to be innocuous.

In 1967, the Haskell Laboratory, in an unpublished report [19], noted the effects of vinyl acetate inhalation at 91-186 ppm (319-651 mg/cu m) on four dogs. Dogs inhaled vinyl acetate at 91 ppm (319 mg/cu m) 6 hours/day, 5 days/week, for 6 weeks. Two and one-half weeks after this exposure ended, the same dogs were exposed to vinyl acetate at 79 ppm (277 mg/cu m) for 2 weeks and then at 186 ppm (651 mg/cu m) for 1 week. No circulatory abnormalities or evidence of disturbed metabolism were noted at any of these concentrations, but at 186 ppm eye irritation and tearing were apparent. Microscopic and gross examination at autopsy showed no lesions that the pathologist attributed to vinyl acetate exposure.

In 1970, Gage [20] presented the results of a short-term inhalation study of a number of industrial chemicals including vinyl acetate. Four groups of four male and four female Alderley Park specific-pathogen-free rats, weighing an average of 200 g, were exposed to vinyl acetate at 100, 250, 630, or 2,000 ppm (350, 875, 2,205, or 7,000 mg/cu m) for 6 hours/day, 5 days/week, for 3 weeks in chambers monitored by gas-liquid chromatography. Control rats were exposed to air alone. Throughout the study the animals were observed for changes in body weight, clinical condition, and behavior. Urine samples were collected overnight after the last exposure day, for biochemical tests. The animals were then anesthetized with halothane, and blood was obtained by heart puncture, for hematologic tests. The organs were examined grossly, and fixed lung, liver, kidney, spleen, and adrenal tissues were examined microscopically.

Exposure to vinyl acetate at 2,000 ppm caused eye and nose irritation and respiratory difficulty, and these rats gained less weight than the controls [20]. Microscopic examination showed increased numbers of macrophages in their lungs, but no other microscopic or pathologic changes were reported. Female rats exposed at 630 or 250 ppm showed abnormally low weight gains. The

results of urine and blood tests on rats exposed at 250 ppm were reported as "normal." No signs of adverse effects were seen in rats exposed at 100 ppm. No abnormalities were apparent in the organs of rats exposed at 100, 250, or 630 ppm. Gage commented that vinyl acetate was the only unsaturated ester of a saturated carboxylic acid, among those tested, of sufficient volatility to exhibit what he termed "...typically...low toxicity, high concentrations producing irritation and narcosis." He recommended a "provisional occupational limit" of 50 ppm for vinyl acetate.

In a 1968 abstract, Goldstein et al [21] reported the effects of inhaling vinyl acetate, alone and with acetic acid, on white mice of unspecified number, age, sex, weight, and strain. Gross and microscopic observations were made and toxic and lethal doses and cytochrome oxidase and succinic dehydrogenase activities of the pulmonary tissue were measured by unidentified methods.

Vinyl acetate alone produced a clinical picture of irritation, primarily of the respiratory system [21]. Microscopic examination revealed acute edematous-hemorrhagic or sero-fibrino-hemorrhagic inflammation, with or without foci of edematous or edematous-hemorrhagic pneumonia. Capillaries in the lung parenchyma, septa, and bronchial walls were dilated, and there were interstitial, subpleural, or parenchymal hemorrhagic foci scattered through the lungs. According to the authors, the experiment showed that vinyl acetate was about four times as toxic as acetic acid. They also noted that the risk of intoxication following industrial exposure to vinyl acetate was more than three times that following exposure to acetic acid. No other details were presented. Vinyl acetate acted rapidly after being inhaled by the mice, and most of the mortality from vinyl acetate (number of deaths not reported) occurred during the actual exposure. The activities of succinic dehydrogenase and of cytochrome oxidase in the lungs of animals that had inhaled vinyl acetate were lower than those in control animals; the activities of these two enzymes in the lungs of animals inhaling acetic acid were higher than those in the lungs of control animals. The microscopic lesions and enzyme activities produced by mixtures were similar to those produced by vinyl acetate alone, and the levels of "lethal concentrations" and "absolute toxicity" were reported to be quite similar for vinyl acetate with and without acetic acid. The authors did not define these terms.

The abstract [21] stated that, since the biologic activity of vinyl acetate with acetic acid was greater than that expected from a simple additive effect, the combined action of the two compounds was synergistic. Because this abstract did not contain essential experimental data, its contribution toward establishing an occupational health standard for vinyl acetate is minimal, but the abstract suggested that mixed exposures to vinyl acetate and acetic acid, which could occur readily in the industrial environment, may be more hazardous than exposure to either chemical alone.

Bartenev [22], in 1957, investigated the effects of low concentrations of vinyl acetate on central nervous system (CNS) function and on recorded changes

in reflex activity in the rabbit. The author's purpose was to establish the threshold concentrations that would elicit recordable changes in reflex activity. Using the methods of Lyublina and of Parfenov, the author monitored CNS activity by measuring two indices of the reflex activity of the rabbit foot: (1) the time for muscle tension reflex development to attain a value of 0.7 kg; (2) the muscle tension value when the reflex had been attained.

Six male rabbits, with body weights of 2,020-2,450 g, were exposed to vinyl acetate vapor at 125, 250, or 500 mg/cu m (35.5, 71, or 142 ppm) for 40 minutes. No significant changes were observed at 125 mg/cu m, but five of six rabbits exposed at 250 mg/cu m showed decreased times for development of target reflex muscle tension and decreased reflex strength. Three of the rabbits exposed at 500 mg/cu m exhibited sharp fluctuations in the excitability of the CNS that occurred much earlier than similar changes seen at 250 mg/cu m, accompanied by increased times for development of target reflex muscular tension and decreased reflex strength.

Bartenev [22] also evaluated cerebral cortical activity in three rabbits by recording changes in the respiratory component of their reactions to electrical stimulation of the paw. Two positive conditioned stimuli, the sound of a metronome and light from two flashlights, and a negative one, a dim light from another pair of flashlights, were presented to the rabbits twice before exposure, with 5 minutes between presentations, and twice during the 37 minutes when vinyl acetate vapor was being inhaled.

Exposure to vinyl acetate vapor at 25 mg/cu m (7.1 ppm) usually caused no marked effect on higher CNS activity, but, although it did not disturb differentiation, it clearly enhanced the reaction to the metronome when the stimuli were presented to one rabbit three times during an exposure. This rabbit exhibited the same phenomenon at higher concentrations. 50 mg/cu m (14.2 ppm) caused different changes in the nervous activity of each rabbit, manifested particularly by uncertain differentiation between the two light stimuli. More profound changes occurred during exposure to vinyl acetate at 100 mg/cu m. In this situation, the rabbits failed to respond to the sound stimulus after 20-26 minutes of exposure and to the strong light at the end of the exposure period. At that time, a paradoxical response to the weak light was present. Complete recovery of normal responsiveness to the various stimuli required 2-6 days.

Bartenev [22] concluded that (1) the minimum (threshold) concentration of vinyl acetate vapor that affected the CNS of rabbits, determined by flexor reflex changes, was between 125 and 250 mg/cu m, (2) the threshold concentration of vinyl acetate vapor during a 37-minute exposure that altered the ability of rabbits to differentiate between qualitatively similar but quantitatively different visual stimuli was between 25 and 50 mg/cu m, and (3) inhalation of vinyl acetate at a concentration one-fifth of that causing changes in unconditioned reflex activity induced disturbances in conditioned reflex activity.

Goeva [23], in 1966, studied the acute and long-term effects of ingested vinyl acetate on mice and rats, including its influence on conditioned reflex development in rats. In the first series of acute experiments, the oral median lethal dose, or LD50, of vinyl acetate for 50 white mice was determined to be 1,613 mg/kg; a majority of the mice died within 3-5 days. In the second short-term test, 20 mice were given oral doses of vinyl acetate of 300 mg/kg (about 0.2 of the median lethal dose) daily for 3 weeks. Each mouse received a total of about 6,000 mg of vinyl acetate. Two animals died during the experiment. At the end of the experiment, all surviving mice were given the median lethal dose (about 1,600 mg/kg), and 8 of the remaining 18 died; on these bases, the author concluded that vinyl acetate had moderate cumulative properties.

The long-term experiment on 30 albino rats lasted for 7 months and included one group of control rats and two experimental groups [23]. Rats ingested vinyl acetate in doses of 0.01 or 0.1 mg/kg with their drinking water. No information was given on the stability of vinyl acetate in water. The rats were observed or examined for: general appearance; body and organ weight changes; peripheral red blood cell counts and hemoglobin values; external gas exchange; liver function by Quick's test (excretion of hippuric acid after ingestion of sodium benzoate) and prothrombin time; blood cholinesterase activity; urinary protein, sugar, urobilin, and acetone; and, microscopically, for changes in the lungs, liver, kidneys, heart, spleen, and gastric and intestinal mucosa. Experimental and control animals showed no appreciable differences in any of the parameters measured, ie, oral administration of vinyl acetate at 0.01 and 0.1 mg/kg produced no toxic effects in rats. It should be noted, however, that the acid environment of the stomach results in the rather rapid hydrolysis of vinyl acetate to acetic acid and acetaldehyde.

Goeva [23] also determined the time required for acquisition of conditioned reflexes in rats that had previously ingested vinyl acetate at 0.01 or 0.1 mg/kg in their drinking water for 7 months. Rats that ingested vinyl acetate at 0.1 mg/kg exhibited fewer positive responses to the conditioned stimulus and took longer to acquire conditioned reflexes than controls; thus, the author considered this the threshold dose. No significant differences were observed in the acquisition of conditioned reflexes between control and experimental rats fed vinyl acetate at 0.01 mg/kg.

Maltoni and Lefemine [24], in 1974, and Maltoni [25], in 1976, reported the results of a study involving 96 13-week-old Sprague-Dawley rats exposed to vinyl acetate vapor at 2,500 ppm (8,750 mg/cu m). The authors said this concentration appeared to be the "maximum possible dose for a chronic exposure" [24]. The rats were exposed for 4 hours/day, 5 days/week, for 52 weeks and observed for up to 83 weeks after exposure for tumorigenic effects. None of the rats exposed to vinyl acetate developed tumors; however, six controls developed a variety of tumors [25]. No toxic effects from exposure to vinyl acetate were reported, but only 49 of 96 exposed animals (51%)

survived at 26 weeks; 58 of 68 controls (85%) were alive at that time. The authors did not discuss the reasons for this increased mortality in the rats exposed to vinyl acetate.

In 1976, Bartsch et al [26] reported data comparing the mutagenicity of several olefinic compounds on two strains of Salmonella typhimurium, TA1530 and TA100, in a modified Ames test. Vinyl acetate served as the control substance. Vinyl acetate was combined with mouse liver fractions, with and without an NADPH-generating system, and S. typhimurium in a soft agar layer. No mutagenic effect was detectable with vinyl acetate.

Metabolism

Filov [27], in 1959, discussed the fate of inhaled vinyl acetate in rabbits. The concentrations of inspired and expired vinyl acetate were measured polarographically, but the author did not specify the concentrations used. Blood was removed from the carotid artery periodically during exposure for polarographic analysis for vinyl acetate. Filov reported that vinyl acetate tended to remain in the body after it was inhaled; 70% of the vinyl acetate administered was retained, and an equilibrium was established in the first few minutes after exposure began. Filov found no vinyl acetate in the blood, either during or after its inhalation, which suggested to him that vinyl acetate is rapidly metabolized when it enters the body through the lungs.

Filov [27] also suggested that on hydrolysis vinyl acetate yields acetic acid, a normal body constituent, and vinyl alcohol, which should rapidly tautomerize to yield acetaldehyde, another normal body constituent. The rate of vinyl acetate hydrolysis in blood was investigated by determining its hydrolysis products in body fluids and the mode of their formation. Aqueous and physiologic solutions containing 380 μg of vinyl acetate were added to 2 ml samples of rat and human blood. The mixtures were then analyzed spectrophotometrically at various time intervals for acetaldehyde. Amounts of acetaldehyde in 2 ml of blood ranged from 84 μg immediately after addition of vinyl acetate to 174 μg 4.5 minutes after addition. Filov calculated a theoretical yield of 194 μg of acetaldehyde with complete hydrolysis and concluded that vinyl acetate hydrolyzes rapidly in the blood in vitro to produce acetaldehyde.

