DEVELOPMENT OF PERFORMANCE CRITERIA FOR PROTECTIVE CLOTHING USED AGAINST CARCINOGENIC LIQUIDS

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FOREWORD

The National Institute for Occupational Safety and Health (NIOSH) is responsible for helping ensure that every person in the Nation has safe and healthful working conditions. To accomplish this end, the Institute engages in research on occupational safety and health problems, including the evaluation of hazards and the development of testing and performance requirements for personal protective equipment.

One of the many work-place hazards considered to be significant by the Institute is dermal contact with carcinogenic liquids. At the present time, there are no comprehensive criteria or other guidelines available to assist in the manufacture, selection, and testing of protective clothing materials and garments used to protect against this hazard. Therefore, Arthur D. Little, Inc., is pleased to publish this initial research effort for development of such criteria.

It should be noted that the research described here was contracted under a specific scope of work. Further evaluation and validation of the developed criteria are necessary.

PREFACE

This report addresses three principal topics:

1. An identification of occupational exposures to carcinogenic liquids (Section II).
2. The development of performance criteria for materials used in protective clothing for use against carcinogenic liquids (Section III); and
3. The development of a permeation test method for evaluating clothing materials (Section IV).

Of particular interest are the results of the permeation experiments. In these experiments, clothing materials were evaluated as barriers to several industrially important chemicals suspected of being carcinogenic (e.g., benzene and trichloroethylene). The results suggest that several commercially-available materials may not offer adequate protection in certain applications.

Further, it should be noted that Appendix A is a collection of "overview documents" for each chemical used in the experimental program. Each document is a summary of the primary sources, uses, properties, hazards, and recommended handling procedures of the subject chemical.

Arthur D. Little, Inc., has carried out this research assignment for the National Institute for Occupational Safety and Health (NIOSH) under the direction of Project Officer William F. Todd of the Protective Equipment Section, Control Technology Research Branch, Division of Physical Sciences and Engineering. NIOSH, a research institute of the U.S. Department of Health, Education, and Welfare, was created by the Occupational Safety and Health Act of 1970. As mandated by this Act, NIOSH performs and sponsors research, and develops criteria for recommended standards applicable to the problems of occupational safety and health.

The data collected in this and subsequent investigations are intended to support safety standards needed to ensure the proper protection of workers who handle potentially harmful chemicals.

ABSTRACT

Workers who produce, use, and transport liquid chemicals can be exposed to many compounds capable of causing harm to the human body. The deleterious effects of contacting these liquids can range from acute trauma, such as skin irritation and burn, to chronic degenerative disease, such as cancer. Contacts can extend from one-time splashes to continuous 15-60 minute wettings due to accidental spills or emergency situations. Accordingly, there is a strong need for clothing that will protect workers for at least 60 minutes of continuous contact. However, comprehensive performance criteria for protective clothing is lacking.

In this study, a set of recommended performance criteria was compiled. Further, to fill a void in the coverage of available test methods, a simple experimental procedure was developed to measure the resistance to permeation of protective clothing materials by liquid chemicals. Using this procedure, the barrier properties of several polymeric materials were evaluated against nine carcinogenic liquids (e.g., benzene, trichloroethylene and β-propiolactone). Breakthrough times, steady state fluxes, and chemical solubilities were measured. In many cases, the breakthrough times for widely used materials were less than the recommended 60 minutes.

Such results suggest that many workers may not be protected by currently recommended clothing. However, substantially improved protection could be provided if comprehensive performance profiles were generated and made available for the design and specification of protective clothing. Clothing materials should be subjected to a comprehensive performance evaluation. Evaluations, including permeation testing against the specific chemical to be handled, should be performed over the range of anticipated exposure conditions.

This report was submitted in fulfillment of Contract No. 210-76-0130 by Arthur D. Little, Inc., under the sponsorship of the National Institute for Occupational Safety and Health.

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I. INTRODUCTION

Workers involved in the production, use, and transportation of industrial chemicals can be exposed to numerous compounds capable of causing harm to the human body. These chemicals can be in the form of vapors, mists, dusts, liquids, and solids. Exposures can occur during routine work-place activities as well as during emergency situations, even with chemical processing systems incorporating state-of-the-art designs and controls. One of the most serious hazards of exposure to chemicals is skin contact by liquids. The deleterious effects of certain liquids can range from acute trauma, such as skin irritation and burn, to chronic degenerative disease, such as cancer. This strongly suggests that emphasis should be placed on eliminating skin contacts through measures such as the use of protective clothing.

However, although considerable effort has been expended in the development of many other areas of personal protection, relatively little effort has gone into developing criteria for the proper specification and use of protective clothing. In fact, there is almost no comprehensive information available which describes the properties that clothing materials should have in order to provide protection against harmful liquids. Clothing materials appear to be selected most often on the basis of their resistance to visible degradation by common solvents, acids or alkalies. In many cases the test chemical may not be the chemical of concern (i.e., an analog is used) and, therefore, may not interact with clothing materials in the same way. Further, even if clothing materials resist visible degradation or swelling, a question remains as to the completeness of protection actually provided since permeation of small amounts of liquid can occur without gross interactions with the barrier. This question is especially important when considering resistance to permeation by carcinogenic chemicals which have no established threshold levels for carcinogenicity on skin contact.

While guidelines for safe exposures* have been developed for other toxic chemicals, few such guidelines have been promulgated for carcinogenic chemicals. Accordingly, the Occupational Safety and Health Administration (OSHA) recommends that protective clothing materials be impermeable to carcinogenic liquids.[1] However, OSHA does not offer recommendations for assessing the barrier properties of such clothing materials.

Because of the absence of this important information, the National Institute for Occupational Safety and Health (NIOSH) has sponsored this program to investigate the performance of protective clothing materials against selected carcinogenic chemicals. Emphasis has been placed on studying permeation of chemicals handled in the liquid state. The results of this work, as presented in this report include:

(1) A description of the form and extent of worker needs for protective clothing;

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* Defined as time-weighted average (TWA) concentrations for an 8-hour work day.

(2) A recommended criterion for clothing resistance to permeation and an overview of several other functional requirements;

(3) Recommended test methods for evaluating the performance of clothing materials; and,

(4) Data showing the resistance of currently-used clothing materials to permeation by selected carcinogens.

The next section begins this presentation with a review of occupational exposures to carcinogenic liquids.

II. OCCUPATIONAL EXPOSURES TO CARCINOGENIC LIQUIDS

According to NIOSH, approximately 1500 industrial and research chemicals have been categorized as suspected human carcinogens.[2] This number includes mined, manufactured, processed, synthesized and naturally occurring organic and inorganic compounds. Of these chemicals, fourteen have been classified as highly carcinogenic and are now closely regulated by OSHA.[3] Since NIOSH's listing is too large to permit a comprehensive study of occupational exposures to carcinogenic liquids, ten compounds which are liquid at ambient conditions were selected from the listing for in-depth study. In this study, information characterizing the production, use and transportation of these compounds has been documented and subsequently used to define occupational exposures.

A. SELECTED CARCINOGENIC COMPOUNDS

The carcinogenic compounds selected were identified through a consensus-type process involving specialists in chemical carcinogenesis, occupational safety and health, organic and inorganic chemistry, and the chemical process industries. A large number of compounds were reviewed for carcinogenic activity, the number of workers potentially affected, current industrial importance, chemical type and, of course, physical state at ambient conditions. As a group, the compounds finally chosen show diversity in most of these parameters and thereby include many of the variations found in industrial situations. For example, benzene is a very important industrial chemical, while β-propiolactone use is limited in volume and scope. However, β-propiolactone is considerably more carcinogenic than benzene. The ten chemicals selected for study are identified in Table 1.

B. OVERVIEW DOCUMENTS

Information relating to current production, use, transportation and associated exposure hazards of each of the selected liquids has been compiled and an "overview document" prepared. Each overview document contains information under the following headings.

- Summary
- Selected Properties (i.e., physical, chemical, and carcinogenic)
- Sources (i.e., production sources)
- Uses
- Transportation
- Number of Affected Workers
- Recommended Protective Clothing Materials
- Current Practices in Worker Protection
- References

The ten overview documents are included as Appendix A to this report.

The information contained in these documents was used to define typical occupational exposures to carcinogenic liquids.

TABLE 1

CARCINOGENIC COMPOUNDS SELECTED FOR STUDY

Carcinogenic Compound	Chemical Classification	Source
Trichloroethylene	Alkyl Halide	Eastman Kodak
Epichlorohydrin	Halogenated Epoxide	Eastman Kodak
Coal-tar Creosote	Aromatic	Allied Chemical
Benzene	Aromatic	Eastman Kodak
4,4-Methylenebis (2-chloroanaline) in solvent	Aromatic Amine	–
Ethylenimine	Aliphatic Amine	Dow Chemical
1,1-Dimethylhydrazine	Aliphatic Amine	Tridom/Fluka
2-Nitropropane	Nitroparaffin	Aldrich Chemical
β-Propiolactone	Ester	Tridom/Fluka
Hexamethylphosphoramide	Amide	Aldrich Chemical

C. OCCUPATIONAL EXPOSURES

In reviewing the ten overview documents, conditions for worker exposure to carcinogenic liquids were found to be similar for each chemical. Potential exposures can be described in terms of (1) production and use, and (2) transportation.

1. Production and Use

Because the processes and equipment identified for both the industrial production and the industrial use of carcinogenic liquids are somewhat similar, potential contacts associated with each are discussed together.

a. Closed Processing Systems (Continuous and Batch)

Usually no chemical/worker interactions exist in closed process systems, so there is little potential for routine worker exposure to carcinogenic liquids. However, there are several exceptions:

- In the absence of automatic sampling, the manual collection of process samples can result in one-time splashes or minor spills.
- Minor maintenance operations which do not require a process shutdown, such as the repair of leaky valves or replacement of seals on rotating equipment, can result in continuous exposure to liquid for 15-60 minutes.
- Major maintenance operations which require a process shutdown, such as the periodic opening of and entering vessels for cleaning and inspection, can result in continuous exposure to liquid for 60 minutes or more.

- Emergency conditions which lead to a major spill and/or process shutdown, such as primary equipment failure, can result in continuous wetting for 15-60 minutes.

b. Open Processing Systems (Continuous and Batch)

Open systems are usually not used in the production of carcinogenic chemicals. However, open-vessel continuous and batch processing of carcinogenic chemicals to manufacture other end products is still practiced. The primary hazard associated with open vessel processing is exposure to vapor-phase chemicals; since improved work practices have substantially eliminated the gross exposures to liquids which were prevalent only a few years ago. However, worker exposure to liquid can still result from a number of operations:

- In small processing operations, the manual addition of reactants or removal of product can result in periodic splashes or minor spills.

- The collection of process samples can result in one-time splashes or minor spills.

- Minor maintenance operations which do not require a process shutdown, such as the repair of leaky valves or replacement of seals on rotating equipment, can result in continuous exposure to liquid for 15-60 minutes.

- Major maintenance operations which do not require a process shutdown, such as the periodic opening of and entering vessels for cleaning and inspection, can result in continuous exposure to liquid for 60 minutes or more.

- Emergency conditions which lead to a major spill and/or process shutdown, such as primary equipment failure, can result in continuous wetting for 15-60 minutes.

c. Laboratory-Scale Processing Systems

A considerable amount of laboratory-scale work involves the use of carcinogenic liquids. This work is usually carried out in well-ventilated hoods with the most potent liquids handled only in special glove boxes. From the safety/health point of view, an important aspect of laboratory research is that most operations are manual. Therefore, workers may interact with carcinogenic liquid throughout most operations:

- Opening containers and transferring quantities of liquid from one container to another can result in periodic splashes or minor spills

- Manipulating and handling apparatus can result in periodic or prolonged contact with "wet" apparatus.

- Gloves used in glove boxes are often in contact with liquid and vapor continuously for days or weeks at a time. Therefore, the potential exists for glove materials to become saturated by chemical and thereby provide little or no protection.

2. Transportation

The manipulations involved in loading and unloading carcinogenic liquids are similar for shipment by tank car, tank truck, or barge. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and collecting samples. This routine handling of "wet" connections and associated equipment can result in intermittent contact with liquid for 15 to 60 minutes.

3. Summary

In summary, analyses of industrial operations show that liquid contacts can range from one-time splashes in the collection of process samples to continuous 15-60 minute wettings due to accidental spills or emergency process shutdowns. Accordingly, the protection offered by clothing materials recommended for use with carcinogenic liquids should be compatible with these potential liquid contacts.

III. PROTECTIVE CLOTHING USED AGAINST CARCINOGENIC LIQUIDS

The most obvious function of protective clothing used against carcinogenic liquids is the isolation of workers during occupational exposures. However, protective clothing must also possess a number of other important characteristics. Notably, clothing should resist physical hazards and permit easy execution of the many manual tasks necessary in working with carcinogenic liquids. These, as well as other performance requirements, are discussed in the following pages.

A. PERFORMANCE REQUIREMENTS

Six characteristics pertinent to the performance of protective clothing have been identified through an evaluation of the day-to-day tasks and of typical environmental conditions encountered during the production, use, and transportation of carcinogenic liquids. They are:

- Strength;
- Chemical Resistance;
- Thermal Resistance;
- Dexterity/Flexibility;
- Cleanability; and,
- Aging Resistance.

With the exceptions of cleanability and aging resistance, all are applicable to both disposable clothing items and reusable clothing items. Such items include gloves and outerwear components (i.e., suits, aprons, boots and hats).

As shown in Table 2, each characteristic has been expanded into one or more quantifiable performance requirements. These requirements relate to clothing resistance to physical hazards, to the adaptability of clothing to manual tasks, and to the length of clothing service life. Each requirement can be important by itself or as a supplement to other performance requirements. For example, without adequate strength to resist cut or puncture, the resistance of a clothing material to permeation by carcinogenic liquid could be compromised by sharp edges or points encountered during normal use. Resistance to permeation by liquid, the single most important protection requirement, is included under chemical resistance. At least one measurable, testable parameter can be described for each performance requirement. Both quantitative performance criteria and associated test methods can be specified through use of these parameters.

B. PERFORMANCE CRITERIA

The specification of a performance criterion for each performance requirement would be a very complex undertaking. Such criteria must be based on worker needs and potential hazards in each segment of carcinogenic liquid production, use and transportation. For example, the strength requirements for gloves used in making and breaking the connections required for bulk liquid loading and unloading could differ substantially from the strength requirements for gloves

TABLE 2

PROTECTIVE CLOTHING PERFORMANCE REQUIREMENTS

Characteristics	Specific Requirements
Strength	Tear Resistance Tensile Strength Puncture Resistance Abrasion Resistance
Chemical Resistance	Strength Degradation Permeation Resistance
Thermal Resistance	Strength Degradation
Dexterity/Flexibility	Dexterity (gloves only) Flexibility
Cleanability	Decontamination Washability
Aging Resistance	U.V. Resistance

used in other plant activities. Each operation would probably require a separate specification for strength. The need for such individual attention in developing performance criteria has been confirmed in discussions with two major manufacturers of protective clothing.[4] In addition, the manufacturers voiced the need for standard test methods which would minimize or stop the nonuniform testing and data presentations now practiced.

It was an objective of this program to develop a standard test method and performance criterion pertinent to permeation of carcinogenic liquid through clothing materials and to survey published test methods relevant to the other performance criteria. The results of the survey are presented in Part C which follows. Accomplishments related to permeation are discussed in Section IV.

C. STANDARDIZED TEST METHODS

Published test methods were surveyed for their relevance in evaluating protective clothing used against carcinogenic liquids. Sources included:

- ASTM;
- ANSI;
- AATCC;
- Federal (U.S.) Test Methods;
- British Test Methods;
- Protective Clothing Manufacturers;
- Published NIOSH Reports; and,
- Miscellaneous Sources.

As a result of this survey, test methods were identified for all but three of the clothing performance requirements. Many of the methods are adaptable as published. Several others can be used, but with minor modifications. Specific test methods were not found for permeation resistance, thermal resistance or decontamination. As described in the next section of this report, a special method was devised for permeation resistance. Thermal resistance was related to changes in tensile strength after thermal exposure, and decontamination was correlated with individual chemicals. Brief descriptions of each test method, with suggestions for modifications where appropriate, are presented below. Table 3 provides a summary list of these methods, together with a listing of methods currently used by two protective clothing manufacturers. Manufacturers' information is included for reference only, and illustrates cases in which several test methods are used to measure the same performance characteristic.

The following methods are recommended for consideration as industry standards in the evaluation protective clothing used against carcinogens.

1. Strength

a. Tear Resistance

ASTM D2261 (FEDERAL TEST METHOD 191-5134): TEARING STRENGTH OF WOVEN FABRICS BY THE TONGUE (SINGLE RIP) METHOD.

This test method establishes the tear resistance of a material by using constant-rate-of-extension tensile testing machine, such as an Instron, to pull apart a pre-slit rectangular specimen. The force required to propagate the tear is determined.

b. Tensile Strength

ASTM D1682 (FEDERAL TEST METHODS 191-5100 or -5102): BREAKING LOAD AND ELONGATION OF TEXTILE FABRICS.

This test method establishes the strength of a material in tension by using a tensile testing machine, such as an Instron, to pull apart a rectangular specimen. The minimum force for break and the associated elongation are determined.

c. Puncture Resistance

ARTHUR D. LITTLE TEST METHOD: A TEST METHOD FOR RESISTANCE TO (STATIC) PUNCTURE.*

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* From DHEW (NIOSH) Publication No. 77-134, entitled, "The Development of Criteria for Firefighters' Gloves."

TABLE 3

RECOMMENDED TEST METHODS SUMMARY TABULATION

Clothing Equipment	Test Methods		
		Currently-Used Methods	
	Recommended Methods	Manufacturer #1	Manufacturer #2
A. STRENGTH			
1. Tear Resistance	ASTM D2261 (Fed. 191-5134)	Fed. 191-513, & 191-5134	Fed. 191-5132
2. Tensile Strength	ASTM D1682 (Fed. 191-5100 & 191-5102)	Fed. 191-5100	–
3. Puncture Resistance	ADL Method (See Text and Appendix B)	–	Special
4. Abrasion Resistance	ASTM D1175 (Fed. 191-5308)	Fed. 191-5306	ASTM 1044
B. CHEMICAL RESISTANCE			
1. Strength Degradation	ASTM D543	Special	ASTM D1239
2. Permeation Resistance	New ADL Method (See Text and Appendix B)	Special	ASTM D814
C. THERMAL RESISTANCE			
1. Strength Degradation	Proposed ADL Method (See Text)	Special*	–
D. DEXTERITY/FLEXIBILITY			
1. Dexterity (gloves only)	ADL Method (See Text and Appendix B)	–	Special
2. Flexibility	ASTM D1388 (Fed. 191-5206)	Fed. 191-5200	Fed. 191-5206
E. CLEANABILITY			
1. Decontamination	Special (See Text)	–	–
2. Washability	AATCC 61 (Test IIIA)	–	–
F. AGING RESISTANCE			
1. U.V. Resistance	ASTM G27	ASTM G25	–

*Similar to ADL Method, but lower temperatures used.

This test method establishes the puncture resistance of a material by using the compression mode of an Instron with a specified penetrometer to puncture a specimen. The minimum force required to puncture the material is determined. A copy of this test method is included in Appendix B to this report.

d. Abrasion Resistance

ASTM DD1175 (FEDERAL TEST METHOD 191-5308): ABRASION RESISTANCE OF TEXTILE FABRICS . . . UNIFORM ABRASION METHOD.

This test method, using the Schiefer Abrasion Testing Machine, applies abrasive action uniformly in all directions over the surface of a material specimen. A spring steel abradant is used for woven, felted, pile or knit fabrics; while a cross-cut tungsten abradant is used for coated fabrics. The abrasion resistance of a specimen is specified either in terms of qualitative visual changes or by a more quantitative weight loss criterion.

2. Chemical Resistance

a. Strength Degradation

ASTM D543: RESISTANCE OF PLASTICS TO CHEMICAL REAGENTS.

This test method is based on the immersion of material specimens in selected liquid chemicals for seven days at room temperature. The effects of immersion are specified both in terms of visual changes and by changes in tensile strength per ASTM D1682 (above).

Although D543 recommends fifty (50) standard chemicals for testing, it would be more appropriate to select chemicals related to and including carcinogens of interest. Several of the ASTM standard chemicals should also be included and the immersion temperature elevated to 50°C to accelerate the test to less than seven days.

b. Permeation Resistance

(A recommended test method is described later in this report.)

3. Thermal Resistance

a. Strength Degradation

ARTHUR D. LITTLE PROPOSED TEST METHOD: THERMAL RESISTANCE OF MATERIALS.

Material specimens should be exposed to three elevated temperatures (e.g., 50°C, 100°C, 150°C) for a specified time (e.g., 100 hours). The effects of the elevated temperatures should be specified both in terms of visual changes and by changes in tensile strength and elongation per ASTM D1682 (above).

4. Dexterity/Flexibility

a. Dexterity (Gloves Only)

ARTHUR D. LITTLE TEST METHOD — A TEST METHOD FOR GLOVE DEXTERITY.*

This test method establishes an ability to meet minimum levels of dexterity through successfully gripping stainless steel pins of selected diameters. A copy of this test method is included in Appendix B to this report.

b. Flexibility

ASTM D1388 (FEDERAL TEST METHOD 191-5206): STIFFNESS OF FABRICS, CANTILEVER TEST METHOD.

With this test method, the flexibility of materials is determined by sliding a specimen strip over the edge of a horizontal surface and measuring the length of overhang when the tip of the specimen is depressed under its own weight so as to meet an inclined plane 41.5 degrees below the horizontal surface. A measure of the flexural rigidity of the material is provided by the cube of one-half of the bending length multiplied by the weight per unit area of the material.

5. Cleanability

a. Decontamination

No formal test method was identified for this requirement. Procedures for decontamination are strongly dependent on the chemical causing contamination and therefore a test protocol must be specifically tailored for each chemical.

b. Washability

AATCC 61 (TEST IIIA): ACCELERATED WASHFASTNESS OF FABRICS SUBJECTED TO REPEATED MACHINE WASHING IN A HOME OR COMMERICAL LAUNDRY UNDER VIGOROUS CONDITIONS.

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* From DHEW (NIOSH) Publication No. 77-134, entitled, "The Development of Criteria for Firefighters' Gloves."

This test method provides for an evaluation of the washfastness of materials to the equivalent of five (5) home or commercial launderings, without bleach, at temperatures of 49-60°C. Resistance to washing is specified in terms of visual changes in the material specimen.

6. Aging Resistance

a. U.V. Resistance

ASTM G27: OPERATING XENON-ARC TYPE APPARATUS FOR LIGHT EXPOSURE OF NON-METALLIC MATERIALS — METHOD A — CONTINUOUS EXPOSURE TO LIGHT.

This test method provides for exposure to accelerate simulated outdoor U.V. conditions with controlled temperature and moisture levels. Resistance to U.V. exposure is specified in terms of visual changes e.g., color changes, in the surface of the material specimen.

IV. RESISTANCE OF PROTECTIVE CLOTHING MATERIALS TO PERMEATION BY CARCINOGENIC LIQUIDS

Ideally, protective clothing materials should prevent all skin contact by carcinogenic liquids to which a worker is exposed. In reality, however, such protection is limited in both extent and duration. Carcinogen breakthrough and subsequent permeation of elastomers (the materials most suitable for protective clothing) typically occur at some time after the outer surface becomes wet. The permeation mechanism is composed of three interacting processes. The processes are discussed in the following paragraphs. In addition the permeation test method used in this study and proposed for consideration as the standard method is described. Experimental results pertaining to the permeation of nine chemicals through protective clothing materials are presented. Finally, pertinent permeation theory is reviewed and the development of a mathematical model discussed.

A. PERMEATION MECHANISM

A general review of the permeation mechanism is presented here. A more rigorous treatment of permeation theory, including the basic form of a mathematical model, is presented in Part D of this section.

Permeation of a carcinogenic liquid through an elastomeric material is a three-step process involving (1) the sorption of molecules of the carcinogenic liquid into the contacted (outside) surface of the material, (2) diffusion of the sorbed molecules through the material, and (3) the desorption of the molecules from the opposite (inside) surface of the material. Quite often the inside surface of the material is wet with perspiration; this condition can assist the desorption process. The consequence of these time-dependent processes is the absence of carcinogen at the inside surface of the material for a time after liquid contact with the outside surface, followed by breakthrough and subsequent permeation of the carcinogen to the inside.

Breakthrough [time] is defined as the time elapsed between liquid contact with the outside surface of a material and its detection at the inside surface by analytical techniques. Following breakthrough, the rate of permeation increases until a steady-state rate is established. Figure 1 schematically depicts this sequence. The carcinogen continues to permeate at least as long as the outside surface remains wet and a concentration gradient exists across the material. Breakthrough time and permeation rate are dependent on each material/carcinogen combination and the exposure conditions.

A principal objective of this NIOSH program was to develop a simple and reproducible test method for determining the resistance of protective clothing materials to permeation by carcinogenic liquids. Such a test method was developed and is described below.

B. PERMEATION TEST METHOD

Continuous contact by a carcinogenic liquid, rather than a one-time splash or intermittent wetting, is the "worst case" challenge to protective clothing materials. Accordingly, a simple test

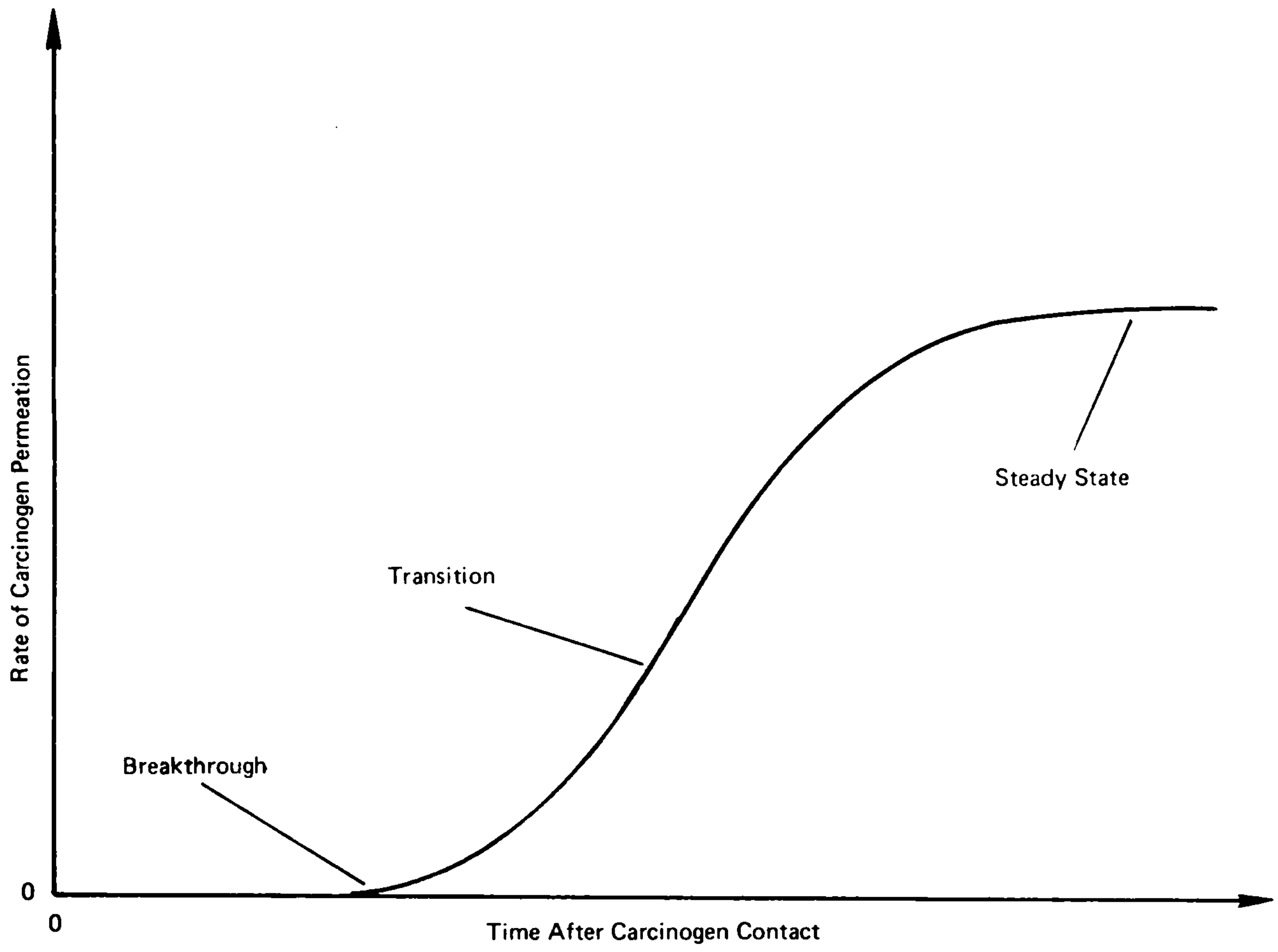

FIGURE 1 TYPICAL PERMEATION RATE THROUGH AN ELASTOMERIC MATERIAL

method has been devised to evaluate the resistances of protective clothing materials to permeation under continuous contact conditions. The method provides a reproducible technique for evaluating materials and also permits direct comparisons among materials. The complete method in a step-by-step ASTM format, including defintions, is presented as Appendix B. A brief overview is given here.