To identify the sites of hydrolysis of vinyl acetate in the blood, the author added 380 μg of vinyl acetate in physiologic solution to 2 ml samples of human or rat whole blood, plasma, or washed erythrocytes; the mixtures were held for 3 minutes and analyzed for acetaldehyde [27]. Whole human blood produced 175 μg of acetaldehyde, while plasma produced 178 μg, and washed cells produced none. In rat blood, 158-165 μg of acetaldehyde were produced; 162-165 μg were produced in plasma, and washed rat erythrocytes produced about 70 μg of acetaldehyde, showing that hydrolysis occurred primarily due to

plasma proteins and partially due to red cells. Incubation of blood plasmas from humans and rats at 62 C for 1 hour destroyed their abilities to hydrolyze vinyl acetate.

Acetaldehyde was detected in the blood of rats that had inhaled vinyl acetate vapor [27]. Because of this finding, and because vinyl acetate was not detected in the blood, the true concentrations of acetaldehyde were measured in the blood of rats that had inhaled vinyl acetate or acetaldehyde until they assumed what was described as the lateral position; they were then decapitated, and blood was collected for acetaldehyde analysis. The mean concentration of acetaldehyde in whole blood of seven rats inhaling vinyl acetate was 45.8 μg%; for seven rats inhaling acetaldehyde it was 30.4 μg%, indicating that vinyl acetate is hydrolyzed rapidly in the blood, with formation of acetaldehyde.

Rostovskii et al [28] reported that the rate constant for hydrolysis of vinyl acetate in aqueous alkali, 2.15 x 10*5 (* means to the power of), is 370 times as high as that for its acid hydrolysis; the concentrations of acid or alkali studied were not reported. Filov's [27] conclusion, that vinyl acetate is metabolized rapidly by enzymatic hydrolysis to acetaldehyde, is consistent with the information showing that vinyl acetate was rapidly hydrolyzed in aqueous alkali. No information was presented in the Filov paper on the concentration of vinyl acetate inhaled or on the distribution of vinyl acetate and its metabolites in the organism, however.

The existence of nonspecific esterases in mammalian blood is well established [29-31]. It is reasonable to assume that they are the probable basis for the hydrolysis of vinyl acetate observed by Filov [27]. These enzymes have not been characterized with vinyl acetate as a substrate; however, Oi and Satomura [32], in 1967, found that vinyl acetate was the most easily hydrolyzed of the acetic acid esters tested with acetylesterase from the fungus Sclerotinia libertiana. Although Oi and Satomura primarily investigated the structure, function, and inhibition of acetylesterase, their results also were consistent with the finding of Filov [27] that vinyl acetate may be rapidly hydrolyzed enzymatically.

In 1970, Boyland and Chasseaud [33] reported the effect of vinyl acetate on glutathione (GSH) levels in rat liver. Liquid vinyl acetate was administered intraperitoneally (ip) at a dose of 0.8 ml/kg (selected as about one-fourth the published LD50) to female Chester Beatty rats weighing 200-380 g. Forty-four control rats, weighing about the same as the experimental rats, were given arachis oil or 0.1 M orthophosphate buffer. GSH assays were performed on homogenized liver samples from three and two experimental rats killed after 30 minutes and 2 hours, respectively; three control animals were killed after 2 hours for GSH assays.

The mean GSH level in control rat livers was 155 mg/100 g of liver [33]. Mean GSH levels of the experimental rat livers, expressed as percentages of control values, were 77% after 30 minutes and 149% after 2 hours, ie, vinyl

acetate produced an initial depression followed by an apparent elevation of rat liver GSH levels. The authors stated that a previous study [34] had shown that vinyl acetate was a slowly reacting substrate for enzyme-catalyzed conjugation with GSH. Chasseaud [35], in 1973, also reported that vinyl acetate underwent enzyme-catalyzed conjugation with GSH. Boyland and Chasseaud [33] concluded that if a compound is a good substrate for glutathione S-transferases, it will lower glutathione levels soon after administration to rats. Although the experiments of Filov [27] indicate that vinyl acetate is rapidly hydrolyzed in blood, the experiments of Boyland and Chasseaud [33] suggest that, following ip administration, vinyl acetate or its metabolites influence the metabolic activity of the liver.

Tiunova and Rumyantsev [36], in 1975, published the results of a study of the inhalation exposure of male albino rats to vinyl acetate. Changes in the synchrony of the activity cycles of liver alanine-aminotransferase and aspartate-aminotransferase (transaminases) were determined over 5 months. The purpose of the study was to test the authors' hypothesis that the desynchronization of fluctuations in enzyme activity during chronic exposures to a chemical stimulus would result in toxic effects, whereas maintenance of synchronization would result in compensation and adaptation.

Three groups of 10 rats each, weighing 120 g, kept in 0.47-cu m metal chambers, inhaled vinyl acetate at 2.4 ±0.2, 13.2 ±0.6, or 68.0 ±2.1 mg/cu m (0.68, 3.75, or 19.3 ppm) 24 hours/day for 4 months. The concentrations of vinyl acetate in the chambers were determined by gas chromatography. Two unexposed groups, one maintained under colony conditions and one kept in chambers similar to those used for exposures, served as controls. The activities of liver alanine- and aspartate-aminotranferase were determined (presumably in serum samples) in all five groups periodically throughout the 5 months (March-July).

In the colony controls, the activities of the two enzymes fluctuated synchronously; control animals placed in the chamber environment showed an altered rhythm of fluctuation, but the enzyme activities were still highly synchronous [36]. Rank correlation coefficients for the activity of the two enzymes were 0.87 in the colony controls ($P=0.01$) and 0.81 in the chamber controls ($P=0.05$). Rats exposed to vinyl acetate at 2.4 mg/cu m also showed a change in the rhythm of fluctuation of enzyme activity, although synchrony was maintained. However, marked and unsynchronized changes developed in the activities of the two enzymes in rats exposed at 13.2 mg/cu m, and especially at 68 mg/cu m; other, undescribed, signs of intoxication were also reported in animals exposed at the latter concentration. Correlation coefficients were not given for the activities of the two enzymes in exposed animals. The authors regarded the modification of the rhythm of fluctuation without loss of synchronization as an indication of adaptive change. They concluded that these biologic rhythms could be used to distinguish adaptive from pathologic changes.

Correlation of Exposure and Effect

Occupational exposure to vinyl acetate occurs primarily via inhalation of the vapor and contact of the liquid or vapor with the skin and eyes. In humans, exposure to vinyl acetate vapor at lower concentrations (68.3-75.6 mg/cu m) has resulted in reversible eye and upper respiratory irritation [4,18]. Dermal exposure to the liquid may result in irritation of the skin [17,18].

Vinyl acetate was lethal to all (presumably six) rats exposed for 2 hours at 28,000 mg/cu m [17], and 4-hour LC50's for exposed rats, guinea pigs, mice, and rabbits ranged from 5,411 to 21,753 mg/cu m [4,14]. No pathologic data were reported for the animals that died from these exposures [4,14,17]. The one beagle exposed to vinyl acetate at 13,388 mg/cu m [4] and all of the rats exposed at 3,500 mg/cu m [17] survived. Upper respiratory difficulty, eye and nose irritation, and increased macrophages in the lungs were noted in rats exposed at 7,000 mg/cu m periodically for 3 weeks [20].

Deese and Joyner [18] found that each of three persons exposed to vinyl acetate at 75.6 mg/cu m experienced hoarseness or coughing and eye irritation; one person became hoarse when exposed at about 15 mg/cu m (14.7).

Ocular effects have also been reported from contact with airborne vinyl acetate. Exposure to vinyl acetate at 840 mg/cu m caused some eye blinking and reddening of the sclerae in a dog [4]; 651 mg/cu m caused eye irritation and tearing in dogs [19]; and 0.5 ml of vinyl acetate caused severe irritation or mild burns when applied to a rabbit's eye [17]. The lowest concentration that caused eye irritation in humans (one of three subjects) was 20.0 mg/cu m [18].

Two reports [17,18] suggested that skin irritation can result in humans after dermal contact with (presumably liquid) vinyl acetate. One report [17] noted that this irritation might result in blisters. Deese and Joyner [18] reported that skin irritation or rash was noted by 3 of 21 vinyl acetate workers. Union Carbide investigators [17] reported that the dermal LD50 in rabbits was greater than 5 ml/kg in a 24-hour covered-skin contact test with liquid vinyl acetate, but they also stated that undiluted vinyl acetate on the skin of the shaved abdomen of a rabbit caused no reaction.

Vinyl acetate has not been characterized as a substrate for mammalian enzymes; however, it was the most easily hydrolyzed of the acetic acid esters tested with acetylesterase from the fungus Sclerotinia libertiana [32]. This was consistent with the finding of Filov [27] that vinyl acetate undergoes rapid enzymatic hydrolysis in vivo, producing end-products that are normal body constituents.

Evidence of possible adverse effects of vinyl acetate on the human nervous system is sparse. Gofmekler [3] found that 0.32 mg/cu m was the minimum concentration of vinyl acetate capable of inducing EEG desynchronization as a

conditioned response; 0.21 mg/cu m did not produce this effect. Goeva [23] found that rats given vinyl acetate in oral doses of 0.1 mg/kg for 7 months exhibited fewer positive responses to a conditioned stimulus and took longer to develop conditioned reflexes than either controls or rats fed 0.01 mg/kg of vinyl acetate. It is questionable whether these particular studies [3,23] demonstrated adverse changes; so it does not now seem appropriate to conclude that vinyl acetate exposure in the work environment at these concentrations will induce biologically significant effects on the nervous system.

The readily identifiable odor of vinyl acetate appears to be one means by which workers are warned of its presence in the work environment. Determinations of the threshold of odor detection have given varying results. For example, Deese and Joyner [18] reported that three of three subjects detected a marked odor of vinyl acetate at 75.6 mg/cu m; a "slight" odor was reported by all of three or four exposed at 14.7 and 1.4 mg/cu m. In an experimental study [4], all of nine volunteers detected the odor of vinyl acetate at 4.6 mg/cu m, but, with one questionable exception, they did not detect its odor at 2.1 mg/cu m. Minimum perceptible (threshold) and maximum imperceptible concentrations for odor detection were determined by Gofmekler [3] to be 1.0 and 0.7 mg/cu m, respectively. These findings indicate that the odor threshold of vinyl acetate probably ranges from 1.0 to 3.3 mg/cu m; their variability probably reflects differences in methods of determination, and possibly in the development by the test subjects of adaptation to the odor. While a noticeable odor of vinyl acetate may indicate a potential hazard, it is not quantitatively reliable.

Olfactory fatigue has also been observed during exposure to vinyl acetate. Vinyl acetate at 68.3-250.3 mg/cu m produced olfactory fatigue in all exposed volunteers [4]. Olfactory fatigue was complete in three of three persons exposed at 68.3 mg/cu m and in one of three at 119.7 mg/cu m after 3-116 minutes; two of three subjects at the latter concentration and four of four at 250.3 mg/cu m experienced partial olfactory fatigue.

The known effects of vinyl acetate on humans and animals are summarized in Tables III-2 and III-3.

Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction

No specific data on the teratogenic or reproductive effects of vinyl acetate were found in the available literature. No mutagenic effects were detectable in S. typhimurium strains TA1530 and TA100 exposed to vinyl acetate [26]. In the single study [24,25] on its carcinogenicity, 96 rats were exposed to vinyl acetate at 8,750 mg/cu m for 1 year and observed until the end of their lives. No evidence was found that vinyl acetate influenced tumor incidence. Several compounds having structures similar to that of vinyl acetate, eg, vinyl chloride, vinyl bromide, vinylidene chloride, vinyl cyanide (acrylonitrile), and vinyl carbamate, have been shown to be carcinogenic or mutagenic [37-48], but there is no evidence to suggest that vinyl acetate

induces similar irreversible processes. No other reports on the carcinogenic or mutagenic potential of vinyl acetate in humans or animals were found in the literature. Vinyl acetate administered ip to rats at a dose of 0.8 ml/kg reduced liver glutathione levels initially [33]. This suggests that a fraction of the dose reached the liver and disturbed glutathione metabolism, perhaps by acting as a substrate for glutathione conjugase. No evidence from either in vitro or in vivo experiments indicates that an oxirane intermediate plays any role in vinyl acetate metabolism, although intermediates containing oxirane rings seem to be important in the metabolism of vinyl halides [44]. Without further research, these aspects of vinyl acetate toxicity cannot be settled.

TABLE III-2

SUMMARY OF EFFECTS OF VINYL ACETATE EXPOSURE ON HUMANS

No. of Persons	Type of Work	Exposure*		Effects	Reference
		Concentration (mg/cu m)	Duration		
4	Volunteers	68.3-250.3	0.5-4 hr	Olfactory fatigue, and/or upper respiratory tract irritation	4
21	Production	ND**-172.6; mean, 30.1	Mean of 15.2 yr	Upper respiratory tract or eye irritation in 6	18
3	Production and sampling	75.6	Short-term	Severe eye irritation, slight cough, hoarseness in 3, marked odor	18
4	"	19.9-23.8	"	Slight eye irritation in 1	18
5	"	14.7-19.9	"	Hoarseness in 1	18
-	"	1.4-17.2	"	No effects	16
3	"	1.4	"	Slight odor detected by 3	18
9	Volunteers	4.6	2 min	Odor detected by 9	4
9	"	2.1	"	Odor detected by 1	4
77	"	1.0	2-3 hr	Threshold of olfactory perception	3
15	"	0.8	"	Threshold of light sensitivity of eye	3
2	"	0.3	"	Threshold of conditioned-reflex desynchronization of brain electrical activity	3

*All exposures were to vinyl acetate vapor.
**ND=not detectable

TABLE III-3

SUMMARY OF EFFECTS OF VINYL ACETATE EXPOSURE ON ANIMALS

Route of Exposure	Species	Exposure		Effects	Reference
		Concentration/ Dose	Length/ Frequency		
Inhalation	Rat	28,000 mg/cu m	2 hr	Death of all	17
"	"	14,000 mg/cu m	"	Death of half	17
"	"	"	4 hr	Death of about half	14
"	"	13,955 mg/cu m	"	Death of half	4
"	"	8,750 mg/cu m	1 yr	No tumors observed by 135 wk	24
"	"	7,000 mg/cu m	3 wk	Eye and nose irritation, low weight gain, increased macrophages in lungs	20
"	"	3,500 mg/cu m	4 hr	No deaths	17
"	"	2,205 mg/cu m	3 wk	Decreased weight gain in females	20
"	"	875 mg/cu m	"	"	20
"	"	350 mg/cu m	"	No effects	20
"	Rabbit	8,789 mg/cu m	4 hr	Death of half	4
"	"	500 mg/cu m	40 min	Changes in reflex strength and development time	22
"	"	250 mg/cu m	"	"	22
"	"	125 mg/cu m	"	No effects	22

TABLE III-3 (CONTINUED)

SUMMARY OF EFFECTS OF VINYL ACETATE EXPOSURE ON ANIMALS

Route of Exposure	Species	Exposure		Effects	Reference
		Concentration/ Dose	Length/ Frequency		
Inhalation	Rabbit	100 mg/cu m	37 min	Conditioned reflexes impaired	22
"	"	25 mg/cu m	"	No effect	22
"	Mouse	5,411 mg/cu m	4 hr	Death of half	4
"	Guinea pig	21,753 mg/cu m	"	"	4
"	Dog	13,388 mg/cu m	"	Nonlethal	4
"	"	840 mg/cu m	"	Blinking, reddened sclera	4
"	"	651 mg/cu m	1 wk	Eye irritation, lacrimation	19
"	"	371 mg/cu m	4 hr	No effect	4
Oral	Rat	2,920 mg/kg	Once	Death of half	17
"	"	0.1 mg/kg in drinking water	7 mo	Slowed formation of conditioned reflexes; no other effects	23
"	"	0.01 mg/kg in drinking water	"	Normal acquisition of conditioned reflexes	23
"	Mouse	300 mg/kg/d, 6,000 mg/kg total	3 wk	Death in 2 of 20	23
"	"	1,600 mg/kg*	Once	Death in 8 of 18	23

TABLE III-3 (CONTINUED)

SUMMARY OF EFFECTS OF VINYL ACETATE EXPOSURE ON ANIMALS

Route of Exposure	Species	Exposure		Effects	Reference
		Concentration/ Dose	Length/ Frequency		
Oral	Mouse	1,613 mg/kg	Once	Death of half	23
Ocular	Rabbit	0.5 ml	"	Severe irritation, mild corneal burns	17
Dermal	"	>5 ml/kg	24 hr	Death of half	17

*Administered to survivors of 6,000 mg/kg experiment

IV. ENVIRONMENTAL DATA

Environmental Concentrations

Few data have been found on the concentrations of airborne vinyl acetate in either industrial or ambient air. Gordon and Meeks [49] found ambient (grab-sample) vinyl acetate concentrations ranging from 0.07 to 0.57 ppm (0.25-2.0 mg/cu m) at four locations in the Texas City, Texas, area. Pervier et al [50] considered air emissions of vinyl acetate from production facilities to be less significant than emissions from other processes surveyed and therefore did not recommend that the Environmental Protection Agency conduct further (in-depth) study of vinyl acetate air emissions.

Deese and Joyner [18], in the course of an epidemiologic study of vinyl acetate workers, reported industrial air sampling results. "Short-term" samples were collected in a midget bubbler and an impinger in series, with toluene (near 5 C) as the collection medium, and "long-term" samples were collected similarly with standard Greenburg-Smith impingers; analyses were performed by gas chromatography. Deese (DE Deese, written communication, May 1978) indicated that the midget impinger samples were breathing-zone samples. The vinyl acetate concentration averaged about 8.6 ppm (30 mg/cu m), ranging from nondetectable to 49.3 pp m (173 mg/cu m). TWA concentrations in three production areas were reported as 8.2, 7.7, and 5.2 ppm (29, 27, and 18 mg/cu m).

Investigators for EI du Pont de Nemours and Company [16] collected air samples in the breathing zones of workers in a vinyl acetate production area. Vinyl acetate was collected in midget impingers containing dimethylformamide and was analyzed by gas chromatography. Samples were collected during two separate periods in summer and winter. The reported TWA concentrations ranged from 0.4 to 4.9 ppm (1.4-17 mg/cu m) with no systematic seasonal variation.

Sampling

Vinyl acetate has been collected by integrative sampling methods such as solid sorbent tubes [51] and midget impingers [18] and by grab-sampling methods, such as sampling bags [49].

Ambient air samples have been collected in polyvinyl fluoride bags for analysis by gas chromatography or infrared absorption spectroscopy [49]. Samples were collected with a 12-volt DC centrifugal blower, in 100-liter and 500-liter bags, requiring sampling periods of 2 minutes and 18-20 minutes, respectively. Two possible disadvantages of this method were noted: contamination of sample by diffusion of bag material and loss of sample by sorption, decomposition, or permeation. An additional disadvantage of this method is that the large sampling bags and the associated pumps are not suitable for personal sampling.

Although often used, midget impingers may be inconvenient for personal sampling because it may be necessary to recharge them with collecting medium frequently (depending on its vapor pressure) and because they may interfere with the movements of the worker, especially when used in series. Handling and transporting absorber solutions is difficult because of the possibility of spills and leaks.

Deese and Joyner [18] used two standard Greenburg-Smith impingers in series or a "fritted glass midget impinger bubbler and a standard midget impinger" in series to collect vinyl acetate. The standard impinger series was used to collect 2-hour samples at a flowrate of 1.5 liters/minute. The midget impinger series was used to collect 10-minute samples at the same flowrate. The temperature of the toluene collecting medium was kept near 5 C with aqueous methanol and dry ice, and vacuum was provided by a portable constant-rate sampler or a sequential sampler. The mean collection efficiency for the first impinger of each series (midget or Greenburg-Smith) was 86.3% at 0 C; mean collection efficiency for the first absorber near 5 C was 84.2%. Gas chromatography was used to analyze the samples.

Solid-sorbent devices are well suited for personal sampling; they are relatively small, and persons wearing them quickly adjust to their presence. They require less careful handling than liquid sorbents and are efficient and easy to use. Charcoal is a widely used general sorbent because it is nonpolar and has an affinity for organic vapors and gases. However, its collection and desorption efficiencies vary from batch to batch, so that it is necessary to determine the collection and desorption efficiencies for each batch.

Celanese Chemical Corporation investigators [51] have developed a method that utilizes a low-flow air sampler pump in conjunction with a collection tube packed with Porapak Q to sample for vinyl acetate. Basically, an air sample is collected in the worker's breathing zone at a flowrate of 40-60 ml/minute; the sample passes through a 3-inch collector tube with a 1-inch backup tube, both packed with Porapak Q (50/80 mesh). The collector tube is removed from the pump connection and locked into the programmed thermal desorber, eg, Century PTD-132, and the sorbent in the collector tube is immediately convection-heated with purge gas, eg, air, drawn through the tube by a device similar to a large stainless steel syringe. After desorption, the "syringe" retains the analyte reconcentrated in a fixed 300-ml volume of purge gas. At any later time, replicate analytical size samples of this gas may be manually or automatically withdrawn from the "syringe" and injected into a gas chromatograph for analysis without sample dilution, since the syringe piston adjusts itself to maintain a constant sample concentration by compensating for the volume of sample withdrawn. The sampling equipment is portable, automatic, and easy to use. Desorption and analysis with a portable gas chromatograph can be performed by on-site (field) personnel, thereby minimizing both the chances of mixup of tubes during transportation to a laboratory and the typical transportation and laboratory delays. Desorption can also be performed at a site remote from that of sample collection.

NIOSH [52] has proposed a solid-sorbent sampling method for vinyl acetate. It is recommended that the sampling rate and volume not exceed 0.1 liter/minute and 3.0 liters, respectively. Chromosorb 107 is the recommended sorbent. Vinyl acetate has been successfully collected by this method over the concentration range of 8.2-206 mg/cu m at a relative humidity of over 80%, but the method is known to be capable of collecting much smaller amounts of vinyl acetate (quantitative limit is 0.5 μg of vinyl acetate/300 mg of solid sorbent). This method, described in Appendix I, is the recommended sampling method.

Chemical Analysis

Vinyl acetate has been determined by polarography [27,53], infrared absorption spectroscopy [49], bromometry [54], paper chromatography [55,56], colorimetry [3,57-59], and gas chromatography [4,16,18,36,51,60-63].

Horacek [53] hydrolyzed vinyl acetate in an alkaline (LiOH) medium and determined the resulting acetaldehyde by polarography. The method was useful for concentrations of vinyl acetate of 0.01-1 mg/ml. The author stated that the method was simple, rapid, and sufficiently precise (not further defined), but interferences included aldehydes and many alkaline cations, eg, Na+, NH4+, K+, Cs+, Rb+, and Ba++. Filov [27] also used a polarographic method to analyze for vinyl acetate, but he did not describe the method in detail.

Long-path infrared Fourier transform absorption spectroscopic analysis was used to measure vinyl acetate at concentrations ranging from 0.07 to 0.57 ppm (0.25-2.0 mg/cu m) [49].

Bokov et al [54] used bromometry to determine vinyl acetate in air. This method was based on the addition of bromine across the double bond of vinyl acetate. The quantity of bromine consumed was indicative of the concentration of vinyl acetate.