1. Test Apparatus

The liquid permeation test cell is sketched in Figure 2. The cell is constructed of Pyrex glass pipe reducer elbows with the small diameter, horizontal sections joined by aluminum flanges. Teflon gaskets are used in all joints. A stainless steel membrane holder is positioned between the aluminum flanges, and, with a membrane in place, divides the cell into two chambers. The membrane holder exposes a one-inch diameter material specimen to a carcinogenic liquid on one surface and to a liquid perspiration simulant or distilled water on the other. The membrane holder is designed to accept and retain a material specimen in either a relaxed or stretched condition. Stainless steel discs are used as covers for the top openings of each chamber. Means of stirring, heating, cooling and temperature measurement can be provided through the cover on each chamber. In addition, samples of the perspiration simulant can be withdrawn — either continuously by pump or batch-wise by syringe — through a porthole.

Glass, Teflon and stainless steel contact the test liquids. Neither contamination of the liquids nor corrosion of the test cell was observed.

2. Test Procedure

Each material specimen to be tested is secured in the membrane holder and the holder is positioned and fastened between the glass elbows. Perspiration simulant (salt solution)* is charged into one chamber of the test cell; the carcinogenic liquid or solution is charged into the other. Stirring of each liquid is begun immediately.

Samples of the perspiration simulant are withdrawn, either continuously or on a predetermined schedule, and analyzed for carcinogen using established analytical techniques. The choice of technique is dependent on the test carcinogen. Both uv spectroscopy and gas chromatography were used successfully.

The test is terminated after a steady-state permeation has been established.

3. Test Data and Sensitivity

The result of the test are data showing changes in carcinogen concentration in the perspiration simulant or the distilled water as a function of time. Several parameters describing the performance of a test material can be derived from these data, including breakthrough time,

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* A salt solution or distilled water was used with equal success in this study. In some cases distilled water was preferred because the salts interfered with the analysis for the carcinogens.

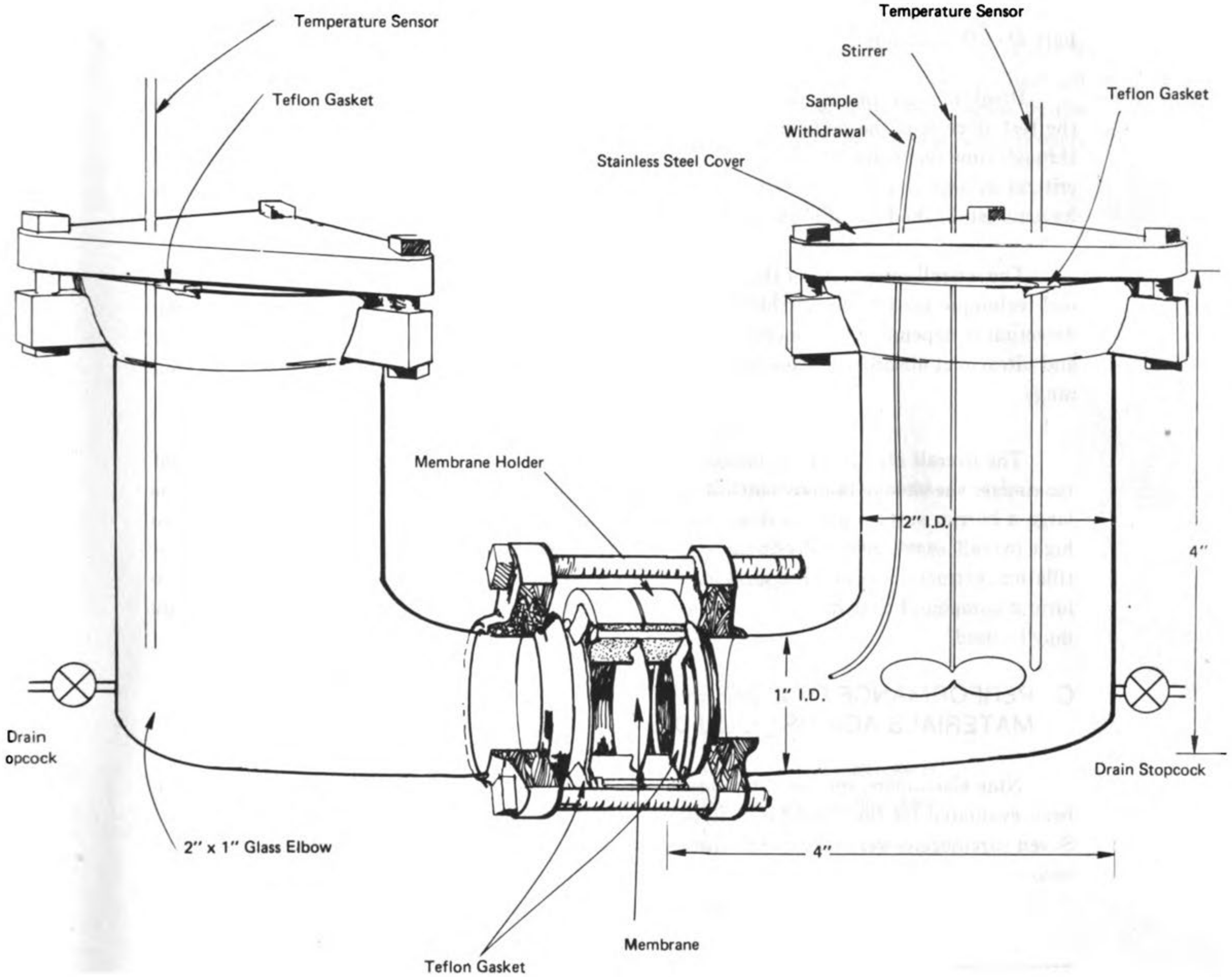

FIGURE 2 SKETCH OF PERMEATION CELL

instantaneous permeation rates (expressed as mass/time) and permeation fluxes (expressed as mass/time/area). Further, by using the results of a separate experiment from which the saturation concentration of a carcinogen in the test material is determined,* a diffusion coefficient for each material/carcinogen combination can be derived. The diffusion coefficient is useful in predicting breakthrough times for materials of different thicknesses, and is discussed in more depth in part D of this section.

Breakthrough time is considered to be the most important piece of information provided by the test since it is the point of failure of the protection offered by a clothing material. Breakthrough time identifies the transition from zero exposure to a detectable exposure level. This is critical in assessing the protection offered by clothing materials since carcinogenic chemicals have no established threshold levels for carcinogenicity on skin contact.

The overall sensitivity of the permeation test is dependent on the sensitivity of the analytical technique used to detect the presence of permeant in the downstream solution. In general, detection is dependent on concentration. For example, in our experiments gas chromatography and ultraviolet absorbancy were used, and the minimum detection limits were in the 1 to 30 ppm range.

The overall sensitivity of the experiment can be improved by operating in a manner that maximizes the change in permeant concentration for any given flux. This is achieved by using as large a barrier surface area to downstream solution volume as is practical. A further means to high overall sensitivity is by increasing the permeant concentration of each sample by distillation, extraction, or other separation technique. Additionally, the permeant may be reacted to form a compound that has a lower minimum detection limit. Finally radiolabelled permeants may be used.

C. PERFORMANCE OF CURRENTLY-USED PROTECTIVE CLOTHING MATERIALS AGAINST LIQUID CARCINOGENS

Nine elastomers, representing most currently available protective clothing materials, have been evaluated for their resistance to permeation by one or more of nine carcinogenic liquids. Seven carcinogens were tested with three elastomers, benzene with nine, and ethylenimine with two.

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* The saturation concentration of a carcinogenic liquid in a clothing material was determined by immersing a weighed specimen of the material in the liquid at ambient temperature (22°c). After seven days, the specimen was removed from the liquid, patted dry, and promptly reweighed. The saturation concentration, c_s (in gm/cm^3 of swollen material), is calculated by using the change in weight of the specimen and the densities of both the dry material and the carcinogen.

Note: The saturation concentration of pure elastomers may differ from those of commercial materials which may be compounded with absorbing fillers, etc.

1. Materials

Table 4 is a listing of the elastomers chosen for evaluation. Test specimens were cut from commercially available protective clothing materials and from U.S. Military Specification sheet stock. In several cases, specimens from both sources were tested. For example, both a neoprene glove (a dip-coated latex) and neoprene sheet (a milled polymer) were evaluated against benzene. While elastomer formulations vary from manufacturer to manufacturer, the choices in Table 4 are believed to be typical of formulations currently in use. With the exception of Viton, all elastomers are selectively recommended for use against one or more of the carcinogens by the protective clothing or chemicals industries. Viton, an elastomer with potentially superior properties, was included as a material of general interest.

TABLE 4

PROTECTIVE CLOTHING MATERIALS

Material	Form
Natural rubber (latex)	Glove
Nitrile rubber (latex)	Glove
(milled)	Military Specification sheet
Neoprene rubber (latex)	Glove
(milled)	Military Specification sheet
PVC-coated nylon	Outerwear
Polyvinyl alcohol (latex)	Glove
(latex)	Cast film*
Polyethylene	Glove
Polyethylene-coated Tyvek	Outerwear
Polyurethane-coated nylon	Outerwear
Viton (milled)	Military Specification sheet
Butyl rubber	Military Specification sheet
Butyl rubber-coated nylon	Outerwear

*PVA films were specially cast for this program.

2. Analytical Detection of Carcinogens

In the permeation test procedure, samples of perspiration simulant (an aqueous salt solution or distilled water) were withdrawn from the downstream chamber of the test cell and analyzed for carcinogen.

For those carcinogens which are detectable by UV spectroscopy, a continuous sampling procedure was used. The downstream solution was withdrawn by a circulating pump (mini-Pump® by Milton Roy), passed through a flow cell capable of monitoring UV absorbance at both 254 nm and 280 nm (duoMonitor® by Laboratory Data Control) and subsequently returned to the test cell. As the experiment proceeded and carcinogen concentration downstream increased, the changing UV absorbance was recorded by a standard laboratory strip-chart recorder. Calibration of the UV detector was accomplished by analyzing aqueous solutions of known carcinogen concentration (usually in the range of 1 to 1000 ppm). A UV intensity versus carcinogen concentration (ppm) calibration curve was then prepared.

For those carcinogens not detectable by UV spectroscopy, 2-cm^3 samples were taken by syringe and analyzed through direct injection into a gas chromatograph coupled with a flame ionization detector. The flame ionization detector was calibrated by analyzing aqueous solutions of known carcinogen concentration (usually in the range of 1 to 1000 ppm). In general, detection limits were 1-10 ppm. Generally, polystyrene-divinyl benzene beads were used as a column substrate. Use of this substrate is particularly advantageous since water elutes more rapidly than organic compounds from the column, resulting in a high quality resolution of the organic constituents. Column substrates were usually packed in stainless steel tubing and conditioned overnight with air at an elevated temperature. Samples were chromatographed as soon as possible after withdrawal from the test cell, especially those species known to be chemically active. The sampling schedule for each carcinogen was determined by factors such as estimated breakthrough time, and the materials ranged from several minutes to several hours. Sampling was continued until carcinogen concentrations of 1000 ppm were obtained.

Because of sampling and subsequent replenishing of the downstream solution with fresh simulant in order to maintain a constant volume through the experiment, mathematical normalization of the raw concentration data was required. The procedure for such calculation is presented in part 7 of the permeation test method found in Appendix B.

3. Primary Test Results

Two sets of data were generated for each of the nine* carcinogenic liquids evaluated.

The first set is the saturation concentrations (or solubilities) of carcinogen in several clothing materials. In addition to being useful in deriving diffusion coefficients, solubility data are useful in prescreening materials for use as protection against a carcinogenic liquid. Typically, a high solubility is indicative of a poor resistance to permeation, although low solubility does not necessarily indicate an acceptable resistance to permeation.

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* Our original plan called for ten liquids but we were unable to obtain samples of MOCA solution.

The second data set is the result of permeation tests with the unused materials. Both breakthrough times and calculated steady-state fluxes are shown for the materials. Steady-state fluxes are included for information only as the values are thickness-dependent. If threshold levels for skin contact are ever defined for carcinogenic liquids, such flux data will be useful in determining the cumulative amount of carcinogen that can permeate after breakthrough. This, in turn, will be useful in determining the service lives of clothing materials.

Except for the results of the benzene and coal-tar creosote experiments, breakthrough is reported to have occurred over a time range. The time range is not an indicator of the reproducibility of the experiment because in general only one test was performed; but rather it accounts for the discrete sampling schedule. That is, breakthrough at the given detection limit occurred within the time range. For example, 15-20 minutes in the breakthrough column indicates that permeant was not detectable in the 15 minute sample but was found in the 20 minute sample. For benzene and coal-tar creosote sampling was continuous, and so the reported data are the actual times that the chemicals were first detectable in the downstream solution. Although the number of tests performed was not sufficient to establish the statistical significance of our results, the data in Table 10 show a high degree of consistency; and we are confident the other results provide an accurate description of the barrier properties of the exposed materials.

Test data are reported on the following pages. In an effort towards conciseness, the format used for these data encompasses a brief description of each carcinogen,* a listing of clothing materials tested, a review of the analytical technique used for detection, and the test results.

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* The Overview Documents in Appendix A should be consulted as references for more complete descriptive information.

a. Trichloroethylene

Trichloroethylene (TCE) is a clear, colorless, liquid alkyl halide which is heavier than water, nonflammable, and has a significant vapor pressure at ambient temperature. Most of the TCE consumed in the United States is used in vapor degreasing operations. This compound is suspected of being a human carcinogen. Nearly 100,000 industrial workers are potentially exposed to TCE.

- Protective Clothing Materials

Nitrile rubber, neoprene rubber, and polyvinyl alcohol (PVA) were evaluated for resistance to permeation by trichloroethylene. All three materials were chosen for evaluation because they are recommended for use against this compound by protective clothing manufacturers.

- Analytical Detection

A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used in conjunction with a 6-in. long x ⅛-in. O.D. Porapak Q column to analyze samples of the perspiration simulant. Analyses of solutions of known trichloroethylene concentration in distilled water yielded a linear calibration curve with a detection limit of 1 ppm. The column temperature was maintained at 150°C.

- Results

Trichloroethylene was slightly soluble in PVA and Viton, moderately soluble in PVC-coated nylon, and very soluble in the remaining materials subjected to immersion testing. These results are summarized in Table 5.

For the thicknesses tested, trichloroethylene broke through each of the three materials within 15 minutes of initial contact. The permeation data are shown in Table 6.

TABLE 5

TRICHLOROETHYLENE SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

Clothing Material	Solubility gm/gm of Material	C_s, gm/cm^3 of Swollen Material
Nitrile rubber[1]	2.17	0.87
Neoprene rubber[1]	1.18	0.73
PVC-coated nylon[2]	0.14	0.15
Polyvinyl alcohol[3]	0.03	0.04
Polyethylene[4]	0.06	0.41
Polyurethane-coated nylon[2]	1.15	0.95
Viton[1]	0.02	0.04
Butyl rubber[1]	1.48	0.87

TABLE 6

TRICHLOROETHYLENE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	Thickness, ℓ (cm)	Breakthrough Time (minutes)[5]	Steady State Flux, J(gm/cm^2/min)
Nitrile Rubber[1]	0.094	10-15	6.0×10^{-5}
Neoprene Rubber[1]	0.079	10-15	5.3×10^{-5}
Polyvinyl alcohol[3]	0.009	< 15	0.8×10^{-5}

1. MIL. Spec. sheet.
2. Outerwear material.
3. Cast film.
4. Glove material.
5. At a minimum detection limit of 1 ppm.

b. Epichlorohydrin

Epichlorohydrin is a colorless, chlorinated liquid epoxide which is flammable and has a moderate vapor pressure at ambient temperature. Most of the epichlorohydrin consumed in the United States is used to produce synthetic glycerine, epoxy resins, epichlorohydrin elastomers, and several minor compounds. Epichlorohydrin is suspected of being a human carcinogen. Approximately 5,000 workers are potentially exposed to liquid epichlorohydrin.

- Protective Clothing Materials

Neoprene rubber, polyvinyl alcohol (PVA), and butyl rubber were evaluated for their resistance to permeation by epichlorohydrin. Neoprene and PVA were chosen for evaluation because they are frequently recommended for use against this compound by protective clothing manufacturers. Butyl was chosen because of low epichlorohydrin solubility (as described below).

- Analytical Detection

A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used in conjunction with a 6-in. long x ⅛-in. O.D. Porapak Q column to analyze samples from the downstream chamber of the test cell. The column temperature was maintained at 150°C. Since epichlorohydrin is known to decompose in acidic solutions, the samples were analyzed immediately after withdrawal. An evaluation of the reaction rate for decomposition showed that immediate analyses were satisfactory in accommodating the decomposition. Analyses of solutions of known epichlorohydrin concentration in distilled water yielded a linear calibration curve with detection limit of 1-5 ppm.

- Results

Epichlorohydrin was least soluble in PVA and butyl rubber and most soluble in the polyurethane. The complete set of solubility data is presented as Table 7.

A range of breakthrough times was observed during permeation testing. Epichlorohydrin broke through PVA in less than 5 minutes, neoprene rubber in 1.3 hours, and butyl rubber in slightly more than 3 days. These data are shown in Table 8.

TABLE 7

EPICHLOROHYDRIN SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

Clothing Material	Solubility	
	gm/gm of Material	C_s, gm/cm^3 of Swollen Material
Nitrile rubber[1]	0.28	0.23
Neoprene rubber[1]	0.44	0.37
PVC-coated nylon[2]	1.03	0.60
Polyvinyl alcohol[3]	Negligible	Negligible
Polyethylene[4]	0.12	0.10
Polyurethane-coated nylon[2]	2.70	0.86
Viton[1]	0.42	0.46
Butyl rubber[1]	0.05	0.05

TABLE 8

EPICHLOROHYDRIN PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	Thickness, ℓ (cm)	Breakthrough Time[5]	Steady State Flux, J(gm/cm^2/min)
Neoprene Rubber[1]	0.076	60-80 min.	11.0×10^{-5}
Polyvinyl alcohol[3]	0.008	< 5 min.	13.0×10^{-5}
Butyl Rubber[2]	0.084	79 hrs.	0.02×10^{-5}

1. MIL. Spec. sheet.
2. Outerwear material.
3. Cast film.
4. Glove material.
5. At a minimum detection limit of 1-5ppm.

c. Coal-Tar Creosote

Coal-tar creosote is an oily mixture of higher phenols, naphthalene, anthracene, and various tar bases. In the United States, creosote oil is used primarily as a wood preservative for railroad ties, telephone poles, and marine pilings. Because it contains compounds such as benzo(a)pyrene, creosote oil is classified as a suspected human carcinogen. It has been estimated that 5000 workers are potentially exposed to creosote oil.

- Protective Clothing Materials

Neoprene rubber, Viton, and butyl rubber were evaluated for their resistance to permeation by trichloroethylene. Neoprene was chosen for evaluation because it is frequently recommended for use against this compound by protective clothing manufacturers. The other two were chosen on the basis of anticipated superior properties.

- Analytical Detection

Most constituents of coal-tar creosote are aromatic and can be readily detected by UV spectroscopy. Continuous monitoring of the perspiration simulant by the UV flow cell was used to detect permeation through clothing materials. By this method, it was possible to detect the presence but not the number or identity of the creosote components which permeated. Accordingly, the development of a UV intensity versus carcinogen ppm calibration curve was not practical. Therefore, only the breakthrough times were obtained for this compound.

- Results

The solubilities of coal-tar creosote were not measured due to its inhomogeneous nature. In addition, certain components of creosote are crystalline at room temperature and therefore cannot be completely removed from the surface of the material specimens.

For the thicknesses tested, neoprene resisted breakthrough for 45 hours. Both Viton and butyl rubber were impermeable for approximately 3½ days, at which time the tests were terminated. These data are presented in Table 9.

TABLE 9

CREOSOTE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	**Thickness, ℓ (cm)**	**Breakthrough Time (minutes)[2]**
Neoprene rubber[1]	0.076	270
Viton[1]	0.043	>5760 (96 hours)
Butyl rubber[1]	0.081	>5400 (90 hours)

1. MIL. Spec. sheet.
2. At a minimum detection limit of 1-5 ppm.

d. Benzene

Benzene is a colorless, aromatic liquid hydrocarbon which is lighter than water, flammable, and has a significant vapor pressure at ambient temperature. The majority of the benzene consumed in the United States is used to synthesize industrial chemicals such as cyclohexane, phenol, styrene, maleic anhydride, nitrobenzene, dichlorobenzene, and dodecylbenzene. Benzene is suspected of being a human carcinogen. More than 100,000 industrial workers are potentially exposed to this compound.

- Protective Clothing Materials

Because of the industrial significance of benzene, specimens of twenty protective clothing materials, representing nine different elastomeric polymers, were evaluated. Materials frequently recommended by protective clothing manufacturers or by the chemical industry — neoprene, nitrile rubber, polyvinyl alcohol (PVA), polyethylene, and polyurethane — are included.

- Analytical Detection

Continuous monitoring by the UV flow cell was used in analyzing the perspiration simulant. Analyses of solutions of known benzene concentration in distilled water yielded a calibration curve with a detection limit of 5-10 ppm.

- Results

Benzene solubilities ranged from 0.03 gm/cm^3 for PVA to 0.7 gm/cm^3 for natural rubber (latex). These data are presented in Table 10.

In the thickness tested, neoprene rubber was the only material currently recommended for use with benzene that prevented breakthrough for more than 10 minutes. Butyl rubber was successful in preventing breakthrough for an hour or more, while Viton delayed breakthrough for more than 8 hours. These data are also presented in Table 10.

PVA exhibited a unique behavior: a quick breakthrough time and subsequent steady-state permeation for 4 to 6 hours was followed by a significant reduction in permeation rate. Such a phenomenon is attributed to a time-dependent sorbance of water by the PVA with resulting interference with diffusion.

TABLE 10

BENZENE SOLUBILITY IN AND PERMEATION THROUGH SELECTED CLOTHING MATERIALS

	Solubility @ 22°C			Breakthrough Time (min)[6]		Steady State Flux (gm/cm^2/min)	
Material	gm/gm	C_s, gm/cm^3 of Swollen Material	Thickness ℓ (cm)	Run 1	Run 2	Run 1	Run 2
Natural rubber[1]	3.2	0.7	0.028	2	1.5	50×10^{-5}	50×10^{-5}
Nitrile rubber[1]	–	–	0.023	6	5.5	50×10^{-5}	60×10^{-5}
Nitrile rubber[2]	1.1	0.5	0.041	5	5.5	50×10^{-5}	50×10^{-5}
Neoprene rubber[2]	–	–	0.041	6	7	50×10^{-5}	50×10^{-5}
Neoprene rubber[2]	0.9	0.5	0.076	24.5		23×10^{-5}	
Neoprene rubber[2]	–	–	0.16	60		8×10^{-5}	
Neoprene rubber[2]	–	–	0.241	186		5×10^{-5}	
Neoprene rubber[1]	–	–	0.038	6		30×10^{-5}	30×10^{-5}
Neoprene-coated fabric[1]	–	–	0.069[5]	15	23	8×10^{-5}	6×10^{-5}
Neoprene/natural rubber[1]	2.8	0.7	0.046	3	5	40×10^{-5}	50×10^{-5}
Neoprene (milled)[1]	–	–	0.036	6.5		52×10^{-5}	
PVC-coated nylon[3]	–	–	0.043	6	6.5	15×10^{-5}	15×10^{-5}
Polyvinyl alcohol[1]	0.03	0.03	0.023	10	10	0.8×10^{-5}	
Polyvinyl alcohol[4]	–	–	0.008	3		3.9×10^{-5}	
Polyethylene[1]	0.3	0.2	0.006	<1	<1	35×10^{-5}	35×10^{-5}
Polyethylene-back Tyvek[3]	–	–	0.009[5]	1	2	22×10^{-5}	22×10^{-5}
Polyurethane-backed nylon[3]	0.6	0.4	0.02	1.5	2	11×10^{-5}	11×10^{-5}
Viton[2]	0.04	0.06	0.16	900		0.05×10^{-5}	
Butyl-coated nylon[3]	–	–	0.056	60		9×10^{-5}	
Butyl sheet[2]	0.6	0.35	0.084	88		13×10^{-5}	

1. Glove material.
2. Military Specification sheet.
3. Outerwear material.
4. Cast film.
5. Material is a membrane/fabric laminate. Thickness is only that of the membrane.
6. At a minimum detection limit of 5-10 ppm.

e. 4,4'-Methylene(bis)2-chloroaniline

4,4'-Methylene(bis)2-chloroaniline (also known as MOCA, a tradename of E.I. du Pont) is normally a solid at ambient temperatures, although limited quantities are available in liquid solution. MOCA has the general characteristics of a primary aromatic amine. Nearly all of the MOCA consumed in the United States is used as a curing agent for liquid-castable urethanes and epoxies. This compound is considered to be a human carcinogen and, accordingly, its use is closely controlled by Federal Regulations.* Approximately 10,000 workers are potentially exposed to all forms of MOCA.

Despite our best efforts, we were not successful in obtaining a sample of a liquid solution of MOCA or product data sheets from any U.S. supplier. Therefore, solubility and permeation experiments were not performed.

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*Note: 29CFR 1910.1005 was revoked at 41FR 35184 (August 20, 1976).

f. Ethylenimine

Ethylenimine (EI) is a colorless, ammoniacal, aliphatic amine which is lighter than water, highly flammable, and very volatile at ambient temperature. The chemical is very reactive and can polymerize with explosive violence under acidic or basic conditions. EI and its derivatives are used in coatings for paper and textiles, in adhesives, in fuels and lubricants, and in agricultural chemicals and pharmaceuticals. This compound is considered to be a human carcinogen and, accordingly, its use is closely controlled by Federal Regulations. Fewer than 100 industrial workers are potentially exposed to liquid ethylenimine.

- Protective Clothing Materials

Neoprene rubber and butyl rubber were evaluated for their resistance to permeation by ethylenimine. Neoprene was chosen for evaluation because it is recommended for use by the sole ethylenimine producer in the United States. Butyl was chosen because of low EI solubility (as described below).

- Analytical Detection

The analytical detection of ethylenimine proved to be difficult due to the compound's extreme reactivity, especially in aqueous solutions. A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used to analyze samples of the distilled water from the test cell. Several Porapak (T,S,Q) stainless steel columns were tried with little success, however, a Porapak QS-glass column did provide the needed sensitivity. Quantification was carried out by planimetry since the recorded peaks from the glass column were skewed. The most sensitive electrometer setting (4×10^{-12}) was required to observe the EI peaks. The column temperature was maintained at 150°C.

Analyses of solutions of known EI concentrations in distilled water yielded a calibration curve with a detection limit of 10-30 ppm.

- Results

Ethylenimine degrades neoprene and Viton very rapidly. However, EI proved to be moderately soluble in natural rubber and butyl rubber. These results are summarized in Table 11.

For the thicknesses tested, EI broke through neoprene in less than 5 minutes. Butyl rubber had a breakthrough time in the interval between the tenth and sixteenth hours after initial contact (range due to discrete sampling schedule). These permeation data are shown in Table 12.

TABLE 11

ETHYLENIMINE SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

	Solubility	
Clothing Material	**gm/gm of Material**	**C_s, gm/cm^3 of Swollen Material**
Natural rubber[1]	0.15	0.12
Neoprene rubber[1]	gummy	–
Viton[2]	decomposed	–
Butyl rubber[2]	0.14	0.12

TABLE 12

ETHYLENIMINE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	**Thickness, ℓ (cm)**	**Breakthrough Time[3]**	**Steady State Flux, J(gm/cm^2/min)**
Neoprene[1]	0.020	<5 min.	–[4]
Butyl rubber[2]	0.084	10 – 16 hrs.	0.45×10^{-5}

1. Glove material.
2. Military Specification sheet.
3. At a minimum detection limit of 10-30 ppm.
4. Steady state was never achieved because degradation of the material was too quick.

g. 1,1-Dimethylhydrazine

Unsymmetrical dimethylhydrazine (1,1-dimethylhydrazine or UDMH) is a clear, colorless, aliphatic amine which is lighter than water, fumes in air, and is highly flammable. UDMH is primarily used as a rocket propellant. This compound is suspected of being a human carcinogen. 250 workers are potentially exposed to liquid UDMH.

- Protective Clothing Materials

Neoprene rubber, polyvinyl chloride (PVC-coated nylon) and butyl rubber were evaluated for their resistances to permeation by UDMH. All three materials were chosen for evaluation because they are frequently cited for use against UDMH by the chemical industry.

- Analytical Detection

A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used in conjunction with a 6-in. long x ⅛-in. O.D. Porapak Q column to analyze samples of the distilled water from the test cell. The column temperature was maintained at 150°C. Analyses of solutions of known UDMH concentration in distilled water yielded a linear calibration curve with a lower detection limit of 10 ppm.

- Results

UDMH was the least soluble in butyl rubber. It dissolved PVA and decomposed (reacted with) Viton and polyurethane. These results are summarized in Table 13.

For the thicknesses tested, UDMH broke through neoprene and PVC-coated nylon in less than an hour after initial contact. Butyl rubber resisted permeation for approximately 1 day. These permeation data are shown in Table 14.

TABLE 13

1,1-DIMETHYLHYDRAZINE SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

Clothing Material	Solubility gm/gm of Material	 C_s, gm/cm^3 of Swollen Material
Nitrile rubber[1]	0.38	0.32
Neoprene rubber[1]	0.30	0.33
PVC-coated nylon[2]	0.35	0.36
Polyvinyl alcohol[3]	Dissolved	–
Polyethylene[4]	Slight weight loss	–
Polyurethane-coated nylon[2]	Polyurethane decomposed	–
Viton[1]	Decomposed	–
Butyl rubber[1]	0.1	0.1

TABLE 14

1,1-DIMETHYLHYDRAZINE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	Thickness, ℓ (cm)	Breakthrough Time[5]	Steady State Flux, J(gm/cm^2/min)
Neoprene[1]	0.076	25-40 min.	45.0×10^{-5}
PVC-coated nylon[2]	0.043	5-10 min.	19.0×10^{-5}
Butyl rubber[1]	0.084	23-27 hrs.	0.29×10^{-5}

1. Mil. Spec. sheet.
2. Outerwear material.
3. Cast film.
4. Glove material.
5. At a minimum detection limit of 10 ppm.

h. 2-Nitropropane

2-Nitropropane is a colorless, liquid nitroparaffin which has a density slightly less than that of water, is flammable, and has a significant vapor pressure at ambient temperature. The primary domestic use for this compound is as a solvent for surface coatings, adhesives, and printing inks. 2-Nitropropane is suspected of being a human carcinogen. Approximately 100,000 industrial workers are potentially exposed to 2-nitropropane.

- Protective Clothing Materials

Nitrile rubber, polyvinyl alcohol (PVA), and butyl rubber were evaluated for their resistance to permeation by 2-nitropropane. PVA was chosen for evaluation because it is frequently recommended for use against this compound by a protective clothing manufacturer. The others were chosen on the basis of anticipated superior properties.

- Analytical Detection

A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used in conjunction with a 6-in. long x 1/8-in. O.D. 5% FFAP column on 100/120 Supelsoport to analyze samples of the perspiration simulant. Analyses of solutions of known 2-nitropropane concentration in distilled water yielded a calibration curve with a detection limit of 10 ppm.

- Results

2-Nitropropane was slightly soluble in PVA, polyethylene, and butyl rubber; and was moderately to very soluble in the remaining materials tested. These results are summarized in Table 15.

For the thickness tested, 2-nitropropane broke through PVA in less than 5 minutes and nitrile rubber in less than 60 minutes. Butyl rubber was effective for 101 hours, at which time the test was terminated. These permeation data are shown in Table 16.

TABLE 15

2-NITROPROPANE SOLUBILITY IN SELECTED CLOTHING MATERIAL AT 22°C

	Solubility	
Clothing Material	**gm/gm of Material**	**C_s, gm/cm^3 of Swollen Material**
Nitrile rubber[1]	0.72	0.41
Neoprene rubber[1]	0.23	0.22
PVC-coated nylon[2]	0.42	0.34
Polyvinyl alcohol[3]	Negligible	Negligible
Polyethylene[4]	0.07	0.06
Polyurethane-coated nylon[2]	0.99	0.54
Viton[1]	1.07	0.66
Butyl rubber[1]	0.02	0.02

TABLE 16

2-NITROPROPANE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	Thickness, ℓ (cm)	Breakthrough Time	Steady State Flux, J(gm/cm^2/min)
Nitrile Rubber[1]	0.09	25-50 min.	20.0×10^{-5}
Polyvinyl alcohol[3]	0.02	< 5 min.	4.4×10^{-5}
Butyl Rubber[1]	0.08	> 101	–

1. MIL. Spec. sheet.
2. Outerwear material.
3. Cast film.
4. Glove material
5. At a minimum detection limit of 10 ppm.

i. β-Propiolactone

β-Propiolactone (BPL) is a colorless liquid ester which is heavier than water, flammable, and moderately volatile at ambient temperature. This compound is considered to be a human carcinogen. Fewer than 20 industrial workers are potentially exposed to liquid BPL.

- Protective Clothing Materials

Natural rubber, polyethylene, and polyurethane were evaluated for their resistance to permeation by BPL. All three materials were chosen for evaluation because they are frequently recommended for use against this compound by protective clothing manufacturers.

- Analytical Detection

A Varian Aerograph Series 2700 gas chromatograph with a flame ionization detector was used in conjunction with a 6-in. long x 1/8-in. O.D. 10% EGSS column on 100/200 GCP to analyze samples of the distilled water from the test solutions of known BPL concentration in distilled water yielded a calibration curve with a detection limit of between 1 and 10 ppm.

Analyses were complicated by the rapid decomposition of β-propiolactone in water. Since the test protocol involves the collection of BPL in an aqueous downstream solution, this decomposition was accounted for in interpreting the results of chromatographic analysis of each sample. Corrected (non-decomposed) β-propiolactone concentrations were found by mathematical treatment of the analytical data. The mathematical treatment is described in Appendix C.

- Results

β-Propiolactone was found to be the most soluble in polyurethane and Viton, and reacted (polymerized) in the presence of polyvinyl alcohol. These results are presented in Table 17.

For the thicknesses tested, polyethylene proved to be the most resistant, and polyurethane the least resistant. None of the three materials resisted breakthrough for 30 minutes. These data are shown in Table 18.

TABLE 17

β-PROPIOLACTONE SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

Clothing Material	Solubility gm/gm of Material	C_s, gm/cm^3 of Swollen Material
Natural rubber[1]	0.09	0.01
Nitrile rubber[2]	0.29	0.23
Neoprene rubber[2]	0.31	0.29
Butyl rubber[2]	0.01	0.01
PVC-coated nylon[3]	0.15	0.16
Polyvinyl alcohol[4]	reacted	–
Polyethylene[1]	0.18	0.15
Polyurethane-coated nylon[3]	1.85	0.75
Viton[2]	0.69	0.60

TABLE 18

β-PROPIOLACTONE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	Thickness, ℓ (cm)	Breakthrough Time[6] (minutes)	Steady State Flux, J(gm/cm^2/min)
Natural rubber[1]	0.030	15-20	0.43×10^{-5}
Polyethylene[1]	0.006	10-30	0.12×10^{-5}
Polyurethane-coated nylon[3,5]	0.003	<5	83.0×10^{-5}

1. Glove material.
2. MIL Spec. sheet.
3. Outerwear material
4. Cast film.
5. Thickness measurement represents polyurethane only.
6. At a minimum detection limit of 2 ppm.

j. Hexamethylphosphoramide

Hexamethylphosphoramide (HMPA) is a water-white, colorless liquid amide with a low vapor pressure at ambient temperature. HMPA's principal industrial application has been as a solvent in the manufacture of du Pont's Kevlar aramid fiber. HMPA is suspected of being a human carcinogen. It has been estimated that no more than 5,000 industrial workers are potentially exposed to this compound.

- Protective Clothing Materials

Nitrile rubber, polyethylene, and butyl rubber were evaluated for their resistance to permeation by HMPA. Butyl rubber was chosen for evaluation because it is recommended for use against this compound by duPont.[1] The others were chosen on the basis of anticipated performances.

- Analytical Detection

Because this compound does not have a significant UV absorbance at 254 or 280 nm, our fixed wavelength, continuous UV flow cell could not be used. Instead, discrete samples of the downstream solution were taken at strategically selected times over the course of each experiment and analyzed by a variable wavelength Beckman DK1A Spectrophotometer at 202 nm. The minimum detection limit was 3 ppm of hexamethylphosphoramide in distilled water.

Attempts to detect HMPA by gas chromatography were futile. Various chromatographic substrates — Porapak Q, Chromosorb 103, Tenax-GC, and OV-101 — were tried both under isothermal conditions (200°C) and with temperature programming. A flame photometric detector operating with a phosphorus filter for detecting the phosphorus moiety in this compound lacked sensitivity.

- Results

HMPA was slightly soluble in polyethylene and butyl rubber, but very soluble in the remaining materials put through immersion testing. In fact, HMPA dissolved polyvinyl chloride and polyvinyl alcohols. These results are summarized in Table 19.

For the thicknesses tested, HMPA broke through polyethylene in less than 25 minutes. Breakthrough times for nitrile and butyl rubbers were between 1 and 1.5 hours. These permeation data are shown in Table 20.

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[1] "Material Safety Data Sheet," E.I. duPont de Nemours Inc., July 1976.

TABLE 19

HEXAMETHYLPHOSPHORAMIDE SOLUBILITY IN SELECTED CLOTHING MATERIALS AT 22°C

Clothing Material	**Solubility**	
	gm/gm of Material	**C_s, gm/cm^3 of Swollen Material**
Nitrile rubber[1]	0.78	0.44
Neoprene rubber[1]	2.72	0.79
PVC-coated nylon[2]	Dissolved	–
Polyvinyl alcohol[4]	Dissolved	–
Polyethylene[3]	0.22	0.17
Polyurethane-coated nylon[2]	2.42	0.76
Viton[1]	2.50	0.84
Butyl rubber[1]	0.08	0.07

TABLE 20

HEXAMETHYLPHOSPHORAMIDE PERMEATION THROUGH SELECTED CLOTHING MATERIALS

Material	**Thickness, ℓ (cm)**	**Breakthrough Time[5]**	**Steady State Flux, J(gm/cm^2/min)**
Nitrile rubber[1]	0.094	1.0-1.5 hrs.	1.3×10^{-5}
Butyl rubber[1]	0.084	1.0-1.5 hrs.	0.002×10^{-5}
Polyethylene[3]	0.006	15-25 min.	0.4×10^{-5}

1. Mil. Spec. sheet
2. Outerwear material
3. Glove material
4. Cast film
5. At a minimum detection limit of 3 ppm

4. Supplementary Test Results

The permeation data presented above relate to new, unused protective clothing materials tested at 22°C (ambient temperature) and in a non-strained condition. In actual use, clothing materials can be exposed to carcinogenic liquids at temperatures other than 22°C, and these materials are usually subject to flexing and stretching (e.g., at finger, elbow and knee joints). In addition, protective clothing is often reworn after contact with a carcinogen. Therefore, several tests were carried out to ascertain whether resistance to permeation is influenced by one or more of these factors.

a. Non-ambient Temperatures

Neoprene was tested against benzene at 7°C and 37°C in order to investigate the influence of temperature on breakthrough and permeation rate. The tests followed the usual protocol except that the test cell was immersed in a water bath at the appropriate temperatures. The results of these tests, in addition to the earlier results at 22°C, are reported in Table 21. The solubility of benzene in neoprene at each temperature is also included.

TABLE 21

BENZENE PERMEATION THROUGH NEOPRENE[1] AT THREE TEMPERATURES

Test Temperature (°C)	Solubility, C_s (gm/cm^3 of Swollen Neoprene)	Breakthrough Time[2] (min)	Steady State Flux, J (gm/cm^2/min)
7	0.49	40	19×10^{-5}
22	0.49	24	23×10^{-5}
37	0.49	16	33×10^{-5}

1. MIL. Spec. sheet, at a thickness of 0.08 cm.
2. At a minimum detection limit of 5-10 ppm.

There was a significant decrease in breakthrough time and an increase in steady state flux as the temperature is increased. This result is not unexpected, and confirms that clothing permeation should be evaluated over the range of temperatures expected under actual use conditions. The constant solubility over this temperature range is not unusual as many other elastomers are known to exhibit similar behavior above their glass transition temperatures.

b. Strained and Strain-cycled Materials

Protective clothing materials can be exposed to carcinogenic liquid while strained or after undergoing strain-cycling. Strained materials represent the condition of stretched materials covering the knee, elbow, and finger joints during flexure. Strain-cycled materials simulate the condition of aged materials which have been stretched and relaxed a large number of times. Neoprene rubber and butyl rubber were each tested against epichlorohydrin and benzene for resistance to permeation under the two conditions:

- Strained Materials

  Each material specimen was stretched to 120% of its unstrained length and then clamped, while stretched, in the permeation test cell.

- Strain-cycled Materials

  Each material specimen was stretched to 120% of its unstrained length and then folded to 80% of its length. Each unstrained specimen was cycled through this sequence 1,000 times before being clamped, while unstrained, in the permeation test cell.

As in the earlier tests, benzene permeation was monitored by means of a UV flow cell detector and epichlorohydrin was detected by discrete sampling, followed by gas chromatography.

The results of these permeation tests are presented in Table 22 along with the data from the tests in which materials were tested in an unused condition. Inspection of the data in each group shows that, for the material thicknesses tested, neither straining nor strain-cycling had a significant effect on resistance to permeation. This conclusion, however, must be considered to apply to only these materials and conditions and may not hold in other circumstances.

c. Pre-exposed Materials

To simulate the situation of rewearing protective clothing that had previously been contacted by carcinogenic liquid, specimens of neoprene and butyl rubber were saturated with benzene and then air dried for 18 hours before evaluating their resistance to permeation. Permeation tests then followed the usual protocol. The results of these tests are presented in Table 23 along with our earlier results for unused materials.

From these data, there do not appear to be significant differences between the performance of pre-exposed, dried materials and unused materials. This conclusion, however, must be checked for each combination of material and carcinogen.

TABLE 22

PERMEATION THROUGH STRAINED AND STRAIN-CYCLED CLOTHING MATERIALS

Carcinogen	Material[1]	Test Condition[2]	Thickness, ℓ (cm)	Breakthrough Time[3]	Steady State Flux J ($gm/cm^2/min$)
Benzene	Butyl Rubber	relaxed	0.076	54 min	20×10^{-5}
	Butyl Rubber	strained	0.073	53 min	18×10^{-5}
	Butyl Rubber	cycled	0.076	52 min	28×10^{-5}
	Neoprene	relaxed	0.080	24 min	23×10^{-5}
	Neoprene	strained	0.076	25 min	32×10^{-5}
	Neoprene	cycled/relaxed	0.080	24 min	35×10^{-5}
Epichlorohydrin	Butyl Rubber	relaxed	0.084	79 hr	0.02×10^{-5}
	Butyl Rubber	strained	0.073	~100 hr	0.01×10^{-5}
	Butyl Rubber	cycled/relaxed	0.076	80-100 hr	0.01×10^{-5}
	Neoprene	relaxed	0.076	60-80 min	11×10^{-5}
	Neoprene	strained	0.076	~70 min	11×10^{-5}
	Neoprene	cycled/relaxed	0.080	80-110 min	11×10^{-5}

1. MIL. Spec. sheet.
2. Strained: tested at 120% of unstrained length; Cycled: tested unstrained after 1000 cycles of stretching to 120% of unstrained length, followed by folding to 80% of unstrained length.
3. At a minimum detection limit of 5.10 ppm.

TABLE 23

PERMEATION OF BENZENE THROUGH PRE-EXPOSED[1] CLOTHING MATERIALS

Clothing Material	Pre-exposed (?)	Thickness, ℓ (cm)	Breakthrough Time[3] (min)	Steady State Flux, J ($gm/cm^2/min$)
Neoprene[2]	Yes	0.076	26	31×10^{-5}
	No	0.076	24	23×10^{-5}
Butyl Rubber[2]	Yes	0.084	51	20×10^{-5}
	No	0.084	54	20×10^{-5}

1. Material specimens saturated with benzene and then air-dried for 18 hours.
2. MIL. Spec. sheet.
3. At a minimum detection limit of 5-10 ppm.

D. MATHEMATICAL MODEL

To assess the practicality of predicting permeation resistance of protective clothing materials on the basis of limited data, two mathematical models were evaluated. In the following paragraphs, these models are described. The discussion begins with a review of simple diffusion theory.

It is concluded that due to the complexities associated with carcinogen permeation through multi-component barriers (e.g., rubber products) and through barriers that are swollen or react with the liquid, such modeling appears to be impractical at this time.

1. Permeation by Simple Diffusion

Permeation of a carcinogen through a barrier is a three-step transport process involving (1) the sorption of molecules of the carcinogen into the contacted surface of the barrier, (2) the diffusion of the sorbed molecules through the barrier, and (3) the desorption of the molecules from the opposite surface of the barrier. In some cases involving liquid contact with a clothing material, the diffusion step is the rate controlling step in the permeation process, and therefore, is the topic of the remainder of the mathematical model discussion.

The rate of mass diffusion through a unit surface area of a clothing barrier (or membrane) is proportional to the concentration gradient of the carcinogen (permeant) across the barrier. This relationship is most often expressed by Fick's law:

$$J = -D \frac{dc}{dx} \qquad (1)$$

where

J is the mass flux in gm/hr/cm^2;

D is the diffusion coefficient in cm^2/hr;

c is the carcinogen concentration *in the membrane* in gm/cm^3; and

x is the distance, in cm, from the contacted membrane surface.

The minus sign in the equation accounts for a decreasing c as x increases.

An objective of experimentation is to determine the diffusion coefficient, D, for each carcinogen/clothing material pair. Such would allow prediction of the carcinogen flux for each material over a wide range of conditions. Such a prediction is appropriate since permeation criteria for protective clothing might, in several years, be specified as a maximum allowable flux rather than a breakthrough time.

Integration of equation (1) results in a relationship which is useful for determining the diffusion coefficient from test data. Where D is not a function of carcinogen concentration, membrane thickness or contact time (such as during the steady-state permeation of a non-reactive gas), this integration is straightforward and yields equation (2):

$$J = D \frac{C_1 - C_2}{\ell} \qquad (2)$$

where

C_1 is the permeant concentration in the upstream (higher concentration) surface of the membrane (at $x = o$);

C_2 is the permeant concentration in the downstream surface of the membrane (at $x = l$); and,

l is the membrane thickness.

In cases where D is a function of concentration, an integral diffusion coefficient $\bar{D}$ can be defined as:

$$\bar{D} = \frac{1}{C_1 - C_2} \int_{C_2}^{C_1} D \, dc \qquad (3)$$

Examples of D as a function of concentration would include:

$$D = D_0 (1 + f(c)) \quad \text{or} \quad D = D_0 \, e^{f(c)} \qquad (4)$$

where D_0 is the zero-concentration diffusion coefficient. Such a concentration dependence usually occurs when organics, such as carcinogenic liquids, diffuse through polymeric materials. The result of integrating equation (1) with an integral diffusion coefficient is equation (5):

$$J = \bar{D} \frac{C_1 - C_2}{\ell} \qquad (5)$$

D or $\bar{D}$ can be determined by measuring both C_1 and the permeation flux, C_2 is considered to be 0 when permeation tests are carried out such that downstream membrane surface (at $x = l$) is continuously exposed to and washed by a fluid in which the concentration of the permeant is far below saturation. In the case of the diffusion of a neat chemical, C_1 is the solubility of the compound in the polymer (i.e., $C_1 = C_s$) and can be determined by a separate, long-term immersion experiment. The rate of permeation can be determined by analytical methods such as continuous monitoring of the UV absorbance of the downstream fluid or analysis by GC or scintillation counting (in the case that the permeant is radiolabelled) of discrete samples taken periodically from the downstream fluid during an experiment. Flux can then be directly calculated from the measured rate of permeant uptake in the solution on the downstream side of a known membrane area.

Regardless of the analytical method used, determination of varying diffusion coefficients require that breakthrough time, a steady-state rate of permeation, and several interim rates of permeation in the transition between breakthrough and steady-state all be measured. A graphical representation of membrane permeation is presented in Figure 3 in terms of measured concentration versus membrane contact time.

In practice, the determination of a varying diffusion coefficient is not straightforward. Therefore, techniques have been developed for calculating this parameter at particular stages of the permeation process. The breakthrough or short time diffusion coefficient, D_o, and the steady-state diffusion coefficient, D_s, are of principal importance to predicative models. In the following paragraphs, the significance of these diffusion coefficients and methods for their determination are described.

- Short-Time Diffusion Coefficient (D_o)

D_o, the zero-time diffusion coefficient, is the constant which appeared earlier in equation (4). It has been shown that when the C_1/C_s ratio approximates 0 at the start of an experiment, the diffusion coefficient D approximates D_o.[5] Since this concentration ratio remains relatively small for a finite time before and around breakthrough, D_o can be used in predicting fluxes near the breakthrough time.

The following method for determination of D_o is taken from the Holstein solution to the diffusion equation which is based on work by Rodgers[6] and later confirmed by Meares.[7] When the general diffusion coefficient is constant, Holstein's solution is:

$$\frac{d\phi}{dt} = 2\left(\frac{A\,C_1}{V}\right)\left(\frac{D}{\pi t}\right)^{1/2} \sum_{M=o}^{\infty} \exp\left[\left(-\frac{\ell^2}{4Dt}\right)(2M+1)^2\right] \qquad (6)$$

where ϕ is the concentration of permeant in a fixed volume, V, of fluid washing, A, the exposed membrane surface area at $x = l$.

When t is small, only the first term of the summation is significant and equation (6) may be simplified and written in logarithmic form:

$$\ell n\left(t^{1/2}\frac{d\phi}{dt}\right) = \ell n\left[\frac{2AC_1}{V}\left(\frac{D}{\pi}\right)^{1/2}\right] - \frac{\ell^2}{4Dt} \qquad (7)$$

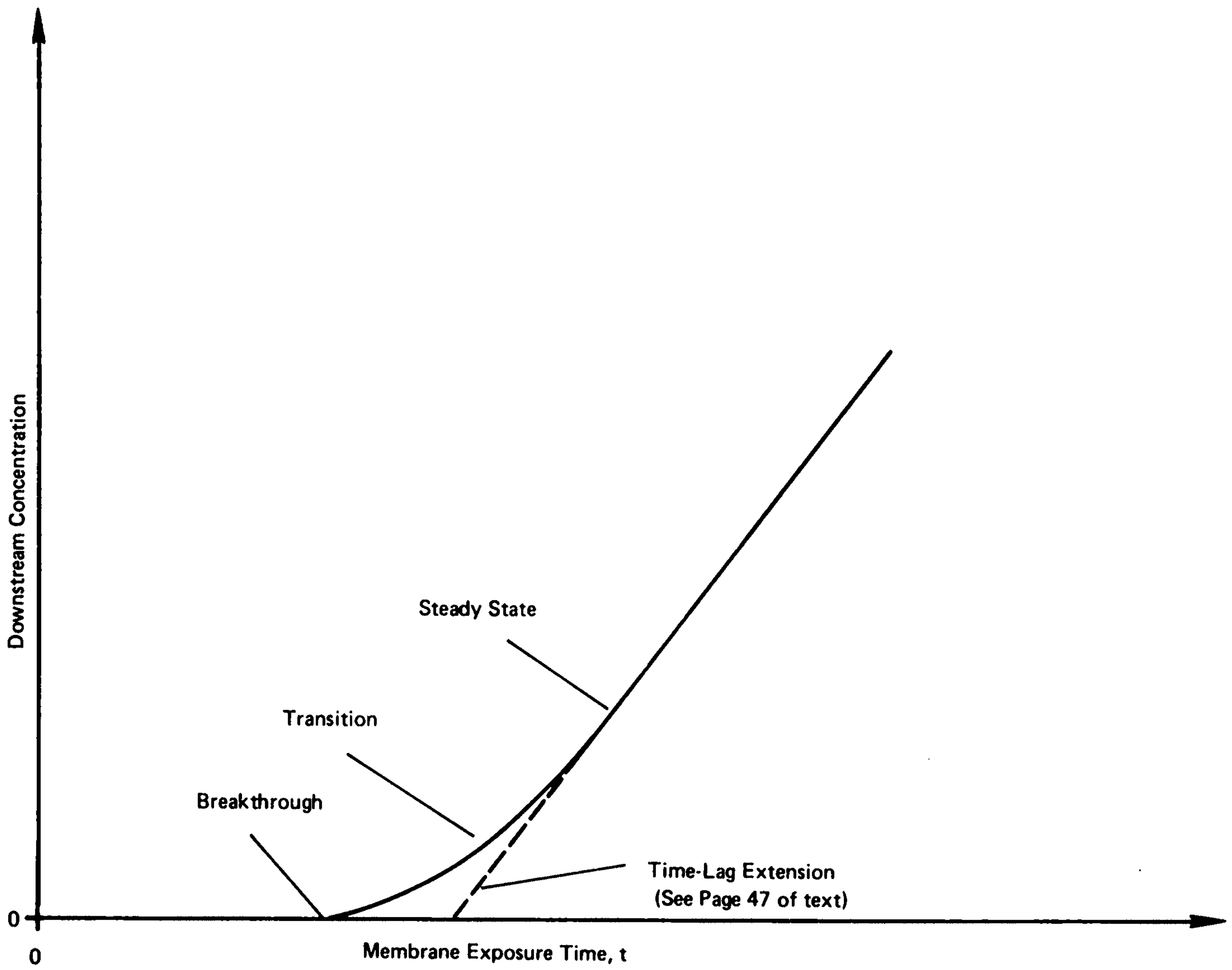


FIGURE 3 TYPICAL PERMEATION THROUGH AN ELASTOMERIC MEMBRANE

When D is constant, a graph of $\ell n\left(t^{1/2}\frac{d\phi}{dt}\right)$ versus 1/t is a straight line of slope $-\frac{\ell^2}{4D}$ from which D can be calculated directly. In addition, once D is known, C_1 can be calculated from the intercept of the line on the zero-time axis (On semilog paper, the intercept on the zero-time axis is $2\left(\frac{AC_1}{V}\right)\left(\frac{D}{\pi}\right)^{1/2}$.