Several colorimetric methods have been used for determination of small amounts of vinyl acetate in air. The complexation of mercuric acetate with vinyl acetate was the basis of one colorimetric method [57]. Mercuric acetate was added to a solution containing vinyl acetate in ethyl alcohol; after 1 hour, diphenylcarbazide in ethanol was added to form a violet complex with the excess mercuric acetate. The sensitivity was reported as 0.05 mg/liter of sample. To determine the concentration of vinyl acetate in air in the presence of aldehydes, Andronov and Yudina [58] mixed a sample with hydroxylamine hydrochloride and ferric chloride and used phenolphthalein as the colorimetric agent. The sensitivity of this method was stated to be 1 μg in 3.5 ml. Another colorimetric method [59] was based on vinyl acetate's oxidation to formaldehyde by permanganate or periodic acid. Chromotropic acid was then used for colorimetric determination of the formaldehyde at 574 nm. Gofmekler [3] mixed a sample of vinyl acetate with alkaline hydroxylamine to

form acetohydroxyamino acid, which produced a color ranging from light yellow to purple in the presence of ferrous chloride. The sensitivity of the method was reported to be 0.025 μg/ml.

Horacek [55] used paper chromatography to separate the hydroxamate derivatives of caprolactam, vinyl acetate, acrylic acid, and metacrylic acid esters. The method was described as rapid and relatively sensitive; the amount of monomer in the aliquot was determined colorimetrically by adding a ferric salt.

Osokina and Erisman [56] described an analytical method for vinyl acetate that involved reacting a salt of mercury with the vinyl acetate, followed by separation of the resulting mercury compound by paper chromatography. The addition of the mercury was found to proceed more rapidly in an alcoholic medium. The minimum amounts of vinyl acetate detectable in various alcohols ranged from 0.3 to 1.0 μg.

The most widely used method for analyzing vinyl acetate is separation by gas-liquid chromatography with flame-ionization detection. Analysis by gas chromatography generally involves either direct injection of a portion of the sample from a sampling container or injection of an aliquot of sample desorbed from a suitable sorption material. The choice of column materials and operating parameters for vinyl acetate analysis depends on the relative retention times of the possibly interfering compounds.

West et al [61] reported using a U-shaped 5-mm x 2-meter glass tube containing 20% beta,beta'-oxydipropionitrile on 30/60 mesh Chromosorb to measure vinyl acetate retention times at a column temperature of 53 C. In another retention behavior study of vinyl acetate, Germaine and Haken [63] used a gas chromatograph with a 12-foot x 1/4-inch aluminum column packed with 10% methyl silicone polymer (SE-30) on 60/80 mesh, acid-washed, and silanized Celite 560 and operated at 150 C.

Bollini et al [62] used gas-liquid chromatography with flame-ionization detection to determine the amount of vinyl acetate monomer in a mixed aqueous suspension of polyvinyl acetate and butyl acrylate-vinyl acetate copolymer. They used a 1/8-inch x 6.6-foot steel column containing 10% polyphenylether OS-138 on Chromosorb W-AV (80/100 mesh) at 90 C. The authors' major criticism of this system was that the injection chamber of the chromatograph might become encrusted after approximately 10 injections.

To separate vinyl acetate from other organic compounds, Smith and Dahlen [60] used a column of tetraamylsilane and dimethyldioctylsilane on 60/100 mesh Celite 545 at a column temperature of 95 C. Values obtained with this method had only a 0.4% error when compared with the known amounts of vinyl acetate used.

Deese and Joyner [18] also used a gas chromatograph equipped with a flame-ionization detector to measure vinyl acetate concentrations. A 6-foot x 1/4-

inch stainless steel column packed with 80/100 mesh Porapak Q was used at 200 C. Preliminary evaluation using known concentrations of vinyl acetate showed a 99.2% mean accuracy (range, 80.9-110.2%) with this method; it was stated to be accurate and reliable for the low concentrations (0.4-49.3 ppm) encountered in the study.

A 4-foot x 1/8-inch stainless steel column packed with Chromosorb 101, 80/100 mesh, has been used at 110 C for monitoring vinyl acetate in air by Celanese Chemical Corporation investigators [51]. May et al [64] found Porapak Q to be a suitable packing in a pyrolysis gas chromatographic system for a 5% vinyl acetate-vinyl chloride copolymer. Two other reports [4,16] noted that airborne vinyl acetate was analyzed by gas chromatography, but details of the analytical methodology were not presented.

NIOSH [52] has proposed a method for analyzing vinyl acetate in workplace air samples by gas chromatography with flame-ionization detection. Samples are collected on Chromosorb 107 and thermally desorbed with helium at 150 C. The desorbed vapors are injected onto a chromatographic column packed with 10% FFAP on 80/100 mesh Chromosorb W AW. This method has been found suitable for quantifying vinyl acetate in concentrations as low as 0.5 μg/300 mg of Chromosorb 107. The pooled relative standard deviation of the sampling and analytical method was 8.1% for 50 samples over the concentration range of 8-200 mg/cu m. This method is described in detail in Appendix I.

There are a number of direct-reading devices that can be used to determine vinyl acetate in workplace air. Combustible gas meters and colorimetric tubes, although they are not sensitive enough to determine vinyl acetate at concentrations as low as the recommended ceiling limit, may be useful for leak detection and other emergency situations.

NIOSH [65] has evaluated nine commercially available, portable combustible gas meters. These instruments are not specific for vinyl acetate, but their utility for measuring concentrations of vinyl acetate can be enhanced by calibrating them under temperature and other conditions resembling as closely as possible those at the sampling site.

Colorimetric tubes capable of semiquantitative measurements of vinyl acetate in air are manufactured by Draeger [66] and by Gastec [67]. The Draeger tubes are sensitive to vinyl acetate at 50 ppm with 10 strokes of the pump, and the Gastec tubes can detect vinyl acetate at 10 ppm with a single stroke of the pump. This sensitivity can be increased by increasing the number of strokes, down to about 5 ppm, the minimum detection limit for these devices. Ethyl acetate and other esters of acetic acid will interfere.

NIOSH [68] has also evaluated several portable, direct-reading analyzers. At least three of these are suitable for determination of vinyl acetate concentrations at or below the recommended occupational exposure limit. The Wilks-Miran infrared analyzer is capable of detecting vinyl acetate down to about 0.02 ppm [69]. The Century organic vapor analyzer is capable of

detection over the range of 1-10,000 ppm, depending on the scale selected [70]. The photoionization meter produced by HNU Systems, Inc, can detect vinyl acetate, as well as many other gases and vapors, over the concentration range of 0.1-2,000 ppm, using energy sources of 10.2 and 9.5 electron volts (eV) [71]. Although none of these devices is specific for vinyl acetate, the HNU photoionization meter with 9.5-eV energy source will discriminate out all compounds with ionization potentials above 9.5 eV; this includes most potential interferences, eg, ethyl acetate (10.11 eV), methane (12.6 eV), vinyl chloride (9.996 eV), acetic acid (10.36 eV), ethylene (10.5 eV), acrylonitrile (10.91 eV), and acetonitrile (12.2 eV) [9].

NIOSH recommends a gas chromatographic method with flame-ionization detection for analysis of vinyl acetate in workplace air. The recommended method is described in detail in Appendix I. This method has the advantage of permitting analysis by a quick instrumental method either on-site or in a laboratory remote from the site of sample collection. It is efficient and economical, since sampling tubes may be reused after analysis is completed. Most potential interferences can be eliminated by altering chromatographic conditions. Although this analytical method has not yet been approved or validated by NIOSH, it shows promise of being suitable for determination of vinyl acetate in workplace air at the concentrations required by the recommended standard, with acceptable precision and accuracy.

Hazard Control By Process and Design Engineering

(a) Ventilation

Engineering design of operations and process equipment involving vinyl acetate should be oriented toward controlling inhalation and skin and eye contact with the liquid or vapor. Properly designed and maintained ventilation systems should prevent dispersal of vinyl acetate into the workroom atmosphere and the accumulation of vinyl acetate on surfaces. These goals can be met with properly constructed and maintained closed systems. If closed systems are not feasible, local exhaust ventilation systems should be provided at potential contamination sources to direct airflow away from the employees' breathing zones. These systems should be designed to remove the vapor with proper allowance for makeup air and should prevent mere recirculation of contaminated air. Guidance for design of such systems can be found in Industrial Ventilation--A Manual of Recommended Practice [72], in Fundamentals Governing the Design and Operation of Local Exhaust Systems (ANSI Z9.2-1971) [73], and in NIOSH's Recommended Industrial Ventilation Guidelines [74].

Ventilation systems require regular inspection and maintenance to ensure effective operation. Inspections should include measurements of system function, eg, airflow at collection hoods, static pressure at branch ducts, or pressure drop across filters and fans. Whenever measurements indicate unacceptable functional decrements in a system, the equipment should be

inspected more closely and immediately repaired or otherwise restored to an acceptable state of function. A water or oil manometer can provide a convenient, continuous method for evaluating airflow. The manometer should be marked to indicate design airflows. The continued effectiveness of vapor control systems should be evaluated by sampling and analyzing air in the general workroom, in operators' breathing zones, and around potential contamination sources whenever the ventilation system or work operations or processes are changed.

Ventilation systems, as well as all other equipment in vinyl acetate manufacture or use facilities, must be designed and operated in a manner cognizant of the high flammability of this compound. Electrical motors and other electrical components must be explosion-proof. Moving parts of the system, eg, fan blades, must be constructed of nonsparking materials.

(b) Storage and Handling Areas

Manufacturing, processing, storage, and transfer equipment must be constructed of materials resistant to corrosion by vinyl acetate. One vinyl acetate manufacturer recommends carbon steel, lined carbon steel, or aluminum and has noted that brass, bronze, or lead compounds are not acceptable construction materials [51]. Small samples should be stored in brown bottles [12]. Storage in outdoor or detached bulk storage areas is preferable to indoor storage. Bulk storage areas must be diked to contain any spills, and sump pumps in these areas must be explosion-proof. Storage and manufacturing areas must be constructed so that spilled or leaked vinyl acetate does not run into sanitary sewers, where it may present an explosion or fire hazard. Facilities in which large quantities of vinyl acetate are processed or stored should be protected by automatic sprinkler or deluge systems [5,51].

Vinyl acetate storage areas should be separated from areas containing oxidizing and polymerization-initiating compounds. Vinyl acetate should also contain a suitable polymerization inhibitor, such as hydroquinone or diphenylamine, when stored [8,12]. Any recommendations of the manufacturer regarding the necessity for the presence of dissolved oxygen should be followed [12].

The storage of vinyl acetate poses certain problems related to vent size, diking, and separation distances, which, in turn depend on other variables, such as tank size or design. Storage areas should therefore be designed in consultation with qualified fire protection engineers [5].

Loading and unloading operations are particularly hazardous because of the high flammability hazard associated with vinyl acetate. Moving liquids, especially bulk liquids, produce buildups of static electricity. These must be controlled by bonding and grounding barge, railroad car, and tank truck terminals.

V. WORK PRACTICES

Storage, Handling, and Use

Vinyl acetate is extremely flammable and potentially explosive; its flashpoint has been reported as -5.5 C (22 F) [5], and the explosive limits, in air by volume, have been reported as 2.6-13.4% [5]. Other pertinent physical and chemical properties are listed in Table XI-1. Because of this extreme flammability, smoking and the unregulated use of open flames or other ignition sources, including matches, must be prohibited in vinyl acetate work areas. Flashlights, if used, must be of a type approved by the Mine Safety and Health Administration for use in hazardous atmospheres [12].

Electrical systems and all electrical equipment in vinyl acetate work areas must conform with the provisions of 29 CFR 1910, Subpart S [75].