When D is not constant, a graph of $\ell n\left(t^{1/2}\frac{d\phi}{dt}\right)$ versus 1/t is a curve. The limiting slope of the curve at the start-up when the C_1/C_2 ratio is small (at t = o when the permeant has not significantly penetrated the upstream membrane surface) is $-\frac{\ell_2}{4D_0}$. Thus, having found D_o, an integrated form of equation (7) can be used to calculate either the total mass permeating the membrane over a selected time or the time for a selected flux level to be reached:

$$\phi = 2\,\frac{C_1 A\ell}{V(\pi)^{1/2}}\,e^{-u^2}\left[\frac{1}{u} - \frac{(\pi)^{1/2}\,(\mathrm{erfc}(u))}{e^{-u^2}}\right] \qquad (8)$$

where

u is defined as equal to $\frac{\ell_2}{4D_0 t}$ and erfc(u) is the error function often used in the solution of certain types of integrals.[5]

- Steady-State Diffusion Coefficient (D_s)

Following a transition period after breakthrough, a constant concentration gradient is established across the membrane and the flux becomes constant. Under such a condition, a steady-state diffusion coefficient, D_s, can be calculated directly from equation (9):

$$J = D_s\,\frac{C_1}{\ell}, \qquad (9)$$

assuming C_2 is small compared to C_1.

The steady state coefficient may be useful in the selection of clothing materials in cases where some limited exposure to a permeating chemical may be acceptable.

- Time-Lag Diffusion Coefficient (D_L)

Another technique for calculating a diffusion coefficient is the time-lag method. The time-lag coefficient, D_L, is determined by extending the steady state portion of the permeation curve (see Figure 3) to the time axis. The time, T_L, at the intercept is substituted into equation (10):

$$D_L = \frac{\ell^2}{6T_L} \qquad (10)$$

and D_L is then calculated. D_L is the general diffusion coefficient, D, in equations (2) and (6).

D_L is valid only for those barriers in which the diffusion coefficient is constant. However, it does provide a good approximation to D_s in some cases and a fair approximation to D_o for those barriers in which the diffusion coefficient is variable.

Since the flux shortly after breakthrough is of most concern in evaluating clothing materials, a computer program, based on equation (8), which uses permeation test data to calculate D_o was written. With D_o known, equation (8) can then be used to predict permeation rates both at non-tested times and for other material thicknesses.

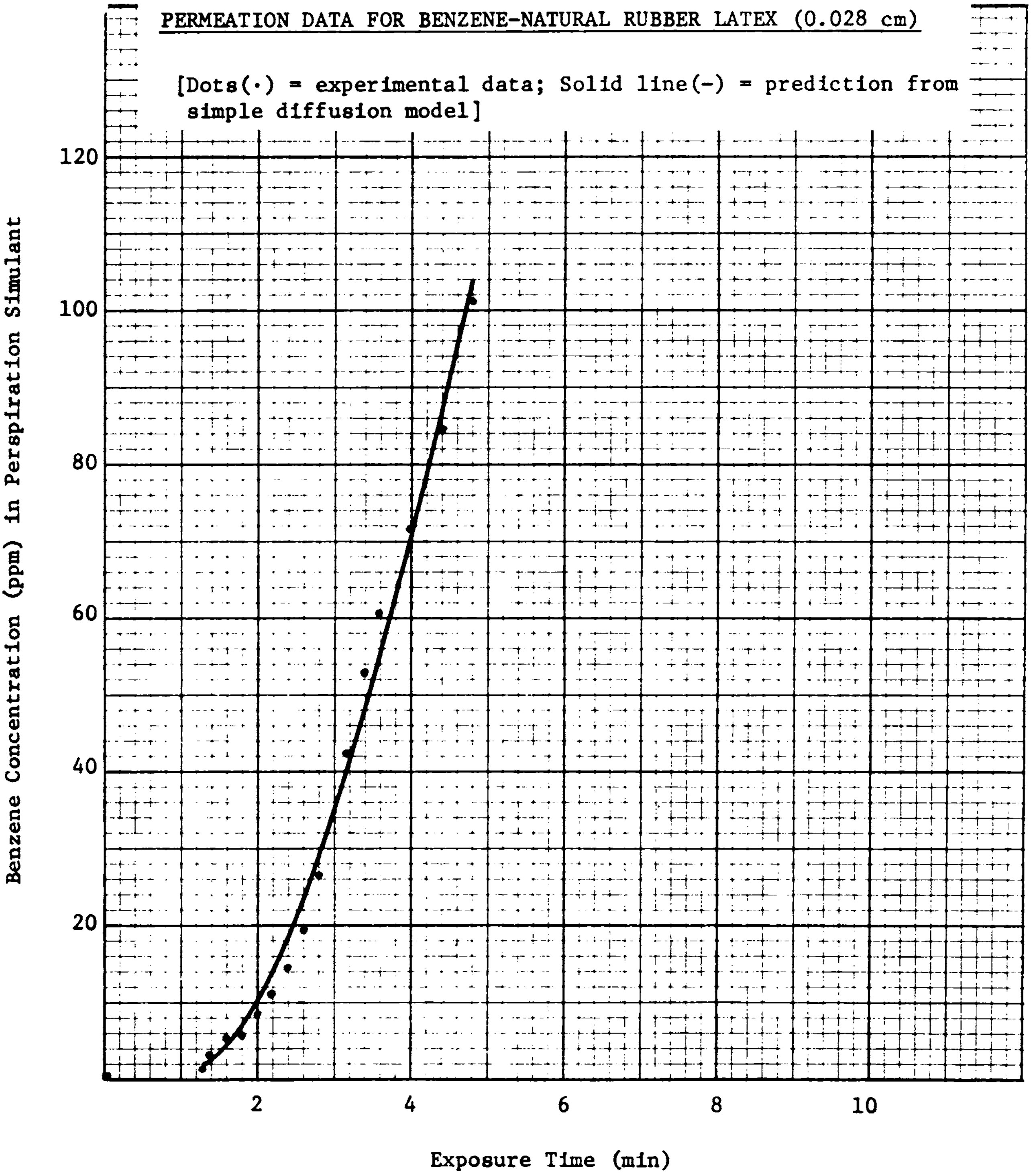
This model has been evaluated for its applicability in predicting the performance of protective clothing materials. Data from benzene experiments were used.

Figures 4, 5, 6, and 7 depict actual short-time experimental data — filled circles — for benzene permeation through natural rubber (latex), polyethylene, Viton and nitrile rubber (latex), respectively. The computer program reduced each set of test data to a predicted continuous permeation curve based on the calculated short-time diffusion coefficient, D_o. As shown, the computer predictions were quite good for natural rubber, polyethylene and Viton. However, the model was not successful in predicting proper breakthrough for the nitrile rubber. The model also failed for several of the other materials tested and listed in Table 10. Apparently, a complicating mechanism is affecting the simple diffusion process. This mechanism appears to be absorbance of benzene by fillers, stabilizers, etc., added to the clothing materials during processing. This is reasonable since the three successful materials are known to contain little or no additives; while the unsuccessful materials are known to contain higher levels of additives. As discussed in the next section, the expansion of the model to include additive/permeant interactions is more complex and requires more experimental data for resolution of the constants.

2. Permeation Through Filled Elastomers

Fillers (e.g., silica and carbon black) are often added to elastomers in the form of small particles to improve mechanical durability and elastic properties. Such fillers also affect the barrier properties of elastomers — to the extent that permeation through filled elastomers has been studied by several investigators. Many parameters, including the solubility of permeant in the elastomer, the type and size of each filler, the loading of each filler and the nature and level of permeant interaction with each filler, have been identified as important. Moreover, past investigators have segregated filled elastomers into two categories to assist in characterizing their barrier properties. These categories are based on the degree of "wetting" of the dispersed filler particles by the bulk elastomer (also referred to as the "polymer" in this discussion). "Wetting" is a term used to describe the nature of the interface between the filler and the polymer. If the surface area of each filler particle is completely and intimately coated with polymer, the filler is

FIGURE 4

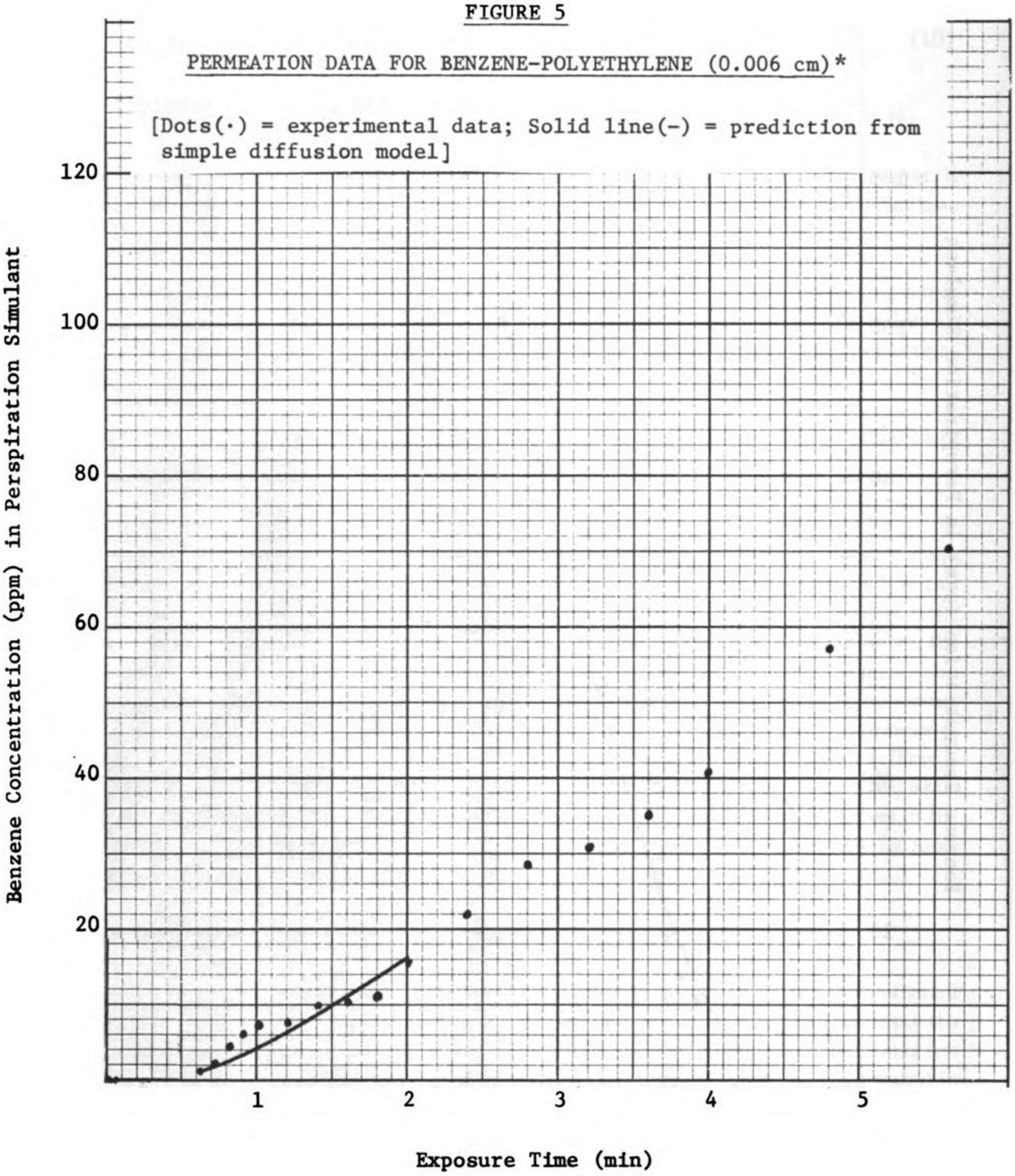

PERMEATION DATA FOR BENZENE-NATURAL RUBBER LATEX (0.028 cm)

[Dots(·) = experimental data; Solid line(-) = prediction from simple diffusion model]

FIGURE 5

PERMEATION DATA FOR BENZENE-POLYETHYLENE (0.006 cm)*

[Dots(·) = experimental data; Solid line(-) = prediction from simple diffusion model]



*Thickness of material.

FIGURE 6

PERMEATION DATA FOR BENZENE-VITON (0.16 cm)

[Dots(·) = experimental data; Solid line(–) = prediction from simple diffusion model]

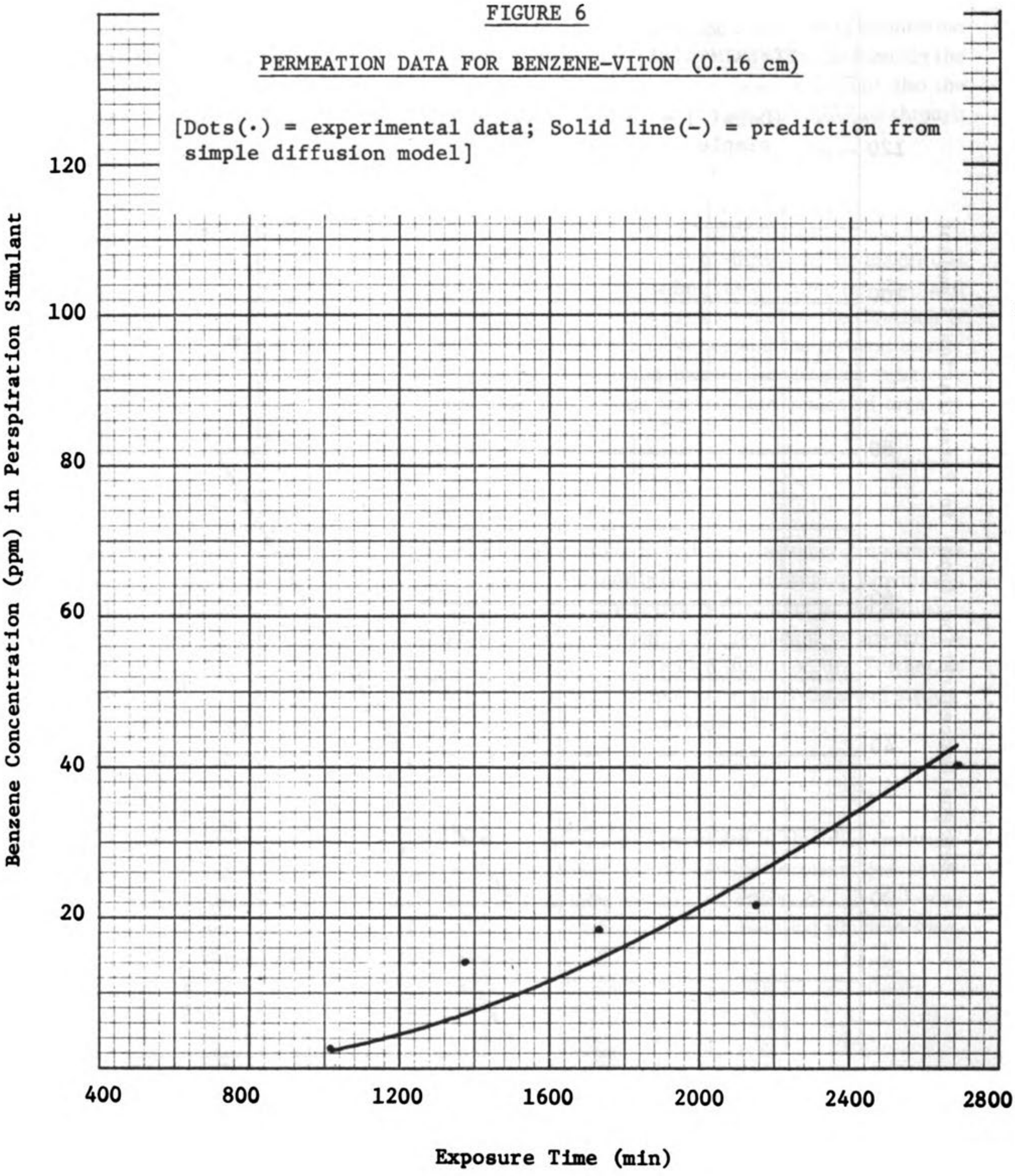
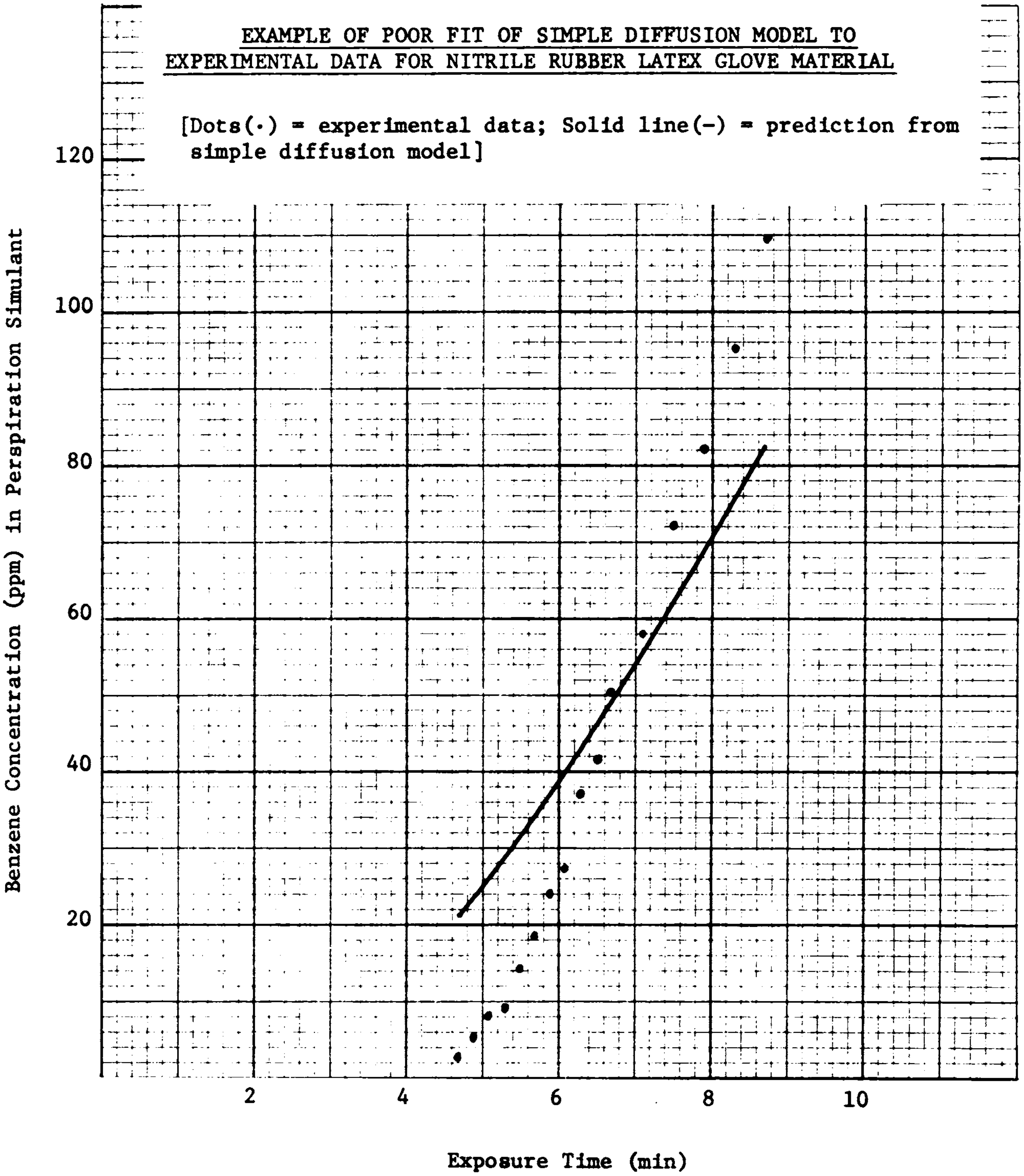


FIGURE 7



EXAMPLE OF POOR FIT OF SIMPLE DIFFUSION MODEL TO EXPERIMENTAL DATA FOR NITRILE RUBBER LATEX GLOVE MATERIAL

[Dots(•) = experimental data; Solid line(–) = prediction from simple diffusion model] said to be thoroughly wetted. If the polymer does not contact the external surface or does not penetrate the pores, the filler is not thoroughly wetted. In the former case, analyses of permeation usually take into account only the physical obstruction to diffusion provided by the filler. In the later case, not only must the physical obstruction by the filler be accounted for, but also the extent and rate of permeant sorbed by the filler (known as its activity) and the diffusion through the air spaces (so-called vacuoles) must be considered.

a. Wetted Fillers

Inert, thoroughly wetted fillers provide a physical obstruction to diffusion. The magnitude of the obstruction is directly dependent on both the percent loading (i.e., volume fraction) and shape of each particle. Regarding shape, the projected surface area normal to the direction of permeant diffusion is most important. The projected area can be varied and the permeation rate modified by judicious specification of filler shape. Analyses of permeation data are relatively straightforward by simple diffusion theory once the volume fraction and projected area are known.

b. Unwetted Fillers

Analysis and mathematical modeling of permeation through an elastomeric membrane which contains active, unwetted filler is much more complex because, in addition to providing a physical obstruction, the filler and associated vacuoles are active participants in the diffusion process. The unwetted filler may immobilize a certain portion of the permeant by irreversible sorption, while the vacuoles present a second medium through which diffusion occurs. Further, as with unfilled materials, there exist two diffusion regimes of importance: short-time and steady-state. Steady-state diffusion through a filled elastomer is discussed first.

- Steady-State Diffusion

Once steady-state has been reached, the concentration of permeant in the filler and vacuoles as well as in the bulk polymer are at a level which is dependent on the permeant concentration (C_o) outside the membrane. The diffusion process is then described by the following relationship which is actually an expanded form of the simple diffusion equation which includes terms for each of the three elastomer components:

$$\frac{dC_a}{dt} + \frac{dC_b}{dt} + \frac{dC_c}{dt} = D_a \frac{d^2 C_a}{dx^2} + \theta D_b \frac{d^2 C_b}{dx^2} + D_c \frac{d^2 C_c}{dx^2} \qquad (11)$$

where:

a represents the filler component;

b represents the pure polymer component;

c represents the vacuole component;

C_i is the concentration of carcinogen (permeant) in component "i" in terms of gm/cm^3 of *total membrane volume* where i refers to a, b, c, etc.

D_a, θD_b and D_c are the diffusion coefficients for each component (D_b is the diffusion coefficient in the pure polymer, and is related to its value in the filled polymer by the factor θ, which accounts for tortuosity of the diffusion path).

The total permeant concentration for three components a, b, and c in a unit volume (cm^3) of a filled polymer (C_p) can be represented by equation (12):

$$C_p = C_a + C_b + C_c = \left(k_a v_a + k_b v_b + k_c v_c\right) C_o \tag{12}$$

where

k_i is the Henry's Law Coefficient relating the concentration of the permeant in component i (C_i) to the concentration of the permeant outside the elastomer (i.e., $k_i = C_i/C_o$); and,

v_i is the volume fraction of each component in the *total membrane volume*.

With equation (12), equation (11) may be simplified to read:

$$\frac{dC_p}{dt} = \left(\frac{D_a k_a v_a + \theta D_b k_b v_b + D_c k_c v_c}{k_a v_a + k_b v_b + k_c v_c}\right) \frac{d^2 C_p}{dx^2} \tag{13}$$

In equation (13), the expression in parentheses is an overall diffusion coefficient which is noted as the steady-state diffusion coefficient, D_s. The steady-state diffusion coefficient is useful in describing the long term barrier properties of protective clothing.

- Short-time Diffusion

The initial, transient regions of the permeation process are more important than steady-state when considering protection from carcinogens. In the short time, the behavior of a filler as a permeant sorber (i.e., immobilizer) can significantly influence the protection offered by a clothing material.

Mathematical modeling of elastomeric membranes containing active filler is complex because independent measurements must be made to quantify filler parameters such as degree of wetting, permeant absorbance rate, capacity for permeant and projected surface area. Also, polymer/filler interactions may occur as a permeant moves through a membrane. The overall result of these parameters is a diffusion coefficient which is a function of permeant contact time and position across the membrane until steady-state is reached. One basis for discussion of the process is the so-called "moving-boundary theory of diffusion."

- Moving-Boundary Theory of Diffusion

In spite of the complexities, an effort has been made to represent these short-time physical occurrences mathematically by the development of the moving-boundary theory of diffusion. This theory is based on the premise that diffusion is accompanied by an instantaneous and irreversible immobilization of the initial permeant molecules resulting in a sharp concentration boundary or front. The boundary separates a region in which all available filler sorption sites are occupied by permeant from a region in which none are occupied. This concept is illustrated in Figure 8. The boundary moves through the elastomer as time passes until a continuous, concentration gradient is established across the membrane.

The discontinuity in the concentration gradient implies that a discontinuity exists in the expression for the diffusion coefficient. Therefore, permeation is not simple (i.e., it is non-Fickian). Considerably more complex mathematics are involved. Crank has developed a general solution for moving-boundary diffusion;[5] and with that as a guide, we have prepared a preliminary solution for the problem of carcinogen permeation through filled clothing materials.

- Problem Statement

Before considering the solution, we mathematically define the physical problem. Figure 8 provides illustration and clarification for this definition. As our example membrane, an elastomer of thickness l is considered. The distance into the membrane normal to the upstream surface contacting a high concentration of carcinogen (permeant) is denoted by x. The concentration of permeant at $x = 0$ is noted as C_1. The concentration of the permeant at the discontinuity, where $x = X$, is C_X. (Note that C_X is the concentration in the filler component and was noted as C_a in our earlier discussion of steady-state diffusion.) Both C_1 and C_X must be determined by independent experiments. It is assumed that the two diffusion coefficients, one on each side of the discontinuity, are constant but not equal. For $x < X$, the coefficient is D_1; while, for $x > X$, the coefficient is D_2. Also, at the time t after upstream contact with the carcinogen, the discontinuity occurs at $X = X(t)$, where $X(t)$ is a function of t. Also at time t, the permeant concentration in the region $0 \leq x \leq X$ is denoted by c_1 and in the region $x > X$, by c_2. At the discontinuity, the concentration c_1 and c_2 must be equivalent and the permeant leaving $x < X$ must equal the permeant entering $x > X$. Thus at $x = X$, $c_1 = c_2 = C_X$ and equation (14) is applicable:

$$D_1 \frac{\partial c_1}{\partial x} = D_2 \frac{\partial c_2}{\partial x} \tag{14}$$

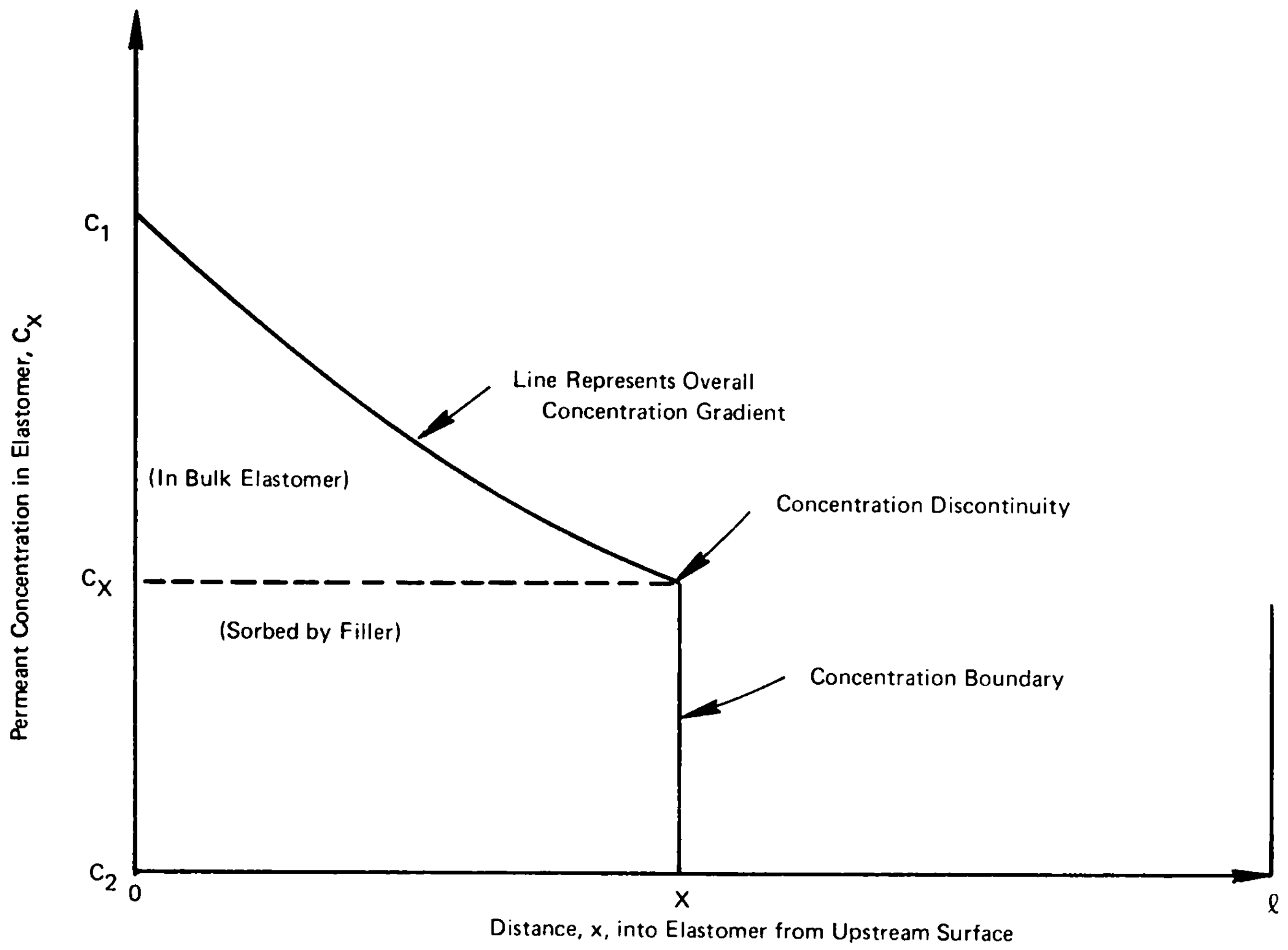


FIGURE 8 GRAPHIC REPRESENTATION OF THE CONCENTRATION GRADIENT DURING THE SHORT-TIME TRANSIENT PHASE OF CARCINOGEN PERMEATION THROUGH AN ELASTOMERIC MEMBRANE CONTAINING AN ACTIVE FILLER

This partial differential equation requires a trial and error solution. In the process, a number of boundary conditions must be identified and specified. Further, the solution to equation (14) provides the sought-after mathematical model for moving-boundary diffusion through clothing materials.

- Problem Solution

The general solution to equation (14) is:

$$\frac{C_X - C_1}{f'\left(\frac{Z}{2\,D_1^{1/2}}\right)} + \frac{C_X - C_2}{f''\left(\frac{Z}{2\,D_2^{1/2}}\right)} = 0 \qquad (15a)$$

where

C_2 is the concentration of permeant at $x = l$;

Z is a constant in the equation, $X = Zt$, relating the location of the discontinuity, X, to time, t; and,

f' and f'' are functions defined by the following relationships:

$$f'\left(\frac{Z}{2\,D_1^{1/2}}\right) = \pi^{1/2}\,\frac{Z}{2\,D_1^{1/2}}\,\exp\left(\frac{Z^2}{4\,D_1}\right)\,\text{erf}\left(\frac{Z}{2\,D_1^{1/2}}\right) \qquad (15b)$$

$$f''\left(\frac{Z}{2\,D_2^{1/2}}\right) = \pi^{1/2}\,\frac{Z}{2\,D_2^{1/2}}\,\exp\left(\frac{Z^2}{4\,D_2}\right)\,\text{erfc}\left(\frac{Z}{2\,D_2^{1/2}}\right) \qquad (15c)$$

where, as above, erf $\left(\frac{Z}{2\,D_1^{1/2}}\right)$ and erfc $\left(\frac{Z}{2\,D_2^{1/2}}\right)$ error functions used in the solutions of the integral equations.

If D_1 is assumed to be constant and D_2 is assumed to be zero (i.e., there is no permeant diffusion at concentrations less than C_X and all diffusion at concentrations greater than C_X follows the simple diffusion mechanism. Both are reasonable assumptions in the short-time permeation regime), equation (15a) can be simplified to:

$$\frac{C_X - C_1}{f'\left(\frac{Z}{2\,D_1^{1/2}}\right)} + C_X - C_2 = 0 \qquad (16)$$

In addition, if the downstream surface at X = l is continuously washed by a solution very dilute in permeant, C_2 can be approximated by zero. Then equation (15a) simplifies even further to:

$$\frac{C_X - C_1}{f'\left(\frac{Z}{2\,D_1^{1/2}}\right)} + C_X = 0 \qquad (17)$$

For each permeant/elastomer pair, C_X, C_1, D_1, and Z are unknown. C_X and C_1 can be determined by solubility tests, while D_1 is the D_S taken from steady-state diffusion data. With these experimental data, Z can be calculated from equation (17). In fact, once Z is known, the breakthrough time of the moving boundary can be determined by substituting l for X in the relationship $X = Zt^{1/2}$. Additional manipulations of the various equations contributing to the development of the equation (15a) permit the generation of an additional equation which describes the overall concentration profile across a membrane at any time after carcinogen contact with one surface.

c. Conclusion

In order to adequately model diffusion through filled, commercial grade elastomeric clothing materials, complex, and specialized theories (e.g., moving boundary) must be used. To solve the mathematical expressions of such theories requires in-depth data on the elastomers, fillers, and other additives relevant to solubilities of the permeant in each and their interactions. Such data are not available; and their acquisition would require experimentation at a level beyond that considered appropriate at this stage of test method development. Therefore, development and evaluation of mathematical models for carcinogen permeation were carried no further in this study.

E. DISCUSSION

In the thicknesses tested, a number of protective clothing materials provided resistance to permeation for the recommended one hour minimum on continuous contact with liquid. However, there were many materials that resisted permeation for only several minutes. (See Table 24.) Breakthrough times of a carcinogenic liquid varied with each material/carcinogen combination. Several materials satisfactorily resisted one or more of the nine liquids tested, but provided little resistance against others. These results clearly confirm the need for quantitative evaluation of each material/carcinogen combination by a standard permeation test method prior to the issuance of recommendations for suitable protective clothing materials.

The results of permeation tests carried out at non-ambient temperatures were also telling. Marked changes in breakthrough times were found over a relatively modest and routine temperature range. This indication highlights the need for criteria which require permeation testing over the entire range of anticipated clothing use conditions.

The test method developed for evaluating the resistance of clothing materials to permeation by carcinogenic liquids is straightforward, reproducible, and yields accurate, meaningful data. The sensitivity of the test is dependent on the analytical technique used to analyze the downstream solution for carcinogen content. In the tests reported here, 1-10 ppm sensitivities were regularly achieved using either UV spectroscopy or gas chromatography.

Solubility data obtained from separate immersion tests supplemented the results of the permeation tests. It appears that a high carcinogen solubility correlates with short breakthrough times and high fluxes. Accordingly, such tests are useful in prescreening materials prior to permeation testing. Further, the numerical value of solubility (saturation concentration) could be used in conjunction with a complex mathematical model in determination of the diffusion coefficient for individual material/carcinogen combinations. Using the diffusion coefficient, predictions of clothing performance at conditions other than those of actual test can be made.

TABLE 24

SUMMARY OF BREAKTHROUGH TIMES OF SELECTED CHEMICALS THROUGH PROTECTIVE CLOTHING MATERIALS AT 22°C

Carcinogen	Detection Limit (ppm)	Clothing Material		Breakthrough Time (min)
		Composition	Thickness (cm)	
Trichloroethylene	1	Nitrile rubber	0.094	10-15
		Neoprene rubber	0.079	10-15
		Polyvinyl alcohol	0.009	<15
Epichlorodydrin	1-5	Polyvinyl alcohol	0.008	< 5
		Neoprene rubber	0.076	60-80
		Butyl rubber	0.084	4740
Coal-Tar Creosote	1-5	Neoprene rubber	0.076	270
		Butyl rubber	0.081	>5400
		Viton	0.043	>5760
Benzene	5-10	Polyethylene	0.006	<1
		Polyurethane-coated nylon	0.02	2
		Natural rubber	0.028	2
		Nitrile rubber	0.041	5
		PVC-coated nylon	0.043	6
		Polyvinyl alcohol	0.023	10
		Neoprene rubber	0.076	25
		Butyl rubber	0.084	88
		Viton	0.16	900
Ethylenimine	10-30	Neoprene rubber	0.02	<5
		Butyl rubber	0.084	600-960
1,1-Dimethylhydrazine	10	PVC-coated nylon	0.043	5-10
		Neoprene rubber	0.076	25-40
		Butyl rubber	0.084	1380-1620
2-Nitropropane	10	Polyvinyl alcohol	0.02	<5
		Nitrile rubber	0.09	25-60
		Butyl rubber	0.08	>6060
β-Propiolactone	10	Polyurethane-coated nylon	0.003	<5
		Natural rubber	0.03	15-20
		Polyethylene	0.006	10-30
Hexemethylphosphoromide	3	Polyethylene	0.006	15-25
		Butyl rubber	0.084	60-90
		Nitrile rubber	0.094	60-90

V. CONCLUSIONS AND RECOMMENDATIONS

The study has achieved its objective: the development of performance criteria and an evaluation program for protective clothing used against carcinogenic chemicals. From our findings we conclude that the opportunity exists to significantly raise the level of protection afforded workers who may potentially contact harmful chemicals — especially carcinogens. We believe the establishment of standard tests by which the performance of protective clothing can be judged is the single, most important step towards that goal. Practical, quantitative standards will encourage product development by manufacturers and permit users to select, specify, and purchase clothing on well-founded bases. Initial steps towards development of comprehensive performance standards have been taken in this study. Further work is needed and warranted in several areas. Our conclusions and recommendations follow.

A. PERFORMANCE STANDARDS

1. Conclusion

We conclude that a comprehensive, widely-accepted set of standard tests is needed to stimulate the development of protective clothing and well-founded bases for its purchase.

2. Discussion

Production processes, handling and transportation procedures, and recommended safety practices associated with ten carcinogenic chemicals were reviewed. In no case were quantitative standards found for the selection and specification of clothing used for protection against the chemicals. Therefore, users or those who specify protective equipment have no means of comparing articles of clothing prior to purchase, and in general must rely on the recommendations of clothing manufacturers and chemical producers. However, such recommendations may not be based on the results of adequate experimentation. In fact, our analyses found several cases in which materials were poor barriers against chemicals for which they were recommended, and their use could result in contact of a harmful agent with the skin of the wearer.

3. Recommendation

We recommend that the set of test methods delineated in Section III.B. be considered for adoption as standards by which protective clothing used against harmful chemicals are evaluated. The tests challenge the strength; chemical aging, and thermal resistances; dexterity; and cleanability of clothing materials. The standards would serve as the logical bases for an improvement in the level of protection available to workers who may potentially contact harmful chemicals.

The scope of this study limited laboratory work to the performance of only one of the twelve tests — permeation. Although the remaining eleven tests are commonly used in the evaluation of materials, the applicability and practicality of their use in the selection of clothing to be used as barriers to harmful chemicals have not been established. Therefore, we recommend an experimental program be carried out to fully evaluate the appropriateness of each test of the proposed standards.

B. FUTURE AVAILABILITY OF TRADE RECOMMENDATIONS FOR CLOTHING TO BE USED AGAINST CARCINOGENS

1. Conclusion

We conclude that the breadth of specific usage recommendations for protective clothing from chemical and clothing suppliers will be reduced as more is learned about the potential harmful effects associated with contacting certain chemicals.

2. Discussion

We have demonstrated that currently available trade recommendations for protective clothing selection may be inadequate to select a barrier against carcinogens. Recommendations were found to be general, qualitative (e.g., "against aromatics use Neoprene"), and may not be based on any experimentation, much less the results of permeation tests. (In spite of such deficiencies, such guidelines are routinely used because they are all that are available.)

In the future, however, even those recommendations may disappear from commercial literature. The reason: the potential for liability litigation against the supplier of the information. The withdrawal of recommendations will probably first occur where carcinogens are concerned since their threshold limits have not been established, and since a manufacturer cannot guarantee that an item of clothing is impermeable.

Consequently, the burden of materials selection will fall on the user. Larger user organizations may have the means to support the extensive clothing materials evaluation program which would be required, but many moderate and small organizations do not. A system through which all users can obtain quantitative information relevant to their selection and use of protective clothing is needed.

3. Recommendation

We recommend the establishment of a protective clothing materials "data bank" to serve both manufacturers and buyers as a source of information pertinent to the protection of workers from potentially harmful chemicals, including carcinogens. Full details of the operation and scope of the bank would best be determined by a comprehensive study of the needs and capabilities of the involved industries and government agencies.

However, factors which should be included are:

- only data generated by accepted, standard test methods would be accepted,
- data would be compiled according to clothing material, toxic chemical, test conditions, and acceptable and non-acceptable use conditions.

- data would be available to all persons responsible for protecting the worker from harmful chemicals. This includes safety directors, plant managers, union representatives, and government officials and inspectors. Technical bulletins would issue from the bank,

- as needs change or more information becomes available, new tests should be developed,

- spot checking of test results and commercially available clothing would be carried out to insure standards are met.

Coupled with the adoption of standard test methods, we believe institution of the data bank concept will result in the marked improvement of worker protection.

C. MINIMUM PERFORMANCE AGAINST CARCINOGENS

1. Conclusion

No standard exists for the minimum time of protection that an item of clothing must provide workers. We conclude that, especially when dealing with carcinogenic chemicals which have no established threshold levels for carcinogenicity, a minimum standard is needed.

2. Recommendation

We recommend that for general purpose protective clothing a standard of at least 60 minutes be adopted. For clothing designed for use in emergency situations (e.g., spills or equipment failure) and planned, long-term exposure, we recommend a standard of eight hours.

We propose for consideration that standards must be met under "worst case," direct, continuous challenge conditions. That is, a material in its actually-used thickness must prevent the breakthrough of the test chemical in "analytically detectable quantities" for the times suggested above. As with other fields of investigation involving carcinogens, the quoted phrase must be defined in a manner appropriate to the conditions of protective clothing usage.

D. PERMEATION TEST

1. Conclusion

As part of this study, we defined a simple permeation test procedure for measuring the barrier properties of clothing materials. From the results of more than 50 permeation tests, we conclude that the method yields data which accurately and quantitatively describe the behavior of permeant/barrier pairs.

2. Recommendation

This program was not designed to perform sufficient numbers of experiments to establish the level of reproducibility of the method. We therefore recommend the performance of additional experiments for the establishment of the level of significance of the results. Further, the method should be refined and optimized, and a "round-robin" evaluation program involving both industrial and government laboratories should be designed and executed, and the results analyzed.

E. RAPID SCREENING OF CANDIDATE MATERIALS

1. Conclusion

We conclude that the results of tests involving the immersion of candidate materials in harmful liquids and gases can be used for screening purposes in order to reduce the number of permeation tests.

2. Discussion

This study was performed using chemicals representing each of several classes of organic compounds (e.g., aromatics — benzene, and amides — hexamethylphosphoramide). Consequently, generalizations from the data are limited. However, one trend which did emerge was a relationship between high chemical solubility in a material and short breakthrough time of the chemical through the material. (The converse relationship — long breakthrough time for a chemical of low solubility — cannot be concluded from our data.) Solubility determinations are more readily carried out than permeation experiments.

3. Recommendation

We recommend further evaluation and consideration of the solubility test as a screening procedure to narrow the field of materials to undergo permeation challenge. The scope of the study should include an investigation of the relationship of the polarities of the chemical and the barrier material on solubility and breakthrough time.

F. TEST CONDITIONS

1. Conclusion

We conclude that the temperature at which articles of clothing are used can have a significant effect on their barrier properties.

2. Discussion

Results of permeation experiments carried out at 7°, 22°, and 37°C show a marked influence of temperature on the effectiveness of a polymeric barrier material. In fact, benzene breakthrough times for a neoprene barrier (0.076 cm thick) were 40 and 16 minutes at 7°C and 37°C, respectively.

3. Recommendation

We recommend that future investigation and performance standards pertinent to protective clothing include the requirement that tests be run at the extremes of the temperature range expected to be encountered during use of the clothing.

G. TEST SPECIMENS

1. Discussion

Most of our permeation experiments were performed using test specimens cut from sheet stock which conformed to military specifications. Thus, we are confident of the uniformity of the specimens used throughout the study. On the other hand, the use of such materials precluded testing of seams and closures which often are the weak points of the protective barrier. Further, results from tests of sheet stock may not be representative of clothing made from the same material since the two items can be made by different processes. For example, sheet stock is usually milled, whereas gloves are usually made by dip coating.

2. Recommendation

We recommend further permeation tests be carried out using specimens from actual clothing in order that comparisons with the results of our tests can be made. An important part of such an investigation should be testing of seams and closures. We see such a study as a logical extension of this study, and as a result of its completion, a sound basis for the specification of protective clothing performance and construction standards will have been produced.

H. LEATHER

1. Discussion

Leather, which was not included in this study, is commonly used in protective clothing, gloves, and footwear. Because the nature of leather produces an appearance of "drying" after contact with many liquids, items made of leather may not be discarded and an unhealthy situation can go undetected. For example, footwear is often subjected to repeated contacts with chemicals that are readily absorbed. Over time, desorbtion occurs. The path of desorbtion is just as likely to be inward as outward; thus potentially, the skin can be in direct contact with harmful chemicals for prolonged periods.

2. Recommendation

We recommend that an evaluation of the barrier properties and chronic exposure aspects of leather clothing, especially footwear, receive high priority in future work plans.

I. PESTICIDES AND OTHER HARMFUL CHEMICALS

1. Conclusion

We conclude that the test criteria may be applied to other harmful chemicals, including pesticides and corrosives, in addition to carcinogens.

2. Discussion

In recent years, the deleterious effects of several pesticides on production workers and their families have been well documented by the FDA and OSHA. Agricultural workers also come into contact with the harmful chemicals. Many of these workers may be unaware of the potential for bodily harm and unfamiliar with the selection and use of protective clothing.

3. Recommendation

We suggest that performance criteria developed in this study be applied to the testing of protective clothing used against the implicated pesticides. Furthermore, we recommend the initiation of a comprehensive program having the objectives of: (i) determining the adequacy of protective clothing materials presently used by agricultural workers; (ii) screening and ranking protective clothing materials that are used against implicated pesticides according to barrier properties determined by experimentation; and (iii) combining the results of items (i) and (ii) with presently available pesticide-user information into a "guidelines for protection from pesticides" handbook.

J. NIOSH CRITERIA DOCUMENTS

1. Conclusion

We conclude that the most immediate mechanism for the education of users as to the most appropriate materials for use against a potentially harmful chemical is the NIOSH Criteria Document for a recommended occupational exposure standard.

2. Recommendation

We recommend that NIOSH expand the coverage and usefulness of its criteria documents by including quantitative performance profiles of each material recommended for use in protection against the subject chemical.

Testing of materials for documents presently in preparation or planned should be scheduled so that timely inclusion in their first printings could be achieved. For those chemicals already covered by a document, material evaluations could be performed and results included in second printings or a separate publication.

VI. APPENDICES

Appendix	Contents
A	Overview Documents
B	Test Methods
C	A Correction for Decomposing Compounds
D	References (to text)

APPENDIX A

OVERVIEW DOCUMENTS

TRICHLOROETHYLENE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Trichloroethylene (TCE) is a clear, colorless liquid alkyl halide which is heavier than water, nonflammable and has a significant vapor pressure at ambient temperatures. Trichloroethylene is primarily produced by the catalytic oxychlorination of ethylene or dichloroethylene under high pressure and temperature. Most of the TCE consumed in the United States is used in vapor degreasing operations. Minor amounts are used in liquid cleaning operations, in polyvinyl chloride production, in three textile finishing operations and in adhesive and surface-coating products. TCE is currently suspected of being a human carcinogen. Although nearly 100,000 workers in the United States can potentially contact liquid TCE, industry programs for worker protection have been minimal.

B. SELECTED PROPERTIES

Table A-1 contains data describing selected physical properties, chemical properties, and the carcinogenicity of trichloroethylene. These data are intended to provide a general characterization of TCE and should prove helpful in interpreting exposure hazards to industrial workers. TCE is typically produced, shipped, stored, and used in the liquid state.

C. SOURCES(1,2,3)

There are currently five plants producing trichloroethylene in the United States. The combined annual capacity of these facilities is 475 MM pounds; however, in 1975, actual production was only 60% of capacity. Due to continuing inroads into traditional TCE applications by substitute solvents, this production level is not expected to increase.

TCE is produced by two processes. One uses acetylene as the primary feedstock; the other uses either ethylene or ethylene dichloride as the primary feedstock.

1. Acetylene Process

Historically, acetylene was used in the production of all trichloroethylene. However, due to the relatively high cost of acetylene as a feedstock, this process is now in disfavor and only one of the five plants uses this feedstock. In the process, acetylene is chlorinated to 1,1,2,2-tetrachloroethane. The intermediate is then dehydrochlorinated by treatment with calcium hydroxide or by pyrolysis to yield trichloroethylene.

2. Ethylene Process

Ethylene is now considered the most economical feedstock for TCE. The direct process feed, however, usually consists of ethylene dichloride rather than ethylene. The ethylene dichloride is

TABLE A-1

SELECTED PROPERTIES OF TRICHLOROETHYLENE

<table>
<tr><td rowspan="3">Physical Properties*</td><td rowspan="2">Physical State @ 20°C, 760 mm Hg</td><td rowspan="2">Boiling Point @ ~760 mm Hg</td><td rowspan="2">Vapor Pressure @ 20°C</td><td rowspan="2">Polarity</td><td colspan="2">Solubility @ 20°C</td></tr>
<tr><td>Water</td><td>Organic Solvents</td></tr>
<tr><td>Liquid</td><td>87.0°C</td><td>60.0 mm Hg</td><td>Non-polar</td><td>1000 ppm</td><td>Generally Miscible</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><td colspan="2">Chemical Reactivity (A Qualitative Assessment)</td><td colspan="2">Stability (On Exposure to an Ambient Atmosphere)</td></tr>
<tr><td colspan="2">Low</td><td colspan="2">Volatile, but Generally Stable</td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><td colspan="2">Human</td><td colspan="2">Experimental (Animal)</td></tr>
<tr><td colspan="2">No Specific Data Available</td><td colspan="2">● Liver Carcinomas Induced in Mice on Oral Administration
● No Carcinogenicity in Rats on Oral Administration</td></tr>
</table>

*Data are from several sources and were compiled by Arthur D. Little, Inc.

first produced by the chlorination of ethylene. The TCE product is then produced by the catalytic oxychlorination of ethylene dichloride under high pressure and temperature.

The final product of both processes is recovered by distillation. This step usually results in a product which is 99.9 weight percent pure. The TCE product is transferred to mixing tanks for addition of a stabilizer and then to storage tanks for shipment to end users. Most producers make one grade of trichloroethylene — that used in degreasing operations. However, some special high purity grades are also available.

Most process operations are carried out in completely enclosed systems. Nonetheless, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts), and frequently, product transfer operations are all potential sources for liquid leaks and subsequent worker exposure. Maintenance personnel contact liquid trichloroethylene when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills or process upsets (i.e., plant shutdowns).

D. USES(1,2,3,4)

Eighty-seven percent of the trichloroethylene consumed in the United States is used as the active solvent in the vapor degreasing of fabricated metal parts. The remainder is used in liquid cleaning operations, in polyvinyl chloride production, in three textile finishing operations and in adhesive and surface-coating products.

1. Vapor Degreasing

Vapor degreasing is a cleaning process in which organic "grease" is removed through the condensation of hot solvent vapors on a cold metal item. Recent data indicate that there are currently 10,000 facilities in the United States utilizing 15,000 TCE vapor degreasers. Eighty-five percent of these degreasers are "open-top" units and the remaining fifteen percent are enclosed, conveyorized units. The operation of each of these units provides ample opportunity for worker exposure and subsequent contact with TCE. Often degreased items are manipulated manually while wet.

2. Liquid Cleaning

Trichloroethylene is also used as the solvent in liquid cleaning operations. This process involves the application of liquid TCE to a metal item by direct rubbing or wiping, spraying or soaking. It has been estimated that there are 2,300 such "cold" cleaners currently in use.

3. Polyvinyl Chloride Production

Trichloroethylene is used as a chain-terminating agent in the production of some forms of polyvinyl chloride (PVC). This application is limited, however, to fewer than one third of domestic PVC plants. All process operations involving PVC are carried out in enclosed systems.

4. Textile Finishing

Three primary uses for trichloroethylene in textile finishing are:

- As a carrier solvent in the application of surface treating agents such as water repellents;
- As a scouring agent in finishing wool products; and,
- As a solvent for dissolving plastic basting threads from finished garments.

Such operations are often carried out batch-wise with some worker exposures probable, especially where wet or damp materials are handled at the end of the finishing processes.

5. Other Uses

Trichloroethylene is also used as a coalescing aid in the manufacture of polyvinyl acetate adhesives. Further, TCE is used in special formulations for government-specification surface coatings. These uses are minimal.

E. TRANSPORTATION[1]

Methods of transporting trichloroethylene follow typical industry practices. Most TCE is transported by rail, truck or barge. Internal pipeline transfers for captive use within a chemical complex are the major exceptions. Smaller containers are available for some commercial and laboratory applications.

The operations involved in loading and unloading liquid TCE are similar for all three primary modes of transportation. A typical sequence requires that workers manually make and break connections, open and close valves, and monitor fill levels. Routine handling of "wet" connections and other equipment necessitates direct contact with liquid TCE.

F. NUMBER OF AFFECTED WORKERS[1]

Because of numerous variations in process design, plant size and age, job descriptions, and worker habits. it is impractical to determine the number of workers potentially contacting liquid trichloroethylene for each process or plant. The data presented in Table A-2 below represent estimates of the total number of workers in the United States, assigned to on-site TCE operations and thereby potentially exposed to TCE vapor.

TABLE A-2

WORKERS POTENTIALLY EXPOSED TO TRICHLOROETHYLENE VAPOR

Process Category	Number of Workers
Sources	~700
Uses	~89,000
Transportation	~2,500

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS[5,6]

Protective clothing manufacturers recommend the following materials for protection against liquid trichloroethylene:

- Nitrile Rubber (NBR)
- Neoprene
- Polyvinyl Alcohol (PVA)
- Polyethylene
- Polyurethane

Typically, the chemical industry recommends that neoprene and vinyl (PVC) be used in protecting against TCE.

H. CURRENT PRACTICES IN WORKER PROTECTION[7,8]

Industry has not taken specific precautions to insure worker isolation from liquid trichloroethylene. Statements such as "avoid prolonged or repeated contact with skin" or "handle with reasonable care" are common in industry literature. Implementation of these precautions is presumed to involve the use of industry-recommended clothing materials.

I. REFERENCES

1. "Technology Assessment and Economic Impact Study of an OSHA Regulation for Trichloroethylene," Draft Report Prepared by Arthur D. Little, Inc., for the U.S. Department of Labor, July 1976.

2. Faith, Keys and Clark, "Industrial Chemicals," Wiley Interscience, 4th Edition, 1965.

EPICHLOROHYDRIN: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Epichlorohydrin is a colorless, chlorinated liquid epoxide which is flammable and has a moderate vapor pressure at ambient temperature. Most epichlorohydrin is produced by the chlorohydrination of allyl chloride. The majority of epichlorohydrin consumed in the United States is used to produce synthetic glycerine, epoxy resins, epichlorohydrin elastomers, and several minor compounds. Epichlorohydrin is a suspected human carcinogen that has been shown to induce sarcomas in mice upon subcutaneous administration. Approximately 5,000 workers in the United States can potentially contact liquid epichlorohydrin.