Storage areas must be operated in accordance with the regulations applying to flammable liquids in 29 CFR 1910.106. Containers should be stored safely to minimize breaks and leakage. Vinyl acetate should be stored at temperatures below 37.8 C (100 F) to prevent acid buildup [12]. Storage areas should not contain sources of high temperature or be exposed to sunlight or other penetrating electromagnetic radiations [12]. Vinyl acetate polymerization can be retarded by adding a suitable inhibitor, such as diphenylamine or hydroquinone [5,8]. The maximum safe storage period depends on the amount and type of inhibitor added [5] and the amount of dissolved oxygen present [12]; the manufacturer's recommendations for oxygen content and maximum storage periods should be observed. The US Department of Transportation (DOT) compatibility guide for bulk liquid chemical transportation by water lists vinyl acetate as incompatible with nonoxidizing mineral acids, sulfuric acid, nitric acid, ammonia, aliphatic amines, and alkanolamines [76]. Vinyl acetate has been found to react with certain desiccants such as silica gel and alumina gel [5]. When desiccants are used, they should be tested for reactivity with vinyl acetate.

During the transfer of vinyl acetate from metal tanks or containers to other metallic vessels, the two vessels must be bonded and grounded to prevent the buildup of static electricity and possible spark generation. Failure to do so has caused explosion resulting in fatal injuries [77,78]. Inert gas purging of enclosed containers should be performed during transfer operations to prevent formation of explosive mixtures of air and vinyl acetate. Pressurized air should never be used for emptying vessels containing vinyl acetate [5].

Containers used to transport vinyl acetate should bear labels warning of the possibility of irritation to skin, eyes, and respiratory tract and providing information on the proper storage and handling of vinyl acetate.

DOT regulations require that vinyl acetate be tagged with a label classifying it as a flammable liquid (49 CFR 172).

Metal drums and other containers of vinyl acetate should be opened only with nonsparking tools. Fittings should never be struck with anything that may cause a spark [5]. When containers have been emptied, all openings should be closed tightly [5]. Vessels to be discarded should be steamed to remove traces of vinyl acetate and rendered impossible to reuse by crushing or piercing.

Maintenance of Equipment

The duties of maintenance and repair workers pose special problems with regard to the evaluation of their potential exposure to vinyl acetate. Often the very circumstances that require the maintenance or repair work, and under which work must be done, will negate some of the normal control procedures. Therefore, these activities should be very carefully supervised. Maintenance and repair workers should use and wear appropriate protective equipment and clothing and should follow standard operating procedures or directives provided along with required special work permits (see below). They should be trained to recognize and control the hazards to which they may be subjected.

All tank maintenance and repair work should be performed under a permit system or its equivalent. Immediately before such work begins, the air in the tank should be tested. If the concentration of vinyl acetate vapor is found to be at or below the recommended ceiling limit, a work permit authorizing the maintenance and repair work should be issued, and the work should be started as soon as all potential vinyl acetate sources have been blocked and the work area has been posted with signs saying that work is in progress. If the concentration of vinyl acetate vapor is found to be above the recommended limit, the tank should be steamed to remove residual vinyl acetate [5]. The tank should then be cooled, preferably by rinsing with water and draining, and purged with fresh air. A work permit should not be issued until tests show that the vinyl acetate concentration in the tank is below the recommended limit. If the work is interrupted before completion, the tank air should be retested and a new work permit issued before work is resumed. The tank atmosphere should be tested frequently while the maintenance and repair work is in progress. If the vinyl acetate vapor concentrations are ever found to exceed the environmental limit, the work permit should be revoked and all work should stop until the concentration of vinyl acetate is reduced to the recommended limit or below and a new permit is issued.

Tanks, equipment, pumps, lines, and valves should be drained and rinsed with water or purged with an inert gas before they are opened and repaired; workers performing this task should use proper protective equipment and avoid contact with any liquid draining or dripping from the equipment. Tanks should be steamed and kept above the boiling point of vinyl acetate (72.7 C) until

residual vinyl acetate vapor has been removed; volatilized vinyl acetate in the steam effluent should not be allowed to contaminate the surrounding areas.

Tank entrances should be large enough to admit a person wearing a safety harness, life line, and respirator in case of emergency. An appropriately equipped worker should be stationed outside the tank to keep the workers in the tank under observation at all times. Tank cleaners or repair workers overcome by vapor should be moved to fresh air immediately, and artificial respiration should be applied if breathing has stopped. A physician should be summoned at once.

Exterior repair work should be allowed only after areas are determined to present no hazard from vinyl acetate vapor. All spark- or flame-producing operations in the vinyl acetate work area must be rigidly controlled by a permit system or its equivalent. All outside welding or burning on tanks or equipment that have contained vinyl acetate should be done only after the containers have been completely purged with steam or filled with inert gas. Purging should continue while repair work is in progress [51].

General Housekeeping

Areas where spills of vinyl acetate have occurred should be posted to prevent entry by nonessential employees and promptly cleaned by means that will minimize inhalation of, or contact with, vinyl acetate. Large spills should first be contained, then flushed with water into an appropriate drainage system where vinyl acetate can be safely stored and either recovered or destroyed. Supervisors should emphasize to employees the need for prompt cleanup of spills, prompt repair of equipment and leaks, proper storage of materials, and proper functioning of dikes and deluge systems. All collected vinyl acetate should be recycled into the process or disposed of in a manner that meets applicable local, state, and Federal regulations.

Emergency Procedures

Specific procedures should be designed for the handling of emergencies involving vinyl acetate, and employees should be trained in these procedures. Complete written procedures for emergencies, revised and updated when necessary, should be readily available to all employees assigned to vinyl acetate work areas. Emergency procedures should provide for transportation of injured personnel to hospitals and should provide for instructions explaining the location, use, and maintenance of first-aid equipment, firefighting equipment, emergency showers, and eyewash fountains. Emergency drills should be held at least annually. All emergency plans should be designed to minimize personal injury.

Properly maintained safety showers and eyewash fountains should be located in or near all areas where exposure to liquid vinyl acetate may occur. In

case of dermal contact with vinyl acetate, the affected area should be flushed promptly with water. In case of ocular contact with vinyl acetate, eyes should be flushed immediately and thoroughly with water at low pressure. Exposed employees should then be taken promptly to the nearest medical facility to determine the need for further treatment. Employees should be made fully aware of these procedures.

For firefighting, carbon dioxide, foam, or dry chemical extinguishers or a spray of water should be used [5]. Use of a stream of water should be avoided to prevent splashing and spreading of fire. Automatic sprinklers and hose lines with spray nozzles should be available for fire control. Appropriate firefighting equipment should also be readily available. It should be noted that vinyl acetate floats on water and that the heat of burning vinyl acetate may initiate violent polymerization which could spread fire [12].

Respiratory Protection

Engineering and administrative controls, along with good work practices, are the preferred means of keeping vinyl acetate concentrations within the permissible exposure limits. However, respirators may be needed to adequately protect employees in some situations, such as emergencies, during nonroutine maintenance, during the time necessary to install and test engineering controls, and during the time necessary to evaluate the impact of a process change on workplace air. Employers should provide each employee in these situations with appropriate respiratory protective equipment in accordance with Table I-1, and ensure that a respiratory protection program is established and observed. Guidelines for such a program are found in 29 CFR 1910.134. Cleanliness and maintenance of respirators should be emphasized. The interior of the facepiece should not be contaminated. Detailed information on respirator selection and usage may be obtained from the Respiratory Protective Devices Manual [79].

Nelson and Harder [80] evaluated the service life of organic vapor cartridges in a vinyl acetate atmosphere by determining the time necessary for 10% of a vinyl acetate influent (3,500 mg/cu m) to break through the cartridge. The flowrate was 53.3 liters/minute, the relative humidity was 50%, the temperature was 20-22 C, and the cartridge contained 26.25 g of activated carbon. Breakthrough time was 81.1 minutes. Because the concentration tested was so great, this study suggests that organic vapor cartridges provide adequate protection at the concentrations at which they are recommended for use in Table I-1 (up to 1,400 mg/cu m).

Other Protective Equipment

The employer must provide all employees occupationally exposed to vinyl acetate with gloves and safety glasses with side shields or goggles and must ensure that they are worn when needed. Long-sleeved cotton coveralls may be

provided and worn to minimize skin contact. Disposable coveralls may be used. Fabrics that generate static electricity should be avoided. In areas where liquid vinyl acetate is handled, suits or aprons and boots impervious to penetration by vinyl acetate should also be provided and worn. Gloves should be constructed of materials resistant to penetration by vinyl acetate. No test data on glove materials were found; one vinyl acetate manufacturer provides neoprene gloves [51], and others have recommended "rubber" [5].

Other personal protective equipment should be provided, used, and maintained as specified in 29 CFR 1910.132-137. Proper protective clothing requires a snug, but comfortable, fit around the neck, wrists, and ankles. The protective equipment and clothing should be cleaned or replaced regularly. Personal protective equipment should be kept in suitable, designated containers or lockers when not in use.

Sanitation and Personal Hygiene

Plant facilities should be maintained in accordance with sanitation requirements listed in 29 CFR 1910.141. Contaminated clothing should be discarded or cleaned by laundering before reuse. Clothing to be reused should be stored in a container that is impervious to vinyl acetate. Personnel who clean such clothing should be informed of the attendant hazards.

Good personal hygiene, including washing hands thoroughly before using toilet facilities, eating, drinking, or smoking, is important to prevent ocular, respiratory, and dermal irritation.

VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

A Threshold Limit Value (TLV) of 10 ppm or 30 mg/cu m (sic) was recommended by the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) in 1969 [81] and adopted in 1971 [82]. A Short-Term Exposure Limit (STEL) or 20 ppm or 60 mg/cu m (sic) was recommended in 1976 [83]. The Documentation of Threshold Limit Values [84] noted 4-hour LC50 values in rats, mice, and rabbits of 4,000, 1,550, and 2,500 ppm, respectively. No evidence of circulatory abnormalities or evidence of altered metabolism was noted in dogs exposed 6 hours/day to vinyl acetate for about 11 weeks at average concentrations of from 91 to 186 ppm. The documentation stated that Gage [20] had found rats unaffected by repeated exposures at 100 ppm and had recommended 50 ppm as a working standard. The documentation also noted a report of 15 years' industrial experience with 21 vinyl acetate chemical operators in whom hoarseness and coughing ("slight irritation") were observed at around 22 ppm. The medical records and multiphasic examinations were stated to have revealed no evidence of chronic effects from concentrations of 5-10 ppm. The Threshold Limits Committee recommended a TLV of 10 ppm, citing the evidence that irritation may be experienced at around 20 ppm but not at 10 ppm and in the light of evidence that neither acute nor chronic effects occur from repeated daily exposures for many years [83].

According to an International Labor Office (ILO) report [85], Australia, Belgium, Finland, the Netherlands, Sweden, and Switzerland have maximum allowable concentrations (MAC's) for vinyl acetate of 10 ppm, or 30 mg/cu m (sic). The MAC for vinyl acetate in the USSR, Poland, and Yugoslavia is 10 mg/cu m (2.8 ppm). The Rumanian limits consist of average and maximum vinyl acetate concentrations of 50 and 100 mg/cu m (14 and 28 ppm), respectively. The ILO report noted that MAC's or ceiling values are used because time-weighted averages (TWA's) should not be applied to fast-acting substances, eg, irritants and narcotics, or to substances that are particularly toxic.

There is no current US Federal occupational standard for vinyl acetate.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Exposures to vinyl acetate in the workplace have produced mainly reversible irritation of the upper respiratory tract and eyes, sometimes accompanied by skin irritation [4,16-18]. The available literature indicates that vinyl acetate typically produces only minor irritation and produces only

minor irritation and produces only minor, perhaps inconsequential, changes in internal organs [4,17-21]. No evidence was found of long-term systemic, carcinogenic, mutagenic, or teratogenic or other reproductive effects in humans or experimental animals.

Three of three persons exposed to vinyl acetate for short periods at 75.6 mg/cu m had upper respiratory tract irritation (hoarseness or cough); one of four exposed at 14.7 mg/cu m experienced hoarseness; and one of three exposed at 20.0 mg/cu m reported eye irritation [18]. All of these symptoms were reversible. Volunteers exposed to vinyl acetate at less than 1 mg/cu m showed changes in ocular light sensitivity and desynchronization of the EEG as a conditioned response [3], but there are no indications that these changes were signs of potentially adverse CNS effects.