B. SELECTED PROPERTIES

Table A-3 contains data describing selected physical properties, chemical properties, and the carcinogenicity of epichlorohydrin. These data are intended to provide a general characterization of epichlorohydrin and should prove helpful in interpreting exposure hazards to industrial workers. Epichlorohydrin is typically produced, shipped, stored and used in the liquid state.

C. SOURCES(1)

In the United States, epichlorohydrin is produced by Dow Chemical and Shell Oil. Total combined capacity in mid-1975 was estimated to be 450 MM pounds per year. In addition, it is thought that Union Carbide and Ciba-Geigy have unused production capacity.

Crude epichlorohydrin is produced by the chlorohydrination of allyl chloride. Raw materials for this process include propylene and chlorine. Refined epichlorohydrin results from further distillation to remove light and heavy impurities.

Most process operations are carried out in enclosed systems. Nonetheless, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts), and frequently, product transfer operations are potential sources for liquid leaks and subsequent worker exposure. Maintenance personnel contact liquid epichlorohydrin when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets (i.e., plant shutdowns).

D. USES(1)

Nearly one-third of the epichlorohydrin consumed in the United States is used in crude form as a raw material for synthetic glycerine. The remainder — some as crude epichlorohydrin, some as refined epichlorohydrin — is used to produce unmodified epoxy resins, epichlorohydrin elastomers and a number of other products such as glycidyl ethers, wet-strength resins for the paper industry, water.treatment resins and ion-exchange resins.

TABLE A-3

SELECTED PROPERTIES OF EPICHLOROHYDRIN

	Physical State @ 20°C, 760 mm Hg	Boiling Point @ 760 mm Hg	Vapor Pressure @ 20°C	Polarity	Solubility @ 20°C	
					Water	Organic Solvents
Physical Properties*	Liquid	115.2°C	13.0 mm Hg	Polar	6.4% (By Weight)	Selectively Soluble

	Chemical Reactivity (A Qualitative Assessment)	Stability (On Exposure to an Ambient Atmosphere)
Chemical Properties*	Reactive Chlorine	Stable

	Human	Experimental (Animal)
Carcinogenicity (including Species and Route of Administration where appropriate)	No Data Available	• Sarcomas in Mice by Subcutaneous Administration[3]

*Data are from several sources and were compiled by Arthur D. Little, Inc.

Glycerine, epoxy resins and epichlorohydrin elastomers are thought to be produced in closed systems. However, it is possible that the minor products are produced by processes based on batch operations.. This permits easy contact with liquid epichlorohydrin unless close attention is given to process containment and worker isolation through protective clothing. The specific number of facilities using epichlorohydrin as a raw material is not available; however, it is estimated to be less than 150.

E. TRANSPORTATION (6)

The methods used in transporting epichlorohydrin follow typical industry practices for flammable materials. Epichlorohydrin is available in tank cars, tank trucks, 55-gallon drums and 5-gallon, 1-gallon, and 1-quart containers. The Shell Oil Company indicates that barge and tanker shipments are available on request. The operations involved in loading and unloading liquid epichlorohydrin are similar for all modes of tank transportation. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and monitoring all fill levels. This routine handling of "wet" connections and associated equipment necessitates direct contact with liquid epichlorohydrin.

F. NUMBER OF AFFECTED WORKERS (5,7)

Because of variations in process design, job design, job descriptions, and worker habits, it is difficult to establish a value for the total number of workers potentially exposed to liquid epichlorohydrin. The data presented in Table A-4 below represent estimates of the workers in the United States assigned to on-site epichlorohydrin operations and thereby potentially exposed to epichlorohydrin vapor.

TABLE A-4

WORKERS POTENTIALLY EXPOSED TO EPICHLOROHYDRIN VAPOR

Process Category	Number of Workers
Sources	~250
Uses	~4500 (This figure may be high)
Transportation	~500

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS (5,8)

Protective clothing manufacturers recommend the following materials for protection against liquid epichlorohydrin:

- Nitrile Rubber (NBR or Buna-N)
- Neoprene
- Polyvinyl Alcohol (PVA)

NIOSH, in its criteria document, recommends that either nitrile rubber, neoprene or natural rubber be used for protection against liquid epichlorohydrin.

H. CURRENT PRACTICES IN WORKER PROTECTION[9]

The chemical industry appears to be taking precautions to insure worker protection from liquid epichlorohydrin through process containment in large-scale systems. However, in small-scale, batch systems where potential contact is unavoidable, industry only recommends that protective clothing be used and subsequently discarded if contaminated.

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4. "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man," 11:131-139, 1976.

5. "Criteria for a recommended standard. . . . .Occupational Exposure to Epichlorohydrin," U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, September 1976.

6. "Epichlorohydrin," Product Bulletin, Industrial Chemicals Division, Shell Oil Company, 1970.

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8. Information sources include:

   Edmont-Wilson, Product Catalogues and Personal Communication;
   Greene Rubber Company, Product Catalogue;
   Pioneer Industrial Products, Personal Communication;
   Granet Corporation, Personal Communication;
   Rainfair, Inc., Personal Communication;
   Los Alamos Scientific Laboratory, Personal Communication; and
   Illinois Institute of Technology, Personal Communication.

9. "Epichlorohydrin: Material Safety Data Sheet," Dow Chemical Company, January 1972.

COAL-TAR CREOSOTE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Coal-tar creosote is an oily mixture of higher phenols, naphthalene, anthracene, and various tar bases. It is heavier than water and has a boiling range of 180-350°C. Creosote oil is a distillate of coal tar, a by-product of the coking of bituminous coal. In the United States, creosote oil is used primarily as a wood preservative for railroad ties, telephone poles, and marine pilings. Minor amounts are used as an extender for fuel oil, as a disinfectant, as a softener for rubbers, and as a chemical intermediate. Because it contains compounds such as benzo(a)pyrene, creosote oil is classified as a suspected human carcinogen. Benzo(a)pyrene has been shown to induce tumors in a number of animal species by different routes of administration — including oral, skin, and intratracheal. There are four major producers of creosote oil in the United States and a larger, but undetermined, number of users. It has been estimated that approximately 5000 workers can potentially be exposed to creosote oil.

B. SELECTED PROPERTIES

Table A-5 contains data describing selected physical properties, chemical properties, and the carcinogenicity of coal-tar creosote. These data are intended to provide a general characterization of creosote oil and should prove helpful in interpreting exposure hazards to industrial workers. Creosote oil is typically produced, shipped, stored, and used in the liquid state.

C. SOURCES(1,2,10)

Allied Chemical, Koppers, U.S. Steel, and Witco Chemical are the primary producers of coal-tar creosote in the United States. In 1972, production was estimated to be just under 150 MM gallons. Creosote oil is a distillate of coal tar, a by-product of the coking of bituminous coal. Coal tar is distilled to creosote oil by either the coke producer or an independent distiller.

Most distilling operations are carried out in enclosed systems. Nonetheless, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts), and product transfer operations are potential sources for liquid leaks and subsequent worker exposures. Maintenance personnel can contact creosote oil when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets (i.e., plant shutdowns).

D. USES(3,4,5,6)

Most of the coal-tar creosote consumed in the United States is used as a wood preservative for railroad ties, telephone poles, and marine pilings. These wood members are saturated with creosote oil under high temperature and pressure. Both the wood and creosote are handled by automated equipment so that worker exposures are minimal.

TABLE A-5

SELECTED PROPERTIES OF COAL-TAR CREOSOTE

<table>
<tr><th rowspan="2"></th><th rowspan="2">Physical State @ 20°C, 760 mm Hg</th><th rowspan="2">Boiling Point @ 760 mm Hg</th><th rowspan="2">Vapor Pressure @ 20°C</th><th rowspan="2">Polarity</th><th colspan="2">Solubility @ 20°C</th></tr>
<tr><th>Water</th><th>Organic Solvents</th></tr>
<tr><td>Physical Properties*</td><td>Oily Liquid</td><td>180-350°C</td><td>~ 2mm Hg</td><td>–</td><td>Slight</td><td>Generally Soluble</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><td colspan="2">Chemical Reactivity (A Qualitative Assessment)</td><td colspan="3">Stability (On Exposure to an Ambient Atmosphere)</td><td rowspan="4"></td></tr>
<tr><td colspan="2">Very Low</td><td colspan="3">Stable</td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><td colspan="2">Human</td><td colspan="3">Experimental (Animal)</td></tr>
<tr><td colspan="2">No Specific Data Available</td><td colspan="3">● Tumor induction by benzo(a) pyrene in nine animal species following different administrations including oral, skin and intratrachael routes.[7]
● Tumor induction in mice by coal-tar creosote.[9]</td></tr>
</table>

*Data are from several sources and were compiled by Arthur D. Little, Inc.

Minor amounts of creosote oil are used as an extender for fuel oil, as a disinfectant, as a softener for rubbers, and as an intermediate for a number of other chemicals such as anthracene, phenanthrene, carbazole, and tar bases. Several of these minor uses are based on batch operations which permit potential contacts with creosote oil unless close attention is given to process containment and worker isolation through protective clothing. The specific number of facilities using creosote oil is not available; however, it is estimated to be less than 250.

E. TRANSPORTATION(4)

Coal-tar creosote is usually shipped in bulk by tank truck, tank car or barge. It is usually loaded warm (50-80°C) by methods which are common to all three modes of transportation. Workers are actively involved by manually making and breaking connections, opening and closing valves and taking samples. Such routine handling of "wet" connections and other equipment necessitates direct contact with creosote oil.

F. NUMBER OF AFFECTED WORKERS(8)

Because of the variations in process design, plant size, job descriptions, and worker habits, it is impossible to establish an accurate number of workers potentially contacting coal-tar creosote. It has been estimated that, at an average of 20 workers per facility, 5000 workers can potentially be exposed to this liquid.

A note concerning the non-industrial application of creosote oil must be made: this compound is available to the public for use on such wood products as fence posts; however, the number of exposures from this use is unknown.

G. RECOMMENDED CLOTHING MATERIALS(2,11)

Protective clothing manufacturers recommend the following materials for use against coal-tar creosote:

- Nitrile Rubber
- Neoprene
- PVC
- Urethane

In its Material Safety Data Sheet, Allied Chemical Company recommends a "non-porous" type protective clothing material. No specific material recommendations are given, however.

H. CURRENT PRACTICES IN WORKER PROTECTION(4)

Since coal-tar creosote is recognized as potentially carcinogenic, very specific procedures are followed by industry in handling creosote. Workers are normally instructed to use long sleeve shirts, cotton clothing, glasses or face shields, and impervious rubber gloves which should be changed frequently.

I. REFERENCES

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2. "Material Safety Data Sheet," Allied Chemical Company, October 1972.
3. "Creosote," a Product Bulletin by the Witco Chemical Corporation, 1970.
4. Personal Communication with Mr. Jim Reid, Technical Service Representative, Allied Chemical Company, Ironton, Ohio, December 22, 1976.
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11. Data Sources:

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    Green Rubber Company, Product Catalogue
    Pioneer Industrial Products, Personal Communication
    Granet Corporation, Personal Communication
    Rainfair, Inc., Personal Communication

BENZENE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Benzene is a colorless, aromatic liquid hydrocarbon which is lighter than water, flammable, and has a significant vapor pressure at ambient temperature. Most benzene is produced from petroleum derivatives, but a minor amount is generated as a by-product from the production of coke. The majority of benzene consumed in the United States is used to synthesize industrial chemicals such as cyclohexane, phenol, styrene, maleic anhydride, nitrobenzene, dichlorobenzene, and dodecylbenzene. The historic use of benzene as a solvent for formulations of surface coatings, inks, and adhesives has been largely discontinued, but solvents currently used in these formulations may contain significant levels (>1%) of benzene contamination. Minor quantities of benzene are still employed in laboratory operations but these are typically conducted under closely controlled conditions. Benzene is currently suspected of inducing aplastic anemia in humans upon long-term vapor inhalation, although the types of jobs described in case histories indicate a probability of cutaneous exposure. Even though more than 100,000 workers in the United States can potentially contact liquid benzene, industry programs for worker protection have typically been minimal.

B. SELECTED PROPERTIES

Table A-6 contains data describing selected physical properties, chemical properties, and the carcinogenicity of benzene. These data are intended to provide a general characterization of benzene and should prove helpful in interpreting exposure hazards to industrial and laboratory workers. Benzene is typically produced, shipped, stored, and used in the liquid state.

C. SOURCES(1,2)

Ninety-five percent of the benzene produced in the United States, approximately 1,400 MM gallons annually, is derived from petroleum. The remaining five percent, approximately 80 MM gallons annually, is produced as a distillate fraction from light oil by-products of coking operations. Details of each production source are provided in the following paragraphs.

1. Petroleum Derivatives

The primary processes used for benzene production are (1) catalytic reforming of low octane naphthas into a high octane reformate containing a high aromatic fraction, (2) hydrogenation of pyrolysis gasoline, a co-product of cracking naphthas and gas oil to ethylene and/or propylene, and (3) hydrodealkylation of toluene.

While there are over 320 petroleum refineries in the Untied States, only 48 produce petroleum-derived benzene. These plants are mostly located in larger refineries where petroleum by-products can be produced economically. Catalytic reforming is used in 32 plants, hydrogenation

TABLE A-6

SELECTED PROPERTIES OF BENZENE

	Physical State @ 20°C, 760 mm Hg	**Boiling Point @ 760 mm Hg**	**Vapor Pressure @ 20°C**	**Polarity**	**Solubility @ 20°C**	
					Water	**Organic Solvents**
Physical Properties*	Liquid	80.1°C	74.6 mm Hg	Non-polar	800 ppm	Generally Soluble
Chemical Properties*	**Chemical Reactivity (A Qualitative Assessment)**		**Stability (On Exposure to an Ambient Atmosphere)**			
	Very Low		Stable			
Carcinogenicity (including Species and Route of Administration where appropriate)	**Human**		**Experimental (Animal)**			
	Aplastic Anemia by Inhalation[3,4]		● Lymphoma in Mice by Inhalation[5] ● No Skin Tumors in Mice by Percutaneous Administration[6]			

*Data are from several sources and were compiled by Arthur D. Little, Inc.

of pyrolysis gasoline is used in seven plants and hydrodealkylation of toluene is used in the remaining plants. Each process requires several reaction vessels, separation and extraction towers, pumps and storage tanks. Such extensive facilities result in a relatively large production/maintenance work force that potentially could be exposed to liquid benzene.

Most process operations are carried out in completely enclosed systems. Nonetheless, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts), and frequently, product transfer operations are all potential sources for liquid leaks and subsequent employee exposure. Maintenance personnel contact liquid benzene when vessels are opened and entered periodically for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills or process upsets (i.e., plant shutdowns).

2. Coke By-Products

By-product gases from coke ovens are condensed to light oil (containing approximately 70% benzene, 25% toluene and 5% xylene by volume) which is then either distilled on-site or sold to refineries for further processing. No chemical reactions are involved in releasing benzene from coal since this compound is naturally present in coal. The carbonization process permits vapor-phase extraction of benzene and other light components.

Arthur D. Little, Inc., has estimated that there are about 65 by-product coke plants currently operating in the United States. About half of the light oil produced is processed on-site in 10 plants to extract benzene. The other half is sold to petroleum refineries for benzene extraction. Approximately 8 off-site plants are currently processing purchased light oil, and all except one of these are also producers of petroleum-derived benzene. Also, at some coke plants, the by-product light oil is used prior to processing as a solvent to extract phenol from plant wastewater.

Worker contact with liquid benzene is possible at all stages of the benzene recovery process (i.e., at both the by-product coke plants and the light oil recovery facilities). Sources and situations of exposure are similar to those noted for the petroleum-derived benzene.

D. USES(2)

Most benzene consumed in the United States is used to synthesize a number of industrial chemicals. The production of these chemicals is accomplished in closed systems with unconverted benzene recycled back to the raw feed. In most instances, the benzene is reacted in the presence of a catalyst at elevated temperatures and pressures to produce a high-purity product containing no significant amounts of benzene.

Benzene is also used as a solvent in laboratories and is found as a contaminant in solvents used in a variety of industrial processes. Many of these processes are based on batch operations and/or manual handling. Both permit easy contact with solution containing benzene unless close attention is given to process containment and worker isolation through protective clothing. An overview of each primary use is presented in the following paragraphs.

1. Industrial Chemicals

There are at least a dozen commercially important industrial chemicals, including those noted below, produced from benzene.

- *Cyclohexane*

  About sixteen percent of the benzene is used to produce cyclohexane which, in turn, is an important intermediate in the production of nylon fibers and resins. Worker contact with benzene is possible at the 10 U.S. plants where benzene is converted to cyclohexane. Most of these plants produce benzene on-site so that transportation and storage is minimized.

- *Cumene/Phenol*

  About twenty percent of the benzene consumed in the United States is used in the production of phenol via cumene as an intermediate. Currently, 15 plants use benzene as a raw material in this synthesis.

- *Ethylbenzene/Styrene*

  Another forty-five percent of the benzene is used to produce ethylbenzene which, in turn, is used to produce styrene. Integration of ethylbenzene and styrene facilities is the rule in the United States; integration of ethylbenzene/styrene and benzene facilities is, however, the exception. Worker exposure to benzene in the ethylbenzene portion of the product chain is associated with the use of benzene as a raw material. Exposure to benzene in styrene production is associated with the formation of small amounts of by-product benzene. There are currently 21 plants producing these two chemicals.

- *Maleic Anhydride*

  Less than four percent of the domestically consumed benzene is used to produce maleic anhydride, an important intermediate for polyester resins and other chemicals. Worker exposure to benzene is possible at the 9 plants in which benzene is used as a feedstock. None of these facilities produce their own benzene, so contact with benzene during transportation and storage operations is possible.

- *Nitrobenzene*

  Another four percent goes into the production of nitrobenzene, which is an intermediate in the production of aniline. All eight plants producing nitrobenzene use direct nitration of benzene; however, process trains do differ in the types of reactors used. Worker contact with benzene is possible in all of these facilities. Further, none of these plants produce benzene, so feedstocks must be imported.

- *Dichlorobenzene*

  Less than one percent of the benzene consumed in the United States is used to produce dichlorobenzene. Ten plants produce dichlorobenzene (including all isomers) using benzene as the starting material. Worker contact is possible at all of these plants.

- *Dodecylbenzene*

  About two percent of the benzene consumed goes into the production of dodecylbenzene. This compound is used principally in detergents. All five plants in the United States provide opportunity for worker contact. None of these facilities produces benzene.

Arthur D. Little has estimated that there are 95 plants producing all benzene-derived chemicals. Typically, benzene is reacted with one or more other chemicals as the first step in a process. Therefore, benzene is generally present only in the upstream portions of processing units.

As is the case with benzene production, worker contact with liquid benzene can occur at relief valves, sample ports, rotating equipment, and feed transfer operations. Cleaning and inspection of process units, as well as emergency spills or shut-downs, also provide opportunities for liquid contact.

2. Solvents

The acknowledged health hazards associated with benzene have encouraged most employers to use alternative solvents. However, many of the alternative solvents are contaminated to various degrees with benzene. The following list identifies several industries in which either benzene or other benzene-contaminated solvents are used:

- Manufacture of adhesives.
- Application of adhesives. . . Solvent-based adhesives are used in the manufacture of a multitude of products including rubber goods, furniture, packaging, floor coverings, shoes, book bindings, boats, and plastic goods.
- Manufacture of gravure printing inks.
- Printing and publishing.
- Manufacture of paint removers.
- Application of paint removers.
- Application of paints.
- Gasoline service stations and terminal facilities. . . Benzene is normally a constituent of automotive gasoline; its presence contributes to the overall octane rating of the product.
- Manufacture of rubber tires.
- Manufacture of miscellaneous rubber products.

- Use in laboratories. . . A variety of laboratories, including clinical laboratories, industrial testing facilities, schools and research laboratories use benzene as a solvent and reagent for numerous applications.

Cumulatively, the number of facilities using benzene or benzene-contaminated solvents numbers in the tens of thousands. Worker contact can range from one-time small spills to periodic or frequent handling of the liquid.

E. TRANSPORTATION(2)

The methods used in transporting benzene follow typical industry practices. Most benzene is transported by rail, truck or barge. Internal pipeline transfers for captive use within a petrochemical complex are the only exceptions. The operations involved in loading and unloading liquid benzene are similar for all three primary modes of transportation. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and monitoring fill levels. This routine handling of "wet" connections and other equipment necessitates direct contact with liquid benzene.

F. NUMBER OF AFFECTED WORKERS(2)

Because of numerous variations in process design, plant size and age, job descriptions, and worker habits, it is impossible to establish an average number of workers potentially contacting liquid benzene for each process or plant. The data presented in Table A-7 below represent estimates of the total number of workers in the United States assigned to on-site benzene operations and thereby potentially exposed to benzene vapor.

TABLE A-7

WORKERS POTENTIALLY EXPOSED TO BENZENE VAPOR

Process Category	Number of Workers
Sources	
• Petroleum derivatives	~2,000
• Coke by-products	~7,000
Uses	>100,000
Transportation	>5,000 (may be already included in source and use data above)

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS [8,9]

Protective clothing manufacturers recommend the following materials for protection against liquid benzene:

- Nitrile Rubber (NBR or Buna-N)
- Polyvinyl Alcohol (PVA)
- Polyethylene
- Polyurethane

Typical chemical industry recommendations for clothing materials only state that insoluble rubber or plastic (such as neoprene) be used for gloves and aprons.

H. CURRENT PRACTICES IN WORKER PROTECTION [9]

Industry has not taken specific precautions to insure worker isolation from liquid benzene. Statements such as "Avoid prolonged or repeated. . . contact with skin." and "Excessive or repeated exposure may cause serious illness." are common in industry literature. Implementation of this precaution is presumed to involve use of industry-recommended clothing materials.

I. REFERENCES

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   Pioneer Industrial Products, Personal Communication
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   Los Alamos Scientific Laboratory, Personal Communication
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4,4'-METHYLENE (BIS) 2-CHLOROANILINE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

4,4'-Methylene (bis) 2-chloroaniline (also known as MOCA, a tradename of E.I. duPont) is normally a solid at ambient temperatures. Nonetheless, limited quantities are available in liquid solution. MOCA has the general characteristics of a primary aromatic amine and is soluble in many organic solvents and lipids. E.I. duPont and the Anderson Development Company are the two major domestic producers. Their production processes are thought to be based on reacting formaldehyde with ortho-chloroaniline. Most MOCA consumed in the United States is used as a curing agent for liquid-castable urethanes and epoxies. It is considered to be a chemical of major commercial importance. MOCA is a moderately toxic substance with proven carcinogenicity in animals. It is also suspected to be a human carcinogen and, accordingly, its use is closely controlled by Federal regulation. The Occupational Safety and Health Administration (OSHA) has estimated that approximately 10,000 domestic workers can potentially be exposed to all forms of MOCA.

B. SELECTED PROPERTIES

Table A-8 contains data describing selected physical properties, chemical properties, and the carcinogenicity of 4,4'-methylene (bis) 2-chloroaniline. These data are intended to provide a general characterization of MOCA and should prove helpful in interpreting exposure hazards to industrial workers.

C. SOURCES(1,2,5,6,11)

In the United States, 4,4'-methylene (bis) 2-chloroaniline is produced by E.I. duPont and the Anderson Development Company. In addition, American Cyanamid has acted as a primary supplier of purchased MOCA for a number of years. Although confirming information is not available, production processes for this chemical are thought to be based on reacting formaldehyde with ortho-chloroaniline. The product is most often available as solid pellets; however, liquid solutions — employing proprietary solvents — are also available. OSHA has estimated that 7.2 MM pounds of MOCA were produced in the United States in 1972. Of this, 2.0 MM pounds were in liquid solution. DuPont has recently estimated a somewhat lower 4.0 MM pounds for worldwide production in 1976. Worker contacts with liquid, MOCA are possible in blending operations which convert solid product to solution. Such operations are most probably carried out in enclosed equipment on a batch basis. Sampling ports, rotating equipment (e.g., seals on pump shafts), and product transfer procedures are all potential sources for liquid leaks and subsequent worker exposure.

Maintenance personnel contact MOCA solutions when vessels are periodically cleaned and inspected. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets.

TABLE A-8

SELECTED PROPERTIES OF 4,4'-METHYLENE (BIS)2-CHLOROANILINE

	Physical State @ 20°C, 760 mm Hg	**Melting Point @ 760 mm Hg**	**Vapor Pressure @ 20°C**	**Polarity**	**Solubility @ 20°C**	
					Water	**Organic Solvents**
Physical Properties*	Solid	110°C	Slight	Polar	Almost Insoluble	Generally Soluble
Chemical Properties*	**Chemical Reactivity (A Qualitative Assessment)**		**Stability (On Exposure to an Ambient Atmosphere)**			
	Low Reactivity: Acts Like a Primary Aromatic Amine		Stable			
Carcinogenicity (including Species and Route of Administration where appropriate)	**Human**		**Experimental (Animal)**			
	Absorbed Through Skin; No Conclusive Carcinogenicity Studies		• Carcinogenic in Mice and Rats on Oral Administration and in Rats on Subcutaneous Administration^{3,4}			

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*Data are from several sources and were compiled by Arthur D. Little, Inc.

D. USES [1,2,6,7]

Nearly all MOCA consumed in the United States is used as a curing agent for liquid-castable urethane rubber and epoxies. Most parts cast from such materials are solids; however, some are cross-linked urethane foams which are used in automotive seating and dashboard safety pads. MOCA, in liquid solution, is required for the preparation of these foams at ambient temperatures. Such uses for MOCA are based on batch casting operations which permit potential contacts with liquid unless close attention is given to process containment and worker isolation through protective clothing. The specific number of facilities using all forms of MOCA is well over 1000. The number of facilities using MOCA in liquid solution is probably less than 200.

E. TRANSPORTATION [6]

In the United States, MOCA in liquid solution is available in well-sealed, small-to-medium volume containers, and drums. Transportation by tank car or tank truck usually does not occur. Since MOCA is a suspected human carcinogen, all shipping containers are well marked and handled with care. The operations involved in filling and withdrawing liquid from these containers are usually carried out in well ventilated areas with attention given to worker isolation through protective clothing.

F. NUMBER OF AFFECTED WORKERS [1,6]

OSHA has estimated that approximately 10,000 workers can potentially be exposed to all forms of MOCA. Only 2000 of these workers are involved with MOCA in liquid solutions.

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS [9,10,11]

Protective clothing manufacturers recommend the following materials for protection against amines such as MOCA:

- Nitrile Rubber (NBR)
- Neoprene
- Polyvinyl Chloride (PVC)
- Polyvinyl Alcohol (PVA)

In one of its older product bulletins, duPont simply states that ". . . gloves and goggles be worn by persons transporting more than small laboratory quantities. . ." Recently, neoprene and butyl rubber have been recommended. Further, duPont references the Code of Federal Regulations for proper practices in worker protection.

H. CURRENT PRACTICES IN WORKER PROTECTION [1,8]

Since the handling of MOCA in all forms is closely controlled, industry is taking more precautions to insure worker protection. The use of nonpermeable gloves, suits and boots is usually recommended. Further, the Code of Federal Regulations states that "employees. . . shall be provided with and be required to wear personal protective equipment adequate to prevent exposure to a carcinogen." However, no materials are suggested as offering proper protection.

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2. "IARC Monographs on Evaluation of the Carcinogenic Risk of Chemicals to Man," 4:65-71, 1973.

3. Russfield, A.B., et al., "The Carcinogenic Effect of 4,4'-Methylene (bis) 2-Chloroaniline in Mice and Rats," Toxicol. Appl. Pharmacol., 1973.

4. Steinhoff, D., and E. Grundmann, "Zur Cancerogen Wirkung von 3,3'-Dichloro-4,4'-Diaminodiphenylmethan bei Rathen," Naturwissenschaften, 58, 1971.

5. Personal Communication with Mr. Joseph Koszka, Vice President, Anderson Development Company, August 5, 1977.

6. Arthur D. Little, Inc., estimates.

7. Hawley, G.G., "The Condensed Chemical Dictionary," Van Nostrand Reinhold Company, 8th Edition, 1971.

8. Code of Federal Regulations, Title 29, Parts 1910.1003-1910.1016.

9. Data Sources:

   Edmont-Wilson, Product Catalogues
   Green Rubber Company, Product Catalogue
   Pioneer Industrial Products, Personal Communication
   Rainfair, Inc., Personal Communication

10. "MOCA," a product bulletin by duPont, November 1964.

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ETHYLENIMINE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Ethylenimine (EI) is a colorless, ammonical, liquid hydrocarbon which is lighter than water, highly flammable and very volatile at ambient temperature. Further, this chemical is very reactive and can polymerize with explosive violence under acidic or oxidizing conditions. EI and its derivatives are used in coatings for paper and textiles, in adhesives, fuels and lubricants, agricultural chemicals, and pharmaceuticals. EI is highly toxic and is considered to be a human carcinogen. Its production, transportation, and use are closely regulated. It has been estimated that fewer than 100 workers can potentially be exposed to the chemical.

B. SELECTED PROPERTIES

Table A-9 contains data describing selected physical properties, chemical properties, and the carcinogenicity of ethylenimine. These data are intended to provide a general characterization of EI and should prove helpful in interpreting exposure hazards to industrial workers. EI is produced, shipped, stored, and used in the liquid state.

C. SOURCES(3,4,9)

In the United States, ethylenimine is produced only by the Dow Chemical Company. Total production is thought to approximate 10 MM pounds per year. Dow's EI process consists of reacting ethylene dichloride and ammonia at elevated temperatures in an acidic environment. This process is completely closed and frequent liquid contacts are not a problem. However, as with most other processes, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts), and product transfer operations are possible sources for leaks. Maintenance personnel can contact liquid ethylenimine when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets (i.e., plant shutdowns).

D. USES(2,3,4,6)

Eighty percent of the ethylenimine produced by Dow is converted captively to polyethylenimine. This derivative is used in the paper and textile industries for improved product characteristics, in adhesives and binders, and as a starting material for surfactants. The remaining EI and its derivatives are used in fuels, coatings, herbicides, pharmaceuticals, ion exchange resins, and photographic chemicals.

According to OSHA, only Dow, Stauffer, PPG, and Ionac handle significant quantities of ethylenimine. Opportunities for exposure are minimal since all process systems are closed and ethylenimine is used only in controlled areas with special handling precautions taken.

TABLE A-9

SELECTED PROPERTIES OF ETHYLENIMINE

	Physical State @ 20°C, 760 mm Hg	**Boiling Point @ 760 mm Hg**	**Vapor Pressure @ 20°C**	**Polarity**	**Solubility @ 20°C**	
					Water	**Organic Solvents**
Physical Properties*	Liquid	57°C	150 mm Hg	Polar	Miscible	Generally Soluble
	Chemical Reactivity (A Qualitative Assessment)		**Stability (On Exposure to an Ambient Atmosphere)**			
Chemical Properties*	Highly Reactive		Polymerizes Readily			
	Human		**Experimental (Animal)**			
Carcinogenicity (including Species and Route of Administration where appropriate)	Highly Toxic, Readily Absorbed on Skin Contact		• Hepatomas and Pulmonary Tumors in Mice on Daily Feeding[7] • Tumors in Rats at Site of Cutaneous Injection[8]			

*Data are from several sources and were compiled by Arthur D. Little, Inc.

E. TRANSPORTATION[2]

In the United States, ethylenimine is available from Dow in cylinders of approximately 5-gallon, 25-gallon, and 50-gallon sizes and in specially equipped tank cars. All of these containers are fitted with special liquid unloading valves, gas pressurizing valves (usually used to provide an inert nitrogen atmosphere during unloading), and perforated tubes filled with NaOH pellets. The NaOH pellets stabilize ethylenimine against the possible presence of small amounts of acidic contaminants. Unstabilized EI cannot be shipped legally.

The operations involved in loading and, especially, unloading are quite detailed. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and monitoring all fill levels. This routine handling of "wet" connections and associated equipment necessitates direct contact with the liquid. Dow insists that only properly trained workers wearing maximum protective clothing and equipment should be involved.

F. NUMBER OF AFFECTED WORKERS[4]

OSHA has estimated that fewer than 100 workers in the United States can potentially be exposed to liquid ethylenimine. This estimate is broken down into source, use and transportation components in Table A-10.

TABLE A-10

WORKERS POTENTIALLY EXPOSED TO ETHYLENIMINE LIQUID

Process Category	Number of Workers
Source	30
Uses	50
Transportation	20

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS[2,4,10]

Protective clothing manufacturers have not made formal recommendations for materials which are resistant to ethylenimine. However, it is generally acknowledged that neoprene has proven most effective over short contact times (i.e., less than 30 minutes).

However, Dow is very specific in recommending Stanzoil R.S.W.-13 neoprene rubber gloves. More general neoprene or rubber (natural) are recommended for other protective clothing components.

H. CURRENT PRACTICES IN WORKER PROTECTION [5]

Industry has taken special precautions to insure worker isolation from liquid ethylenimine. Workers are required to be thoroughly trained in the hazards of EI and outfitted with a full protective ensemble before entering a possible EI exposure area. A full protective ensemble includes respiratory protection, protective outerwear, gloves and boots. Implementation of these requirements is straightforward since the number of workers that can be exposed is relatively small.

I. REFERENCES

1. "Ethylenimine: Material Safety Data Sheet," Dow Chemical Company, March 1972.

2. "Technical Aspects — Ethylenimine," Dow Chemical Company, 1976.

3. Hawley, G.G., "The Condensed Chemical Dictionary," Van Nostrand Reinhold Company, 8th Edition, 1971.

4. Bell, D.R., "Final Environmental Impact Statement: Proposed Regulation (on the) Handling of Certain Carcinogens," Occupational Safety and Health Administration, U.S. Department of Labor, September 1973.

5. Code of Federal Regulations, Title 29, Parts 1910.1003-1910.1016.

6. "Chemical Origins and Markets," Stanford Research Institute, Menlo Park, California, 4th Edition, 1967.

7. Innes, J.R.M., et al., "Bioassay of Pesticides and Industrial Chemicals for Tumorigenicity in Mice: A Preliminary Note," *J. Nat. Cancer Inst.*, **42**:1101-1114, 1969.

8. Walpole, A., "Cytotoxic Agents: The Carcinogenic Actions of Some Monofunctional Ethylenimine Derivatives," *Brit. J. Pharmacol.*, **9**:306-323, 1954.

9. Personal Correspondence with James W. Condor, Health and Environmental Research, Dow Chemical Company, Midland, Michigan, February 8, 1977.

10. Information sources include:

    Edmont-Wilson, Product Catalogues
    Granet Corporation, Products Catalogue
    Pioneer Industrial Products, Products Catalogue

1,1'-DIMETHYLHYDRAZINE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Unsymmetrical dimethylhydrazine (1,1'-dimethylhydrazine or UDMH) is a clear, colorless organic amine which is lighter than water, fumes in air and is highly flammable. Commercial quantities of UDMH are produced from dimethylamine either directly by reaction with chloramine or indirectly by nitrosation followed by reduction of the intermediate, N-nitrosodimethylamine. UDMH is primarily used as a rocket propellant. Minor quantities are used as a chemical reducing agent, as a fuel stabilizer, as a dyestuff intermediate, as an additive in the manufacture of SBR rubber, for oil well casing corrosion control, in the preparation of catalyst systems and as an anti-skinning agent in paints. UDMH is a suspected human carcinogen. This compound is readily absorbed through the skin and may induce tumors. It is estimated that less than 250 workers in the United States can potentially contact liquid UDMH.

B. SELECTED PROPERTIES

Table A-11 contains data describing selected physical properties, chemical properties, and the carcinogenicity of 1,1'-dimethylhydrazine. These data are intended to provide a general characterization of UDMH and should prove helpful in interpreting exposure hazards to industrial workers. UDMH is typically produced, shipped, stored, and used in the liquid state.

C. SOURCES(1,2,5,6,7)

In the United States, commercial quantities of 1,1'-dimethylhydrazine are produced by the Olin Corporation (Agricultural Products Division) and Teledyne McCormick Selph. FMC had been the sole producer of UDMH, but curtailed production due to OSHA's pronouncement that the intermediate, N-nitrosodimethylamine, is carcinogenic. Production quantities appear to be substantially less than 10 MM lbs (1.5 MM gallons) annually.

Most process operations are carried out in closed systems; nonetheless, relief values, sampling ports, rotating equipment (e.g., seals on pump shafts), and product transfer operations are all potential sources for liquid leaks and subsequent worker exposure. Maintenance personnel can contact liquid UDMH when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills or process upsets (i.e., plant shutdowns).

D. USES(2,3)

Most 1,1'-dimethylhydrazine in the United States is used as a major component of rocket propellants. For example, it was a major component of fuel for the Titan group of boosters used in Gemini flights, some of the Apollo flights and a number of satellite launchings. In these situa-

TABLE A-11

SELECTED PROPERTIES OF 1,1-DIMETHYLHYDRAZINE (UDMH)

<table>
<tr><td rowspan="3">Physical Properties*</td><th rowspan="2">Physical State @ 20°C, 760 mm Hg</th><th rowspan="2">Boiling Point @ 760 mm Hg</th><th rowspan="2">Vapor Pressure @ 25°C</th><th rowspan="2">Polarity</th><th colspan="2">Solubility @ 20°C</th></tr>
<tr><th>Water</th><th>Organic Solvents</th></tr>
<tr><td>Fuming Liquid</td><td>63°C</td><td>157 mm Hg</td><td>Polar</td><td>Miscible</td><td>Generally Soluble</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><th colspan="2">Chemical Reactivity (A Qualitative Assessment)</th><th colspan="2">Stability (On Exposure to an Ambient Atmosphere)</th></tr>
<tr><td colspan="2">Highly Reactive</td><td colspan="2">Slight Degradation Over Long-Term Storage</td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><th colspan="2">Human</th><th colspan="2">Experimental (Animal)</th></tr>
<tr><td colspan="2">No Data Available</td><td colspan="2">● Angiosarcomas (Lung) in Mice by Oral Administration[4]</td></tr>
</table>

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*Data are from several sources and were compiled by Arthur D. Little, Inc.

**Experimental data apply to the 1,2-Dimethyl isomer rather than the 1,1-Dimethyl isomer. The occurrence of colon tumors following subcutaneous administration shows that this compound can be transported through the body to induce tumors at remote sites.

tions, government (i.e., NASA, Air Force) employees or contractors are likely to contact liquid UDMH during fuel blending and loading operations.

Minor quantities of UDMH appear to be used as a chemical reducing agent, as a fuel stabilizer, as a dyestuff intermediate, as an additive in the manufacture of SBR rubber, for oil well casing corrosion control, in the preparation of some catalyst systems, and as an anti-skinning agent in paints. It is thought that only a small number of workers can potentially contact liquid UDMH in these applications. Where contacts can occur, they are due to direct handling of small quantities of the liquid. Here, worker isolation through the use of protective clothing is most important.

E. TRANSPORTATION(1)

The methods used in transporting 1,1'-dimethylhydrazine follow typical industry practices for flammable materials. Drums and tank cars are preferred, although tank trucks are used on occasion. Small quantities of UDMH are shipped in glass bottles.

Prior to loading, all shipping containers are visually inspected and then flushed with nitrogen. Such an inert gas is used to eliminate air and thereby reduce the potential for explosive gas mixtures. This precaution is not necessary with small containers.

Direct contact with liquid UDMH can occur with the routine handling of "wet" connectors involved in loading and unloading procedures. These operations require that workers make and break connections, open and close valves, and monitor fill levels.

F. NUMBER OF AFFECTED WORKERS(1)

The data presented in Table A-12 represent estimates of the total number of workers in the United States assigned to on-site UDMH operations and thereby potentially exposed to liquid UDMH.

TABLE A-12

WORKERS POTENTIALLY EXPOSED TO UDMH LIQUID

Process Category	Number of Workers
Sources	~ 75
Uses	~125
Transportation	~ 50

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS(1,10)

The chemical industry recommends the following materials for protection against liquid UDMH:

- Natural Rubber
- Neoprene
- Butyl Rubber
- Polyvinyl Chloride

H. CURRENT PRACTICES IN WORKER PROTECTION[9]

The chemical industry appears to be taking precautions to insure worker protection from liquid UDMH through process containment. However, proper protective clothing has not been clearly identified for use in those situations where potential contact is unavoidable. Only general recommendations are made for the use of impermeable or splash-proof clothing made of materials identified above.

I. REFERENCES

1. "Dimazine — Properties, Applications, Reactions," Product Bulletin, Organic Chemicals Division, FMC Corporation, New York, New York.

2. "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man," **4**:137-143, 1973.

3. "Chemical Origins and Markets," Stanford Research Institute, Menlo Park, California, 4th Edition, 1967.

4. Toth, B., "1,1'-Dimethylhydrazine (unsymmetrical) Carcinogenesis in Mice. Light Microscopic and Ultrastructural Studies on Neoplastic Blood Vessels," *J. Nat. Cancer Inst.*, **50**:181-194, 1973.

5. "1977 Directory of Chemical Producers," Chemical Information Services, Stanford Research Institute, Menlo Park, California.

6. "A Rocket Fuel Shortage Hits the Pentagon," *Business Week*, November 23, 1974.

7. Arthur D. Little, Inc., estimate.

8. "1,1'-Dimethylhydrazine: Material Safety Data Sheet," FMC Corporation, June 1971.

2-NITROPROPANE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

2-Nitropropane is a colorless, liquid nitroparaffin with a density slightly less than that of water, is flammable, and has a significant vapor pressure at ambient temperature. In the United States, 2-nitropropane is produced by the vapor-phase nitration of propane by nitric acid. The primary use for this chemical is as a solvent for surface coatings, adhesives, and printing inks. Minor amounts are used as a solvent for extraction and in the synthesis of other nitro compounds. 2-Nitropropane is a suspected human carcinogen. As an inhaled vapor, it has been shown to induce hepatocellular carcinomas and hepatic adenomas in laboratory rats. It is estimated that approximately 100,000 workers in the United States can potentially be exposed to 2-nitropropane.

B. SELECTED PROPERTIES

Table A-13 contains data describing selected physical properties, chemical properties, and the carcinogenicity of 2-nitropropane. These data are intended to provide a general characterization of 2-nitropropane and should prove helpful in interpreting exposure hazards to industrial workers. 2-Nitropropane is produced in the vapor phase, but is shipped, stored, and used as a liquid.

C. SOURCES(1,2,3,4)

In the United States, 2-nitropropane is produced by IMC Chemicals. Total annual production is thought to be 30 MM pounds. NIOSH has estimated that 12 MM pounds are sold in the domestic market and the remainder is either used captively by IMC or exported.

IMC's production process consists of reacting nitric acid with excess propane at temperatures in the range of 370-450°C and under a pressure of from 8 to 12 atmospheres. The reaction product is a mixture of crude nitroparaffins which are then fractionated to give commercial-grade nitroparaffins, of which 2-nitropropane approaches 50% of the yield. It is understood that this process is carried out in an enclosed system. Relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts) and product transfer operations are possible sources for leaks. Maintenance personnel can contact liquid 2-nitropropane when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets (i.e., plant shutdowns).

D. USES(1,3)

According to NIOSH, "Solvent systems containing 2-nitropropane are used in coatings (e.g., vinyl, epoxy, nitrocellulose, and chlorinated rubber), printing inks, and adhesives. This

TABLE A-13

SELECTED PROPERTIES OF 2-NITROPROPANE

<table>
<tr><td rowspan="3">Physical Properties*</td><td rowspan="2">Physical State @ 20°C, 760 mm Hg</td><td rowspan="2">Boiling Point @ 760 mm Hg</td><td rowspan="2">Vapor Pressure @ 20°C</td><td rowspan="2">Polarity</td><td colspan="2">Solubility @ 20°C</td></tr>
<tr><td>Water</td><td>Organic Solvents</td></tr>
<tr><td>Liquid</td><td>120.2°C</td><td>13.0 mm Hg</td><td>Polar</td><td>1.7% (By Weight)</td><td>Generally Soluble</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><td colspan="2">Chemical Reactivity (A Qualitative Assessment)</td><td colspan="2">Stability (On Exposure to an Ambient Atmosphere)</td></tr>
<tr><td colspan="2">Moderate to Low</td><td colspan="2">Stable</td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><td colspan="2">Human</td><td colspan="2">Experimental (Animal)</td></tr>
<tr><td colspan="2">No Data Available</td><td colspan="2">● Hepatocellular Carcinomas and Hepatic Adenomas in Rats By Inhalation[3]</td></tr>
</table>

*Data are from several sources and were compiled by Arthur D. Little, Inc.

compound contributes to improved drying time, more complete solvent release, better flow and film integrity, retardation of blushing, greater wetting ability, improved electrostatic spraying, and improved pigment dispersion. Exposure to these products can occur in various industries such as industrial construction and maintenance, printing, highway maintenance, shipbuilding, furniture manufacture, food packaging, and plastic products manufacture."

Many of these solvent-containing products are manufactured and used in processes based on batch operations and/or manual handling. Both permit easy contact with the liquid unless close attention is given to process containment and worker isolation through protective clothing. The number of operations involving 2-nitropropane is not available.

Minor amounts of 2-nitropropane are used in the synthesis of other nitro compounds such as amines and chloronitroparaffins.

E. TRANSPORTATION

2-Nitropropane is available in tank cars, tank trucks, 55-gallon drums, and 5-gallon, 1-gallon, and 1-quart containers. The methods used in transporting 2-nitropropane follow typical industry practices for organic solvents. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and monitoring all fill levels. This routine handling of "wet" connections and associated equipment necessitates direct contact with the liquid.

F. NUMBER OF AFFECTED WORKERS(3)

NIOSH has estimated that 100,000 workers in the United States are potentially exposed to 2-nitropropane in the vapor phase. This estimate is broken down into source, use, and transportation components in Table A-14. Although these data represent workers potentially exposed to vapor, they may also be used to represent a maximum number for workers potentially contacting liquid 2-nitropropane.

TABLE A-14

WORKERS POTENTIALLY EXPOSED TO 2-NITROPROPANE VAPOR

Process Category	Number of Workers
Sources	50
Uses	95,950
Transportation	4,000

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS[7]

Only one protective clothing manufacturer recommends a material — polyvinyl alcohol (PVA) — for protection against 2-nitropropane.

The chemical industry has not made specific recommendations for proper protective clothing.

H. CURRENT PRACTICES IN WORKER PROTECTION[3,5]

Industry has not taken specific precautions to insure worker isolation from liquid 2-nitropropane. Only "proper" or "appropriate" protective clothing is recommended.

In its recent Intelligence Bulletin, NIOSH suggests that "Protective full-body clothing should be provided and its use required. . ." The agency does not, however, recommend specific clothing materials.

I. REFERENCES

1. Martin, J.L., and P.J. Baker, "Nitroparaffins," Commercial Solvents Corporation (a reprint from the *Encyclopedia of Chemical Technology,* 13, 1967, by John Wiley & Sons, Inc.).

2. Shreve, R.N., "The Chemical Process Industries," 2nd Edition, McGraw-Hill Book Company, Inc., New York, 1956.

3. "Current Intelligence Bulletin: 2-Nitropropane," National Institute for Occupational Safety and Health, Rockville, Maryland, April 25, 1977.

4. "Chemical Economics Handbook," Stanford Research Institute, Menlo Park, California, January 1977.

5. Arthur D. Little, Inc., estimate.

6. "Storage and Handling of 2-Nitropropane," Technical Data Sheet, Commercial Solvents Corporation.

7. Product Catalogue, Edmont-Wilson Corporation.

β-PROPIOLACTONE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

β-Propiolactone (BPL) is a colorless liquid ester which is heavier than water, flammable, and moderately volatile at ambient temperature. This chemical is highly reactive and is susceptible to self-polymerization at elevated temperatures and under catalytic conditions. BPL is extremely corrosive to skin and is considered to be a carcinogen. BPL is no longer produced in commercial quantities in the United States. Prior to its listing as a suspected carcinogen, BPL was produced by only one company. It has been used as a chemical intermediate for acrylates, as a sterilizing agent, and as a disinfectant. These uses mostly have been discontinued with only small quantities used for sterilization and research. Currently-used quantities apparently are imported. It has been estimated that fewer than 20 workers can potentially be exposed to the chemical.

B. SELECTED PROPERTIES

Table A-15 contains data describing selected physical properties, chemical properties, and the carcinogenicity of β-propiolactone. These data are intended to provide a general characterization of BPL and should prove helpful in interpreting exposure hazards to industrial workers. BPL is shipped and used in the liquid state.

C. SOURCES(2,4,5)

β-Propiolactone is no longer produced in commercial quantities in the United States. However, prior to its listing as a human carcinogen, BPL was produced by the Celanese Chemical Company. Celanese reported producing 50 MM pounds in 1972 through a process based on reacting ketene with formaldehyde.

Currently, small quantities of BPL are available at relatively high cost from The Sigma Chemical Company and from Tridom/Fluka, the U.S. distributor of the Swiss-based Fluka Chemical Company.

D. USES(2,4)

β-Propiolactone was used as a chemical intermediate for acrylates, as a sterilizing agent for blood plasma, vaccines, tissue grafts, surgical instruments and enzymes, and as a vapor-phase disinfectant in enclosed spaces. Most all of these uses have been discontinued with only small quantities currently used for sterilization and research. It is presumed that all such small quantities are purchased through Sigma or Tridom.

TABLE A-15

SELECTED PROPERTIES OF β-PROPIOLACTONE

<table>
<tr><th rowspan="3">Physical Properties*</th><th rowspan="2">Physical State @ 20°C, 760 mm Hg</th><th rowspan="2">Boiling Point @ 760 mm Hg</th><th rowspan="2">Vapor Pressure @ 20°C</th><th rowspan="2">Polarity</th><th colspan="2">Solubility @ 20°C</th></tr>
<tr><th>Water</th><th>Organic Solvents</th></tr>
<tr><td>Liquid</td><td>162°C
(Polymerizes)</td><td>3.2 mm Hg</td><td>Polar</td><td>35% v/v</td><td>Generally Soluble</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><th colspan="2">Chemical Reactivity (A Qualitative Assessment)</th><th colspan="4">Stability (On Exposure to an Ambient Atmosphere)</th></tr>
<tr><td colspan="2">Highly Reactive</td><td colspan="4">Moderately Stable</td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><th colspan="2">Human</th><th colspan="4">Experimental (Animal)</th></tr>
<tr><td colspan="2">Highly Corrosive on Skin Contact</td><td colspan="4">● Carcinogenic in mice by skin application, subcutaneous or interperitoneal injection, and in rats by subcutaneous injection. Carcinogenic to mice after single-dose exposures.[2]</td></tr>
</table>

*Data are from several sources and were compiled by Arthur D. Little, Inc.

The few current uses of β-propiolactone are based on batch operations which permit potential contacts with liquid BPL unless close attention is given to process containment and worker isolation through protective clothing. The specific number of facilities using BPL is not available; however, it is estimated to be less than 10.[5]

E. TRANSPORTATION

Since β-propiolactone is no longer produced in commercial quantities in the United States, bulk transportation of the chemical does not occur. The 1000-ml, 250-ml, and 100-ml quantities that are available are shipped in well-sealed containers. Potential worker exposure is normally not a problem under these conditions.

F. NUMBER OF AFFECTED WORKERS(5)

Because of the small quantities of this chemical that are used in the United States, it is difficult to establish an accurate value for the number of people potentially exposed to liquid BPL. Most all of these uses take place in laboratory environments. It has been estimated that fewer than a total of 20 workers can be potentially exposed in these situations.

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS(1,6)

Protective clothing manufacturers recommend the following materials for protection against liquid β-propiolactone:

- Urethane
- Polyethylene
- Natural Rubber (latex)

Celanese, in its product bulletin, simply states that "nonpermeable gloves. . . as well as adequate protective clothing and protective footwear should be worn when working with BPL. . ." No material recommendations are given.

H. CURRENT PRACTICES IN WORKER PROTECTION(3)

Since the handling of β-propiolactone is closely regulated, industry takes extensive precautions to insure worker protection. Nonpermeable gloves, suits, and boots are recommended. Further, the Code of Federal Regulations states the "employees. . . shall be provided with and be required to wear personal protective equipment adequate to prevent exposure to a carcinogen." Again, no materials are recommended as offering adequate protection.

I. REFERENCES

1. "beta-Propiolactone," A product bulletin by the Celanese Chemical Corporation, 1972.

2. "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man," 4:259-269, 1973.

3. Code of Federal Regulations, Title 29, Parts 1910.1003-1910.1016.

4. Bell, D.R., "Final Environmental Impact Statement: Proposed Regulation (on the) Handling of Certain Carcinogens," Occupational Safety and Health Administration, U.S. Department of Labor, September 1973.

5. Arthur D. Little, Inc., estimate.

6. Data Sources:

   Edmont-Wilson, Product Catalogues
   Green Rubber Company, Product Catalogue
   Pioneer Industrial Products, Personal Communication
   Granet Corporation, Personal Communication
   Rainfair, Inc., Personal Communication

HEXAMETHYLPHOSPHORAMIDE: AN OVERVIEW OF CURRENT OCCUPATIONAL EXPOSURES AND HAZARDS

A. SUMMARY

Hexamethylphosphoramide (HMPA) is a water-white, organic liquid with low vapor pressure at ambient temperature. HMPA's principal industrial application has been as a solvent in the manufacture of duPont's Kevlar aramid fiber. However, small quantities have been used as a solvent in organic and organo-metallic reactions, as an ultraviolet inhibitor in polyvinyl chloride, and as a chemosterilant for insects. Most of these uses are either now or soon will be discontinued. HMPA is a suspected human carcinogen and has been shown to induce cancer in laboratory rats. It has been estimated that no more than 5,000 workers in the United States can potentially contact liquid hexamethylphosphoramide.

B. SELECTED PROPERTIES

Table A-16 contains data describing selected physical properties, chemical properties and the carcinogenicity of hexamethylphosphoramide. These data provide a general characterization of HMPA and should prove helpful in interpreting exposure hazards to industrial workers. HMPA is typically produced, shipped, and used in the liquid state.

C. SOURCES(1,2)

In the United States, hexamethylphosphoramide is produced by E.I. duPont de Nemours and Company, Chemical Samples Company and Fike Chemical Company. Production data are not available. It is presumed that all HMPA production processes are completely enclosed, so that frequent liquid contacts are not a problem. However, as with most other processes, relief valves, sampling ports, rotating equipment (e.g., seals on pump shafts) and product transfer operations are possible sources for leaks. Maintenance personnel can contact liquid HMPA when vessels are periodically opened and entered for cleaning and inspection. Furthermore, direct liquid contacts are probable in responding to emergency situations such as spills and process upsets (i.e., plant shutdowns).

D. USES(1,2,4)

All of the hexamethylphosphoramide produced by duPont is used captively in the manufacture of Kevlar fiber. Small quantities have been used as a solvent in laboratory-scale organic and organo-metallic reactions, as an ultraviolet inhibitor in polyvinyl chloride and polyolefins, and as a chemosterilant for insects. Most of these uses are either now or soon will be discontinued as substitute solvents are identified. Most opportunities for exposure to liquid HMPA occur in laboratory-scale operations.