All of the rats (presumably six) exposed for 2 hours to vinyl acetate at 28,000 mg/cu m died [17]. Four-hour LC50's for rats, guinea pigs, mice, and rabbits exposed to vinyl acetate ranged from about 5,400 to 21,750 mg/cu m [4,17]. A beagle exposed to vinyl acetate at 13,388 mg/cu m [4] and all rats exposed at 3,500 mg/cu m [17] survived. Rats exposed to vinyl acetate at 7,000 mg/cu m for 6 hours/day, 5 days/week, for 3 weeks exhibited respiratory difficulty, eye and nose irritation, and increased numbers of macrophages in the lungs [20]; examination at autopsy showed no visible abnormalities. Dogs exposed to vinyl acetate for 4 hours at 840 mg/cu m demonstrated eye blinking and reddening of the sclerae [4], and those exposed at 651 mg/cu m for 1 week had eye irritation and tearing [19]. No other adverse effects were reported in the dogs.

There is very little information available on the long-term effects of vinyl acetate on humans or animals. Among 21 production workers exposed to vinyl acetate at an average of 30.1 mg/cu m (range, undetectable to 172.6 mg/cu m) for about 15 years, 3 stated that they had experienced skin effects, and there were 6 reports of eye, nose, or throat irritation [18]; no chronic effects were found. Rats exposed 4 hours/day, 5 days/week, for 52 weeks to vinyl acetate at 8,750 mg/cu m and followed for up to 135 weeks did not develop tumors [24,25]; however, their mortality after 26 weeks of exposure was higher than that of unexposed control animals. Although there is some structural identity between vinyl acetate and other vinyl compounds that are known to induce cancer, there is currently no evidence to suggest that vinyl acetate is carcinogenic, mutagenic, or teratogenic, or that it causes reproductive effects in humans or animals.

In contrast to the vinyl halides, vinyl acetate contains an ester moiety. Vinyl acetate appears to be rapidly detoxified by esterases present in mammalian blood [27], ie, by a metabolic route that is not available to the vinyl halides. While it is conceivable that vinyl acetate is oxidized to a reactive oxirane, neither biochemical nor biologic evidence is available to indicate that this pathway plays a significant role in the biotransformation of vinyl acetate.

In the absence of retrospective epidemiologic studies of morbidity and mortality, and because there is no evidence that there are chronic effects in humans resulting from long-term exposure [18], NIOSH concludes that the recommended environmental limit should be based on the reversible irritation that has been associated with workplace exposure to vinyl acetate. The lowest concentration reported to induce any irritant effect (hoarseness) was 15 mg/cu m [18]. Since the toxic action of vinyl acetate, on short-term exposure, is expressed largely by reversible irritation of the respiratory tract and eyes [4,16,18], a ceiling concentration limit is deemed more appropriate than a TWA concentration limit. While hoarseness was experienced by only one of four persons exposed at 15 mg/cu m and eye irritation by one of three at 20.0 mg/cu m [18], the permissible exposure limit for vinyl acetate should protect even the more sensitive workers from these possible adverse effects. Therefore, a ceiling limit of 15 mg/cu m (4 ppm), measured in a 15-minute sample, is recommended as the occupational exposure limit, pending the development of more definitive data.

(b) Sampling and Analysis

Personal sampling, using a low-flow air sampler pump, thermal desorption, and analysis by gas chromatography are recommended for the determination of vinyl acetate. This method is described in detail in Appendix I. The sampling equipment is portable, automatic, easy to use, and relatively inexpensive. Gas chromatography offers the necessary sensitivity, precision, and accuracy and can be used in either field or laboratory situations.

(c) Medical Surveillance

Employees should be given preplacement medical examinations if occupational exposure to vinyl acetate may occur. Because vinyl acetate is an irritant to the upper respiratory tract, eyes, and possibly to the skin [4,16-18], attempts should be made to identify persons with preexisting upper respiratory, eye, and skin problems at the preplacement examination. Since there is no evidence that a chronic hazard may be associated with occupational exposure to vinyl acetate, chest roentgenograms are suggested only for preplacement examinations.

(d) Personal Protective Equipment and Clothing

Several investigators [4,16-18] have reported that vinyl acetate caused dermal and ocular irritation. Reports of dermal effects have mentioned that skin irritation, rash, or blisters resulted from exposure to liquid vinyl acetate and that blisters also occurred from contact with clothing wet with vinyl acetate [17]. Ocular effects from exposure to vinyl acetate included eye irritation or reddened sclerae [4]. None of these reported effects were severe, and all were reversible. Clothing impervious to liquid vinyl acetate, eg, rubber [5], should be worn to prevent skin contact. This clothing should include boots, gloves, coveralls, and face shields (8-inch minimum) with goggles or safety glasses with side shields. Such clothing should be cleaned

inside and out after each use. Emergency showers and eyewash fountains should be readily available in case of accidental contact of the skin or eyes with vinyl acetate. When existing engineering controls are not adequate to reduce concentrations of airborne vinyl acetate to or below the recommended environmental limit, appropriate respiratory protective devices should be used, pending corrective action.

(e) Informing Employees of Hazards

Exposure to vinyl acetate may cause respiratory, ocular, or dermal irritation. The reported irritation has not been severe, but prolonged contact with vinyl acetate may cause blisters on the skin or significant irritation of the eyes [4,17]. Employees who may be exposed to vinyl acetate should be advised of the possible adverse effects of such exposure, methods of preventing exposure, and environmental and medical monitoring and surveillance procedures used to detect hazards. The benefits to workers of participating in these environmental and medical monitoring procedures should be stressed.

(f) Work Practices and Engineering Controls

To minimize respiratory contact with vinyl acetate, engineering controls, preferably process enclosure, should be used when needed to control emissions into the workplace atmosphere. Engineering controls should include local exhaust ventilation for processes known to produce large amounts of airborne vinyl acetate. All vinyl acetate containers should be kept tightly closed when not in use, and should be stored properly, ie, conform to the provisions of CFR 1910.106 for storage of flammable and combustible liquids; this action should prevent breaks, spills, or contact with sources of ignition. Vinyl acetate forms flammable and explosive mixtures with air at temperatures of -5.5 C and above, and has explosive limits, in air by volume, from 2.6 to 13.4% [5], so that it should be kept away from heat, sparks, flames, peroxides, aldehydes, or other agents that might cause a fire or an explosion. Vinyl acetate is incompatible with nonoxidizing mineral acids, sulfuric acid, nitric acid, ammonia, aliphatic amines, and alkanolamines. Spills or leaks should be attended to promptly. Emergency showers or eyewash fountains should be available and used to clean affected areas in case of gross skin or eye contact with vinyl acetate. All employees, including maintenance and repair personnel, should be fully informed of all procedures, routine and emergency, that their specific jobs entail.

The residual vinyl acetate vapor in confined spaces may exceed the recommended environmental limit. To ensure that workers in confined spaces are adequately protected, entry into confined spaces that may contain vinyl acetate vapor should be controlled by a work permit system. Permits should be signed by an authorized employer representative, certifying that the following preventive and protective measures have been taken. The confined space should be cleaned with steam, purged with air, and thoroughly ventilated, inspected, and tested for oxygen deficiency and for vinyl acetate and other contaminants before it is entered. Ventilation should continue while workers are in the

confined space. Personal protective equipment should be readily available to the employee entering a confined space. Another worker stationed outside, equipped with approved personal protective and rescue equipment, should observe and be in communication with the employee working in the confined space.

(g) Monitoring and Recordkeeping Requirements

To minimize exposure of employees to vinyl acetate, employers should anlayze engineering controls, work practices, and sanitation procedures on a continuing basis to ensure that they are operating as effectively as possible.

To ensure that concentrations of airborne vinyl acetate in the workplace do not exceed the recommended environmental limit, employers should conduct an industrial hygiene survey at least annually and as soon as possible after any change likely to result in increased concentrations of airborne vinyl acetate. If such a survey shows that concentrations of vinyl acetate in the workplace are above one-half the recommended ceiling limit, a personal monitoring program should be instituted, and both industrial hygiene surveys and personal monitoring should be repeated every 6 months. If personal monitoring shows that an employee is exposed to vinyl acetate at concentrations above the recommended ceiling limit, control measures should be implemented, the employee should be notified of the exposure and of the control measures being taken, and a personal monitoring program should be instituted, monitoring should be conducted weekly until two consecutive samples show that the employee is no longer overexposed to vinyl acetate. Pertinent environmental monitoring and medical records should be retained for 30 years after termination of employment involving exposure to vinyl acetate.

VII. RESEARCH NEEDS

Epidemiologic Studies

Only one very limited (cross-sectional) epidemiologic report on employees exposed to vinyl acetate [18] has been found in the literature, so that further research is required to assess the effects of long-term occupational exposure to vinyl acetate. Long-term epidemiologic studies that assess the effects of vinyl acetate on the skin, eyes, respiratory system, and general metabolic processes should be performed. These studies should include medical histories, specific pulmonary function studies, and comparison of the morbidity and mortality of exposed populations with those of appropriate control populations. It is essential that accompanying industrial hygiene surveys accurately determine actual exposures in terms of concentrations, durations, and frequencies. Concomitant exposures to other chemicals should also be considered.

Experimental Studies

Studies of both short- and long-term exposures to airborne vinyl acetate at low concentrations should be conducted in at least two animal species. Additional toxicologic experiments should be conducted on a variety of species to characterize, both functionally and anatomically, the nature of any changes induced by vinyl acetate and its metabolites. These studies should simulate occupational exposure regimens, in both the exposure schedule and the routes of exposure (inhalation and skin contact). The results of these studies should provide insights into human susceptibility to the effects of low-level exposure to vinyl acetate. Skin absorption of liquid vinyl acetate in humans should be studied.

Well-designed and controlled behavioral studies should be undertaken to determine whether vinyl acetate affects the CNS, as some studies on humans [3] and animals [22,23] have suggested. Electroencephalographic analyses of humans exposed to vinyl acetate should be conducted to determine whether low concentrations can induce adverse neurologic effects, and animal experiments should be conducted to determine whether or not permanent effects on the CNS can result from exposure to vinyl acetate.

The metabolic fate of vinyl acetate as a function of the concentration and duration of inhalation, including possible oxirane (epoxide) formation and the influence of modifiers of metabolism should be studied. Vinyl acetate's possible role as a substrate for esterases and the possible covalent binding of vinyl acetate or its metabolites to macromolecules should also be quantitatively evaluated.

Carcinogenic, Mutagenic, Teratogenic, and Reproductive Studies

No human or animal studies have been found on the possible teratogenic or reproductive effects of vinyl acetate and, thus, this type of research should be performed. Only one study of mutagenesis using S. typhimurium [26] and one study of carcinogenesis in rats [24,25] have been found. Although the results of these studies showed no mutagenic or carcinogenic potential for vinyl acetate, further studies in several species are recommended because of vinyl acetate's structural similarity to compounds known to induce cancer.

Sampling and Analysis

Improved methods of sampling and analysis for vinyl acetate should be investigated. An accurate and precise sampling system for airborne vinyl acetate, as well as convenient, portable direct-monitoring devices, should be developed further.

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IX. APPENDIX I

METHOD FOR SAMPLING AND ANALYSIS OF VINYL ACETATE IN AIR

This analytical method for vinyl acetate is adapted from NIOSH Method No. P&CAM 278 (classification E) [52]. A Class E method is defined by NIOSH as "Proposed: A new, unproved, or suggested method not previously used by industrial hygiene analysts but which gives promise of being suitable for the determination of a given substance." The proposed validation range is 8-210 mg/cu m in a 1.5-liter sample. Although the method has not yet been validated at 7 mg/cu m, which is one-half of the recommended ceiling limit, it shows promise of being usable for determining vinyl acetate at this concentration.

Principle of the Method

A known volume of air is drawn through a tube containing a Chromosorb 107 to trap the vinyl acetate present. The vinyl acetate is thermally desorbed into a 300-ml chamber. An aliquot of the desorbed vapor is injected into a gas chromatograph. The area of the resulting peak is determined and compared with the areas obtained from the injection of standards.

Range and Sensitivity

(a) Sample loadings of between 2 and 332 μg of vinyl acetate for each sampling device are acceptable. Samples have been successfully collected from dynamically generated atmospheres of vinyl acetate over the concentration range of 8.2-206 mg/cu m when the relative humidity of the sampled air was greater than 80%.

(b) The slope of a typical calibration curve (integrator response vs mass of vinyl acetate in the sample tube) was 687 volt-seconds/g. The sensitivity of the flame ionization detector was 4.04 x 10*-6 coulombs/g of vinyl acetate (* indicates an exponent).

(c) The lowest quantifiable level was determined to be 0.5 μg of vinyl acetate/300-mg bed of Chromosorb 107. At this loading the relative standard deviation of replicate samples was better than 10%.

Interferences

(a) When two or more substances are known or suspected to be present in the air sampled, such information should be transmitted with the sample, because the substances may interfere with the analysis of vinyl acetate.

(b) Any substance that has the same retention time as vinyl acetate at the operating conditions described in this method is an interference. Therefore, retention time data on single or multiple columns cannot be considered proof of chemical identity.

(c) If the possibility of interference exists, separation conditions, eg, column packing, temperature, carrier flow, or detector, must be changed to circumvent the problem.

Precision and Accuracy

(a) The pooled relative standard deviation of the sampling and analytical method was 8.1%. This reflects the precision of sampling and analysis of 50 samples of vinyl acetate collected with calibrated personal sampling pumps from humid atmospheres (>80%) over the concentration range of 8-206 mg/cu m. The relative standard deviation of samples collected from atmospheres averaging 8.6 mg/cu m (range 8.2-9.0) was 9.5%, from atmospheres averaging 24.3 mg/cu m (range 18.6-39.2) was 8.0%, and from atmospheres averaging 181 mg/cu m (range 159-206) was 5.9%.

(b) The concentration of the sampled air was independently determined using a gas-phase infrared analyzer. The samples were collected from humid air and stored at room temperature. The determination averaged 7% high, 5% high, and 4% low when analyzed on days 1, 7, and 14, respectively. Thus, the sample displayed a 0.8%/day storage loss when stored at room temperature. This loss can be attributed to the analyte degrading in the presence of water, because samples spiked with 18 μg of vinyl acetate in "dry" hexane gave 98% recovery when stored for 14 days at room temperature.

(c) The breakthrough volume and therefore the capacity of Chromosorb 107 for vinyl acetate decreased with increasing relative humidity. Under the most adverse conditions tested, 83% relative humidity, the breakthrough volume was found to be 4.0 liters when an atmosphere of vinyl acetate at 113 mg/cu m was sampled at 0.125 liter/minute.

Advantages and Disadvantages of the Method

(a) The sampling device is small, portable, and involves no liquids.

(b) The samples are analyzed using a quick instrumental method and the sampling tubes can be reused after the analysis is completed.

(c) Many of the interferences can be eliminated by altering chromatographic conditions.

(d) The precision of the method is limited by the reproducibility of the pressure drop across the sampling tubes. Variations in pressure drop will

affect the flowrate. The reported sample volume will be imprecise because the pump is usually calibrated for one tube only.

(e) The amount of sample that can be collected is limited by the capcity of the sampling device. When the amount of vinyl acetate found on the backup section exceeds 10% of the amount found on the front section, the possibility of sample loss exists. Migration from the front to the backup section is not a problem because the sections are separated and individually capped immediately after sampling.

Apparatus

(a) Personal sampling pump capable of accurate performance at 0.1 liter/minute. The pump must be calibrated with a representative sampling device in line, and the pump battery must be fully charged prior to being used.

(b) Chromosorb 107 sampling tubes. Individual front and backup tubes (Century Systems Corporation "Flare" tubes or equivalent) are used. The front section is a stainless steel tube 7.3 cm long with a 6-mm outer diameter, a 4-mm inner diameter, and a 45-degree flare at one end. The backup section is a chrome-plated nickel tube 3 cm long with a 6-mm outer diameter, a 4-mm inner diameter, a 45-degree flare at one end and a hose connection at the other end. Each tube has a permanent metal frit in the outlet end of the tube. The front section contains 300 mg of prewashed Chromosorb 107 held in place with a removable metal frit. The backup section contains 50 mg of prewashed Chromosorb 107 held in place with a plug of silylated glass wool. The sampling device is assembled by joining the front and backup sections with a nylon nut and fitting. A hollow nylon ferrule is placed between the two sections. The pressure drop across the tubes must be less than 10 inches of water at a flowrate of 0.1 liter/minute. The Chromosorb 107 is washed in a Soxhlet extractor for 8 hours with water, 8 hours with methanol, and 8 hours with dichloromethane. The sorbent is then dried overnight in a vacuum oven. The tubes are loaded with sorbent and thermally purged for 2 minutes with helium at 150 C. After cooling in a closed container, the ends are capped.

(c) Thermal desorber equipped with thermostatted desorbing oven, 300-ml sample reservoir, and a 2-ml gas sampling loop (Century Systems Corporation Programmed Thermal Desorber or equivalent).

(d) Gas chromatograph equipped with a flame-ionization detector and electronic integrator.

(e) Gas-chromatographic column (20-feet x 1/8-inch outer diameter) made of silanized stainless steel and packed with 10% FFAP on 80/100 mesh Chromosorb W AW.

(f) Vials, 1.5-ml, with aluminum serum cups equipped with Teflon-lined silicone rubber septa.

(g) Microliter syringes, 10-μl and convenient sizes for making standards.

(h) Pipette, 1,000-μl, with disposable plastic tips.

(i) U-tube, glass with at least one hose connection, approximately 75-ml internal volume.

(j) Pump capable of drawing 200 ml/minute through the front section of the sampling device.

(k) Gas bag, 10-liter volume for helium purge gas.

(l) Test tubes with close-fitting plastic caps.

(m) Ring stand with clamps.

Reagents

Whenever possible, reagents used should be ACS Reagent Grade or better.

(a) Vinyl acetate, practical, inhibited with hydroquinone and freshly distilled before use.

(b) Hexane (ultraviolet grade).

(c) Helium, Bureau of Mines Grade A.

(d) Hydrogen, prepurified.

(e) Air, filtered and compressed.

Procedure

(a) Cleaning of equipment. All nondisposable glassware used for the laboratory analysis of vinyl acetate is washed with detergent and rinsed thoroughly with tapwater and distilled water.

(b) Collection and shipping of samples.

(1) Immediately before sampling, remove the plastic caps from the inlet and outlet ends of the sampling tube.

(2) Connect the tube to the sampling pump using a short piece of flexible tubing. The backup section is positioned nearest the pump. The sampling tube is kept vertical during sampling to prevent channeling through the device.

(3) Air being sampled must not pass through any hose or tubing before entering the sampling device.

(4) The temperature, pressure, and volume of air sampled is measured and reported. The volume sampled should not exceed 3 liters, sampled at a flowrate of 0.1 liter/minute or less. Record either the flowrate and sampling time or the initial and final stroke readings and the volumetric stroke factor.

(5) Immediately after sampling, disassemble the two sections, cap the sections with plastic caps, and label the sections. Do not use rubber caps.

(6) For every 10 samples taken, handle one sampling device in the same manner as the samples (uncap, disassemble, cap, label, and transport); however, do not sample any air through this device. Label this device as a blank.

(7) Samples received at the laboratory are logged in and analyzed as soon as possible. Samples stored at room temperature for 14 days exhibit an 11% loss of analyte.

(c) Analysis of Samples

(1) Preparation of samples. Remove the caps from either a front or a back section. Wipe the outside of the tube with a clean laboratory wiper.

(2) Thermal desorber conditions. Typical operating conditions for the thermal desorber are:

(A) 150 C desorbing oven temperature
(B) 70 ml/minute desorbing rate, helium gas
(C) 160 C transfer line temperature
(D) 15 second pressure equalization time

(3) Gas-chromatographic conditions. Typical operating conditions for the gas chromatograph are:

(A) 33 ml/minute helium carrier gas flowrate
(B) 40 ml/minute hydrogen flow to detector
(C) 435 ml/minute airflow to detector
(D) 160 C injector temperature
(E) 160 C manifold (detector) temperature
(F) 60 C oven temperature

Under these conditions, the capacity ratio for vinyl acetate should be 4.4.

(4) Thermal desorption of samples. Wipe off the tube and insert it in the desorbing oven. Desorb with helium at atmospheric pressure. The helium is stored in the 10-liter gas bag. Desorbing with air chars the Chromosorb and renders it unsuitable for reuse.

(5) Injection. Inject a 2-ml aliquot of the desorbed vapors into the gas-chromatographic column. Since the desorbed vapors are stored in a reservoir, as many as five replicate injections of each sample can be made.

(6) Measurement of area. Measure the area of the sample peak with an electronic integrator or other suitable technique of area measurement. The results are read from a standard curve as prepared in subsection (d)(4).

(7) Preparation for next sample. After satisfactory analysis is obtained, purge the thermal desorber with helium for 2 minutes. Remove the tube from the desorbing oven, place it in a test tube and cap the test tube. When the tube is cool, remove it from the test tube and cap it with the plastic caps.

(d) Calibration and Standardization

(1) It is convenient to express the concentration in terms of μg of vinyl acetate/sample tube. Standard curves are prepared by loading clean sampling tubes (front sections) with known amounts of vinyl acetate. The density of vinyl acetate (0.932 mg/μl at 20 C) is used to convert the volume taken to mass.

(2) Preparation of standards. Pipet 1.00-ml aliquots of hexane into clean glass vials. Crimp the vials shut with an aluminum serum cap equipped with a Teflon-lined silicone rubber septum. Inject either 25, 10, 5, or 1 μl of freshly distilled vinyl acetate into each vial. These standard solutions are freshly prepared for each analysis.

(3) Loading the standard. Support a U-tube on a ring stand. Using a short length of tubing, attach the outlet end of a clean front section of a sampling tube to a small pump. The inlet end of the clean front section is attached to the side of the U-tube that has the hose connection. Use the solvent-flush technique to withdraw a 2-μl aliquot of a standard solution. Turn on the pump and inject this 2-μl aliquot into the end of the U-tube farthest from the sampling tube. Sweep enough air through the U-tube (2 minutes at 200 ml/minute, approximately five volume changes) to ensure that all the vinyl acetate is loaded on the sample tube. Stop the pump, remove the sample tube, cap both ends, and label. This tube now contains a known amount of vinyl acetate.

(4) Standardization. Analyze each tube from subsection (d)(3) as in subsection (c)(3). The standard curve is obtained by plotting the amount of vinyl acetate loaded on a tube vs the peak area found. If conditions warrant, prepare standards at higher or lower concentrations.

(e) Calculations

(1) The sample weight in μg is read from the standard curve.

(2) Blank corrections are not expected. If the analysis shows a blank correction is needed, the correction is:

$$WF = Ws - Wb$$

where:

WF = corrected amount (μg) on the front section of the sample tube.
Ws = amount (μg) found on the front section of the sample tube.
Wb = amount (μg) found on the front section of the blank sample tube.

A similar procedure is followed for the backup sections.

(3) The concentration, C, of vinyl acetate in the air sampled is expressed in mg/cu m, which is numerically equal to μg/liter.

$$C = \frac{WF + WB}{V}$$

where:

WF = corrected amount of vinyl acetate found on front section in μg.
WB = corrected amount of vinyl acetate found on backup section in μg.
V = volume of air sampled in liters.

(4) If desired the results may be expressed in ppm at 25 C (298 K) and 760 mmHg.

$$C(ppm) = C\ (\mu g/l) \times \frac{24.45}{86.1} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P = pressure of air sampled in mmHg.
T = temperature of air sampled in degrees C.
24.45 = molar volume at 25 C and 760 mmHg in liters/mole.
86.1 = molecular weight of vinyl acetate in g/mole.