TABLE A-16

SELECTED PROPERTIES OF HEXAMETHYLPHOSPHORAMIDE

<table>
<tr><td rowspan="3">Physical Properties*</td><td rowspan="2">Physical State @ 20°C, 760 mm Hg</td><td rowspan="2">Boiling Point @ 760 mm Hg</td><td rowspan="2">Vapor Pressure @ 20°C</td><td rowspan="2">Polarity</td><td colspan="2">Solubility @ 20°C</td></tr>
<tr><td>Water</td><td>Organic Solvents</td></tr>
<tr><td>Liquid</td><td>233°C</td><td>0.03 mm Hg</td><td>Polar</td><td>Miscible</td><td>Soluble in many polar and non-polar solvents</td></tr>
<tr><td rowspan="2">Chemical Properties*</td><td colspan="2">Chemical Reactivity (A Qualitative Assessment)</td><td colspan="3">Stability (On Exposure to an Ambient Atmosphere)</td><td></td></tr>
<tr><td colspan="2">Low</td><td colspan="3">Stable</td><td></td></tr>
<tr><td rowspan="2">Carcinogenicity (including Species and Route of Administration where appropriate)</td><td colspan="2">Human</td><td colspan="3">Experimental (Animal)</td><td></td></tr>
<tr><td colspan="2">No Data Available</td><td colspan="3">● Nasal Passage Tumors (Squamous Cell Carcinoma) in Rats on Inhalation[3]</td><td></td></tr>
</table>

*Data are from several sources and were compiled by Arthur D. Little, Inc.

E. TRANSPORTATION

In the United States, hexamethylphosphoramide is available in well-sealed, small-volume containers. DuPont performs intra-company transfers by tank car or tank truck.

The operations involved in loading and unloading tank cars or trucks follow normal industry practices. A typical sequence requires that workers be actively involved by manually making and breaking connections, opening and closing valves, and monitoring fill levels. This routine handling of "wet" connections and other equipment often necessitates direct contact with liquid HMPA.

F. NUMBER OF AFFECTED WORKERS[4]

Because of the decreasing amount of hexamethylphosphoramide used in the United States, it is difficult to establish an accurate value for the number of workers potentially exposed. In 1975, NIOSH estimated that 5,000 workers could be exposed to HMPA, with most of these working in laboratory environments.

G. RECOMMENDED PROTECTIVE CLOTHING MATERIALS[2,5,6]

Protective clothing manufacturers have not published recommendations for materials to be used in protecting against liquid hexamethylphosphoramide. However. duPont recommends that butyl rubber or other impervious materials be used for gloves, shoes, boots, suits and hoods when contacting HMPA.

H. CURRENT PRACTICES IN WORKER PROTECTION[2]

DuPont and presumably other HMPA producers and users process the chemical in regulated areas where entry and exit are restricted to a limited number of workers. HMPA and its solutions are treated as "no contact" chemicals and full impervious suits with respirators are recommended.

I. REFERENCES

1. Hawley, G.G., "The Condensed Chemical Dictionary," Van Nostrand Reinhold Company, 8th Edition, 1971.

2. Personal Communication from Donald W. Smith, Administrative Assistant, Environmental Quality Committee, E.I. duPont de Nemours and Company, Wilmington, Delaware, January 12, 1977.

3. "Hexamethylphosphoramide Causes Cancer in Laboratory Animals," *Chemical and Engineering News,* —:17, September 29, 1975.

4. "Background Information on Hexamethylphosphoric Triamide," National Institute for Occupational Safety and Health, October 24, 1975.

5. "Material Safety Data Sheet," E.I. duPont de Nemours, Inc., July 1976.

6. Data Sources:

   Edmont-Wilson, Product Catalogues
   Green Rubber Company, Product Catalogue
   Pioneer Industrial Products, Personal Communication
   Granet Corporation, Personal Communication
   Rainfair, Inc., Personal Communication

APPENDIX B
TEST METHODS

A TEST METHOD FOR RESISTANCE TO STATIC PUNCTURE

1.0 Scope

1.1 This test method determines the resistance to static puncture by measuring the force required to cause a pointed penetrometer to puncture a material specimen.

1.2 This test method defines the test procedure, test apparatus, penetrometer dimensions, and material specimen size, conditioning and position in the apparatus.

2.0 Test Specimens

2.1 Each material specimen to be tested shall be a rectangle at least 3.5 in. (8.9 cm) on a side. Multiple puncture tests may be made on each specimen.

2.2 Each specimen may consist of either a single layer or a composite which is representative of actual glove construction with all layers arranged in proper order. In each test, the specimen's normal outer surface shall be the first contacted by the point of the penetrometer.

2.3 Material specimens may be tested in either a dry or a wet condition.

3.0 Number of Tests

3.1 Three specimens shall be tested for each material with three punctures made on each specimen.

3.2 When it is necessary to evaluate both dry and wet specimens, three specimens shall be tested for each condition.

4.0 Test Apparatus

4.1 The static puncture *test apparatus* shall be a tensile testing machine, such as an Instron or its equivalent, which challenges a material specimen with a uniformly moving pointed penetrometer as shown in Figure B-1. The machine shall meet the requirements described in paragraphs 4.1.1-4.1.4.

4.1.1 The penetrometer shall be motor-driven at rate of travel of 20 in./min (50 cm/min) under load conditions and shall be uniform at all times.

4.1.2 The force applied to the specimen shall be accurate to ±1% up to and including a force of 50 lb (or 25 kg). The force shall be detected by a compression cell and shall be indicated by a dial, scale or automatic recorder.

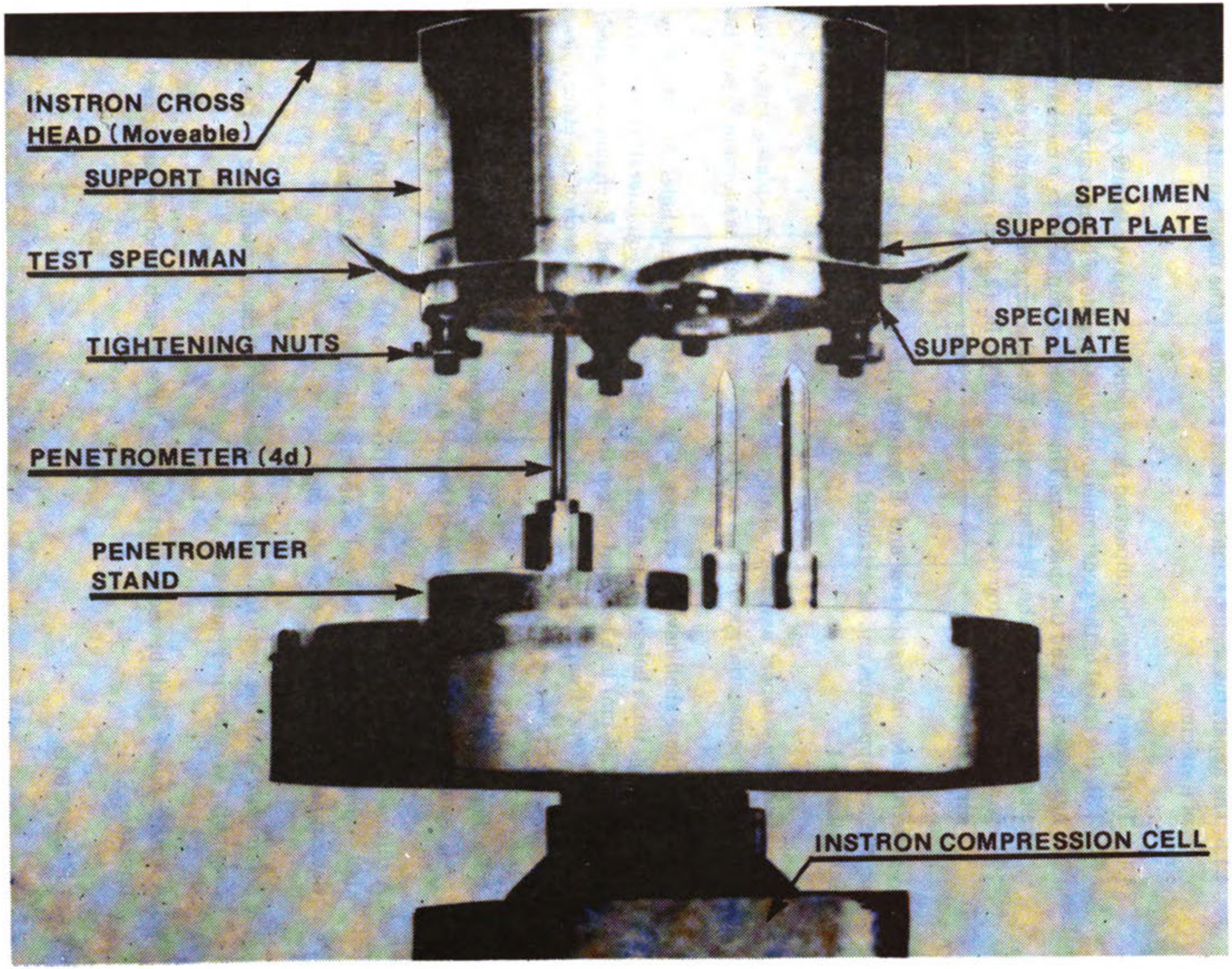

FIGURE B-1 STATIC PUNCTURE TEST APPARATUS

4.1.3 The apparatus shall be able to record or indicate the maximum load at puncture of a specimen.

4.1.4 To prevent damage by impact on the underlying support assembly (see paragraph 4.3), the travel of the penetrometer shall be capable of being stopped once the tip has passed beyond the specimen. This can be accomplished by a mechanical or an electrical stop on the test apparatus. For the support assembly described in paragraph 4.3, the stop is set approximately 1 in. (2.5 cm) beyond the specimen surface.

4.2 A *penetrometer* having the size and dimensions shown in Figure B-2 shall be mounted on the test apparatus and be attached to the compression cell of the machine as shown in Figure B-1.

4.3 The *specimen support* assembly shall consist of two flat metal plates which clamp together so the material specimen is held tightly between them as shown in Figure B-3.

4.3.1 Each plate shall have one or more ¼ in. (0.6 cm) diameter holes. For efficiency in testing, three holes spaced at the points of a 60-degree equilateral triangle having 1-in. (2.5 cm) legs centered within the plate can be used. Each hole is located ¾ in. (1.9 cm) from the plate edge and 1 in. (2.5 cm) from each of the other holes, as shown in Figure B-4.

4.3.2 The specimen support plates shall be connected to a metal support ring which mounts on the movable arm of the test apparatus, as shown in Figure B-1.

4.4 A *thickness gauge* capable of measuring thickness to the nearest 0.001 in. (or nearest 0.01 mm), as specified in Federal Standard 191, Method 5030.2, shall be provided to determine the thickness of each specimen.

4.5 A *template* shall be used to locate the holes for specimen mounting in the support assembly, as shown in Figure B-5.

4.6 A *leather punch* shall be used to cut the four holes in each specimen as located by the template.

5.0 Test Procedure

5.1 Each material specimen shall be conditioned before testing:

5.1.1 Materials to be tested dry shall be conditioned for a minimum of 24 hrs at a temperature of 70±5°F (21±3°C) and a relative humidity of 50±5%.

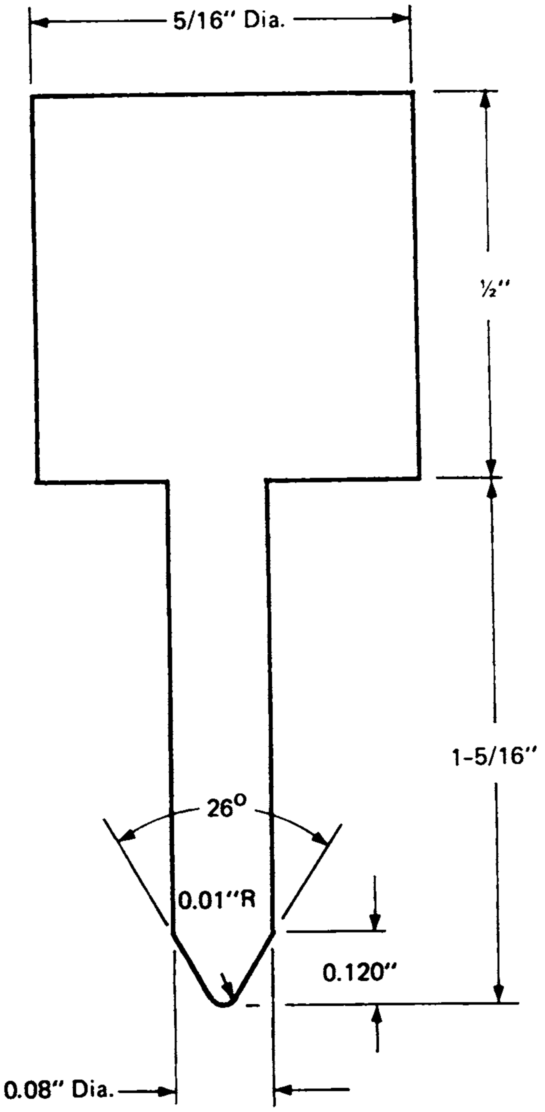

FIGURE B-2 CROSS-SECTION OF 4d PENETROMETER

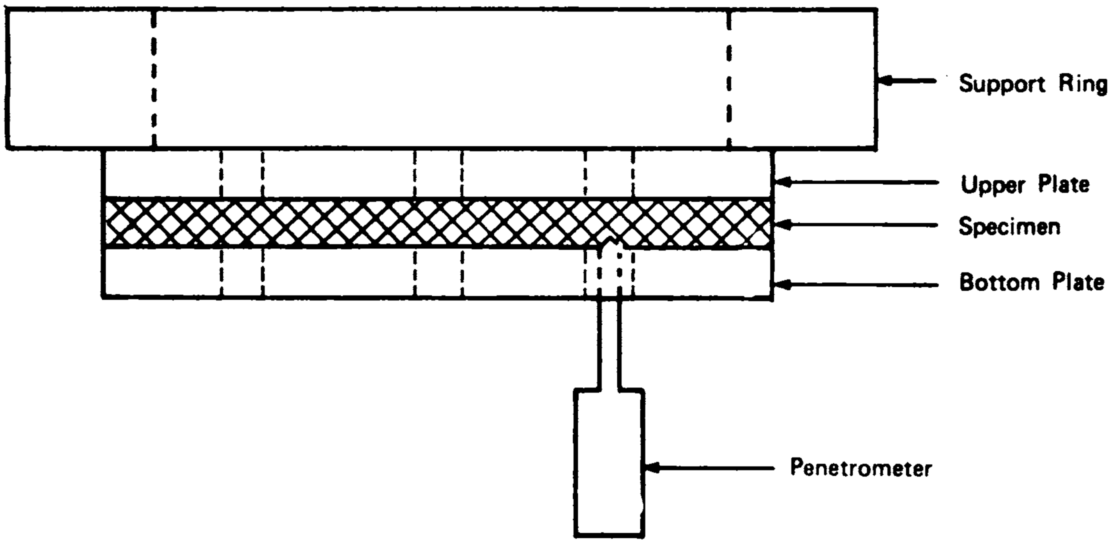

FIGURE B-3 SIDE-VIEW OF SPECIMEN SUPPORT ASSEMBLY

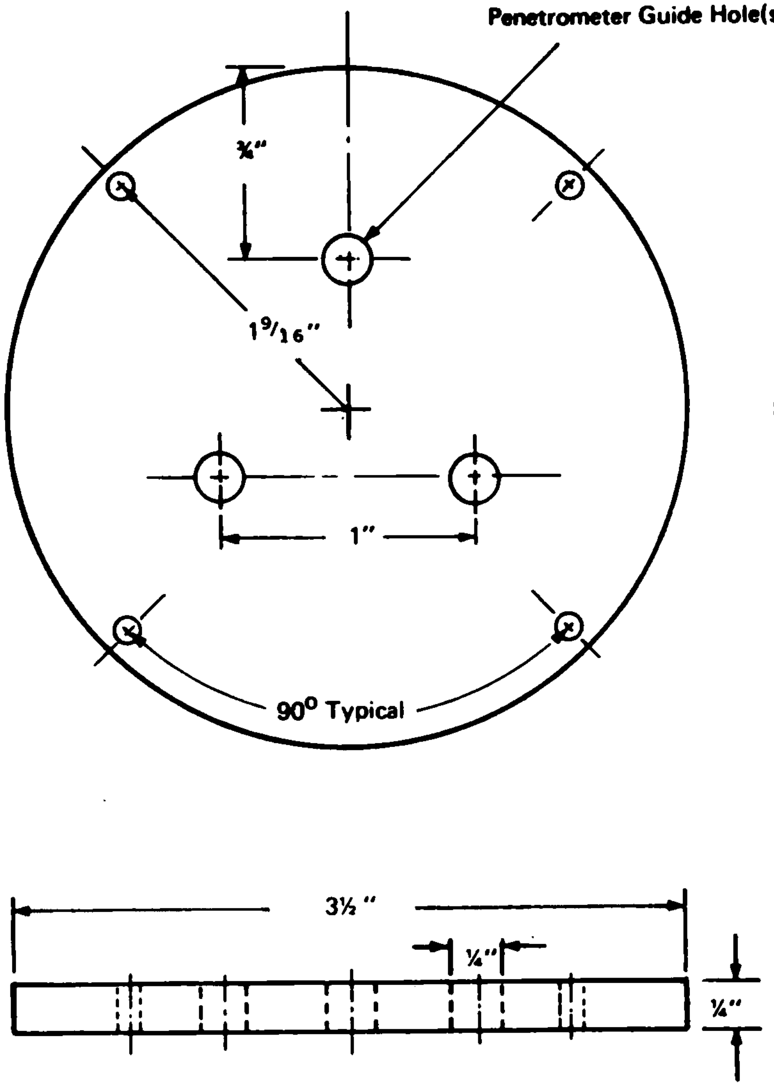

FIGURE B-4 SUPPORT PLATE (Two Required)

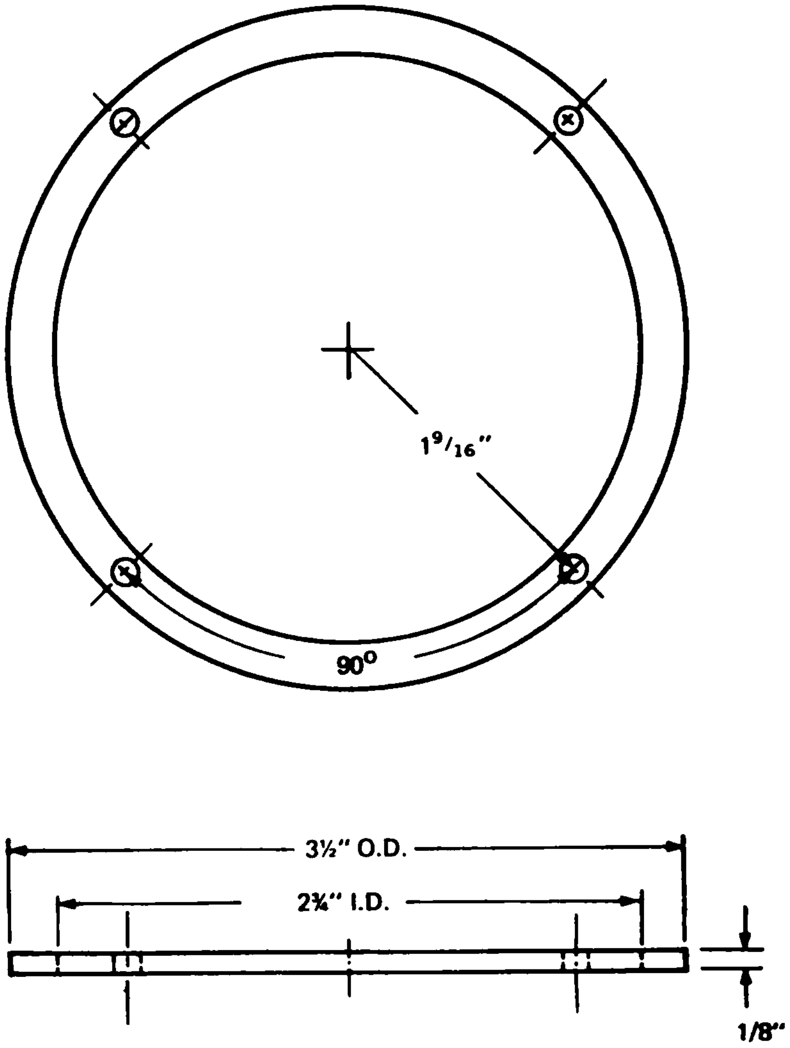

FIGURE B-5 TEMPLATE

5.1.2 Materials to be tested wet shall be immersed in room temperature water (70±5°F, 21±3°C) for not less than 1 hr. The specimens shall be blotted surface-dry between absorbent towels and tested within 5 min of removal from the water.

5.2 The thickness of each conditioned specimen shall be measured to the nearest 0.001 in. (or nearest 0.01 mm). ASTM D120.

5.3 The first specimen to be tested shall be mounted in the support assembly as shown in Figure B-3.

5.3.1 It is important that the two plates be marked and care taken that the holes are aligned prior to testing to avoid damaging the penetrometer and plates.

5.4 The support assembly shall be attached to the movable arm of the test apparatus.

5.5 The penetrometer shall be positioned on the compression cell of the test apparatus as shown in Figure B-1.

5.6 The apparatus shall be set in operation, but stopped when the penetrometer has been driven through the material specimen. (See paragraph 4.1.4.)

5.7 The maximum force registered by the indicating device shall be recorded to the nearest 0.1 lb (or nearest 50 gm) for each determination.

5.7.1 If the specimen has not been penetrated, a maximum force of 50 lb (or 25 kg) shall be recorded.

5.8 After the first test has been run, the penetrometer shall be repositioned under each of the other guide holes and the test repeated until three punctures have been made.

5.9 Additional specimens shall be tested until the requirements of paragraph 3.0 are met.

6.0 Report of Test Results

6.1 The force required for each puncture shall be reported to the nearest 0.1 lb (or nearest 50 gm) for each specimen. The average force for each material shall then be calculated and reported separately for the dry condition and the wet condition.

6.2 The thickness of each specimen shall be reported to the nearest 0.001 in. (or nearest 0.01 mm). The average thickness for each material shall then be calculated and reported separately for the dry condition and the wet condition.

6.3 If possible, observations shall be made and reported on the relative puncture resistance of various layers if the material specimen is a composite of two or more layers.

7.0 Notes

7.1 During the development of a test method appropriate for evaluating the puncture resistance of materials, the following published methods were reviewed for applicability, either in part or in whole:

ASTM Method D781-68 (1973)	Puncture and Stiffness of Paperboard, Corrugated and Solid Fiberboard.
ASTM Method D1048-70	Rubber Insulating Blankets, Spec. for (Paragraph 17.4, Puncture Test).
ASTM Method D1321-70	Needle Penetration of Petroleum Waxes.
ASTM Method D1709-67 (1972)	Impact Resistance of Polyethylene Film by the Free-Falling Dart Method.
ASTM Method D2207-64 (1970)	Bursting Strength of Leather by the Ball Method.
ASTM Method D2582-67 (1972)	Resistance to Puncture — Propagation of Tear in Thin Plastic Sheeting.
Federal Standard, 311, Method 2051	Bursting Strength, Plunger Method.
NBS 10,673	Method for Evaluating and Testing Sharpness of Points (1972).
NBS 10,839	The Skin Puncture Potential of Points Associated with Certain Toys (1972).
NBS 73-123	Resistance of Human Skin to Puncture and Laceration.

A TEST METHOD FOR DEXTERITY

1.0 Scope

1.1 This test method determines the dexterity of gloves by establishing the ability of a gloved-hand to pick up a specified object.

1.2 This test method defines the test procedure, test apparatus, and glove specimen conditioning.

2.0 Test Gloves

2.1 Each glove shall be tested as a complete glove in new (as-distributed) condition. This includes liners and outer coverings when they are considered to be an integral part of the glove design.

2.2 Gloves shall not receive special softening treatments (such as tapping with a mallet or squeezing between rollers) prior to testing.

2.3 Gloves shall be tested in both the dry condition and the wet condition.

3.0 Number of Tests

3.1 Three gloves in the dry condition shall be tested for each material and construction combination.

3.2 Three gloves in the wet condition shall be tested for each material and construction combination.

4.0 Test Apparatus

4.1 The dexterity *test apparatus* shall consist of smooth, stainless steel pins:

4.1.1 "Fine-Grip" test pins shall consist of a pin, 5.0 mm (0.20 in.) in diameter and 40.0 mm (1.6 in.) in length.

4.1.2 "Coarse-Grip" test pins shall consist of a pin, 8.0 mm (0.30 in.) in diameter and 50.0 mm (2.0 in.) in length.

5.0 Test Procedure

5.1 Gloves shall be conditioned before testing.

5.1.1 Gloves to be tested dry shall be conditioned for a minimum of 24 hrs at a temperature of 70±5°F (21±3°C) and a relative humidity of 50±5%.

5.1.2 The finger portions of gloves to be tested wet shall be immersed in room temperature water (70±5°F, 21±3°C) for not less than 1 hr. The gloves shall be tested within 5 minutes of removal from the water.

5.2 The first glove to be tested shall be evaluated in the dry condition as follows:

5.2.1 A trained operator, wearing the test glove and sequentially using each of the four possible combinations of thumb and finger, shall attempt to pick up the "fine-grip" pin by its circumference from a flat surface. To be successful, this attempt must be completed within 30 seconds.

5.2.1.1 This presumes that the trained operator is able to easily carry out these manipulations with an ungloved hand.

5.2.2 If appropriate, the operator shall carry out the same procedure using the "coarse-grip" pin.

5.3 The test glove shall then be evaluated in the wet condition as follows:

5.3.1 The operator shall repeat the test procedure using the "fine-grip" pin. However, the test shall be conducted with the finger portion of the glove held under a stream of slowly running water.

5.3.2 If appropriate, the operator shall carry out the same procedure using the "coarse-grip" pin.

5.4 Additional gloves shall be tested until the requirements of paragraph 3.0 are met.

6.0 Report of Test Results

6.1 A report shall be made of whether each glove material and construction combination is suitable for dry and/or wet "fine-grip" or "coarse-grip" usage.

6.1.1 To be suitable, all three gloves tested for each usage condition must meet the 30-second limitation specified in paragraph 5.2.1.

6.2 Observations on the factors causing failure, if evident, shall be reported for each material and construction combination not meeting the 30-second limitation. This shall include such factors as bulky fingers, excess materials and slippery materials.

7.0 Notes

7.1 During the development of a test method appropriate for evaluating the dexterity of gloves, the following published method was reviewed for applicability, either in part or in whole.

British Standard No. 3791	Clothing for Protection against Intense Heat for Short Periods, Appendix F — Test for Tactility of Gloves.

A TEST METHOD FOR DETERMINING THE RESISTANCE OF A PROTECTIVE CLOTHING MATERIAL TO PERMEATION BY A HARMFUL LIQUID

1.0 Scope

1.1 This test method determines the resistance of a protective clothing material to permeation by a harmful liquid. This is accomplished by measuring the time required for initial penetration through a clothing material by a liquid and then monitoring the subsequent rate of permeation by the liquid.

1.2 This test method determines the resistance of a protective clothing material to permeation by a harmful liquid under the worst-case condition of continuous liquid contact.

1.3 This test method defines the test procedure, test apparatus, and protective clothing material specimen size, conditioning and position in the test apparatus.

2.0 Definitions

2.1 A *Protective Clothing Material* is any material or combination of materials used in a glove, apron, suit, boot, hat or other clothing items whose purpose is to isolate the body from contact with a harmful liquid.

2.2 A *Harmful Liquid* is any liquid, which at normal temperature and pressures, can cause harm to the human body upon skin contact. The liquid can be either a neat liquid or an aqueous or organic solution containing a dissolved chemical. The deleterious effects of these liquids can range from acute trauma such as skin irritation and burn to chronic degenerative disease such as cancer.

2.3 The *Perspiration Simulant* is an aqueous solution containing several components found in normal human perspiration. This solution contains 4.8 gms of sodium chloride, 0.4 gm of calcium chloride, 0.4 gm