X. APPENDIX II

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole

mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 F (21.1 C); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if

possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.
>
> Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill" or "incineration." Warnings such as "comply with local, state, and Federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified

as to type and NIOSH or Mine Safety and Health Administration approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

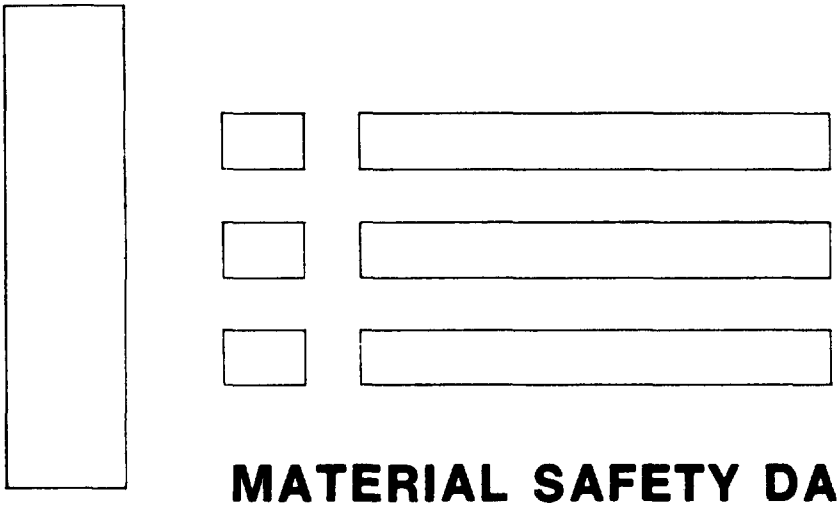
(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous substance. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.



MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION	
MANUFACTURER'S NAME	REGULAR TELEPHONE NO EMERGENCY TELEPHONE NO
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS		
MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA			
BOILING POINT, 760 MM HG		MELTING POINT	
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE	
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT	
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)	
APPEARANCE AND ODOR			

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE			
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER		
EXTINGUISHING MEDIA					
SPECIAL FIRE FIGHTING PROCEDURES					
UNUSUAL FIRE AND EXPLOSION HAZARD					

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY _____

ADDRESS _____

DATE _____

XI. TABLES AND FIGURES

TABLE XI-1

PHYSICAL AND CHEMICAL PROPERTIES OF VINYL ACETATE

Molecular formula	CH3COOCH=CH2
Molecular weight	86.1
Appearance	Clear, colorless liquid
Odor	Pleasant, sweet to sharp, irritating
Boiling point	72.7 C
Melting (freezing) point	-100.2 C
Vapor density (air = 1)	2.97
Specific gravity	0.9338 at 20 C*
Vapor pressure	100 mmHg at 21.5 C (see Figure XI-1)
Refractive index	1.3952 at 20 C
Viscosity	0.43 centipoise at 20 C
Heat of vaporization	90.6 cal/g at 72.7 C
Heat of combustion	5.75 kcal/g
Heat of polymerization	21.3 kcal/mole
Solubility	2.5 g/100 ml water at 20 C; soluble in most organic solvents
Explosive limits (in air, by volume)	2.6-13.4%
Flashpoint (open cup)	-5.5 C
Autoignition temperature	427 C
Conversion factors	1 mg/cu m = 0.284 ppm 1 ppm = 3.5 mg/cu m

*Density at 20 C given as 0.982 in reference 52

Adapted from references 1,2,5-9,12

TABLE XI-2

OCCUPATIONS WITH POTENTIAL EXPOSURE
TO VINYL ACETATE

Chemical-synthesis workers
Equipment cleaners
Equipment repairers
Maintenance workers
Monomer-containing-aerosol producers
Monomer-containing-aerosol users
Monomer loaders and unloaders
Monomer production workers
Monomer samplers and gagers
Monomer transport workers
Polymer compounders
Polymer fabricators
Polymer loaders and unloaders
Polymer packagers
Polymer processors
Polymer production workers
Polymer transport workers
Quality-control-laboratory workers
Warehouse workers

Adapted from references 2,5,8

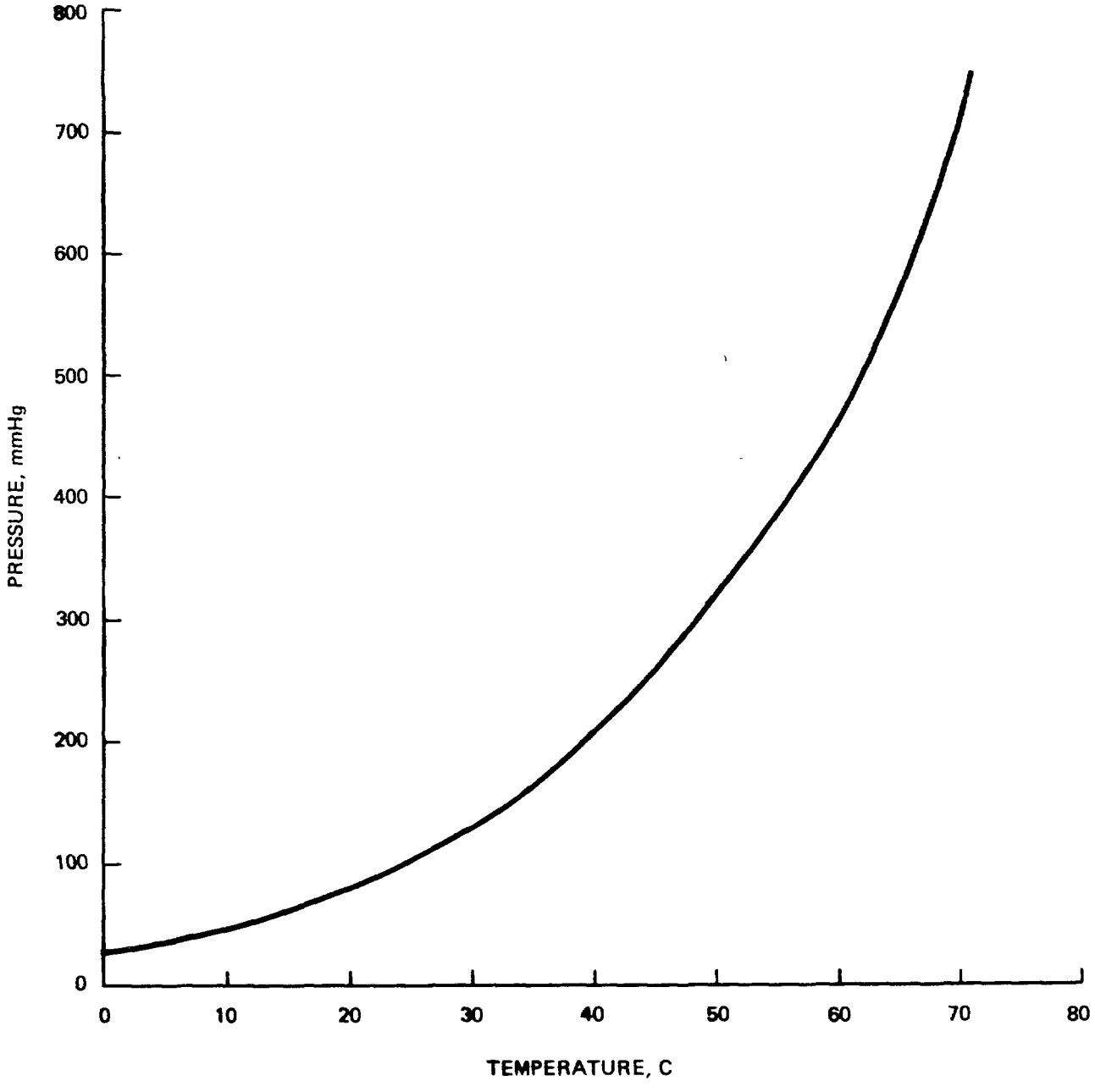


FIGURE XI-1

VAPOR PRESSURE OF VINYL ACETATE VS TEMPERATURE

Adapted from references 1 and 5

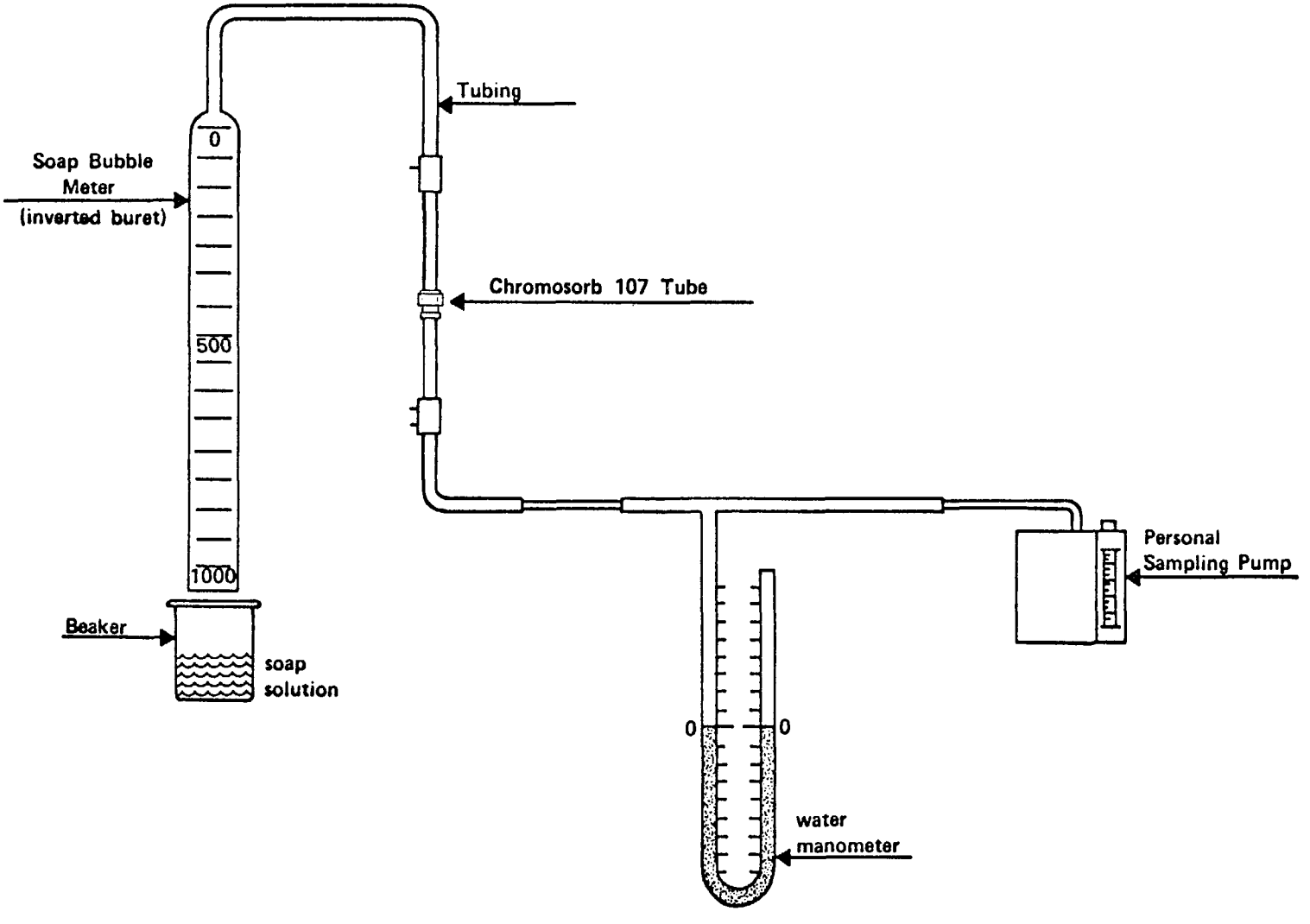


FIGURE XI-2

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH CHROMOSORB 107 TUBE

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DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
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NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
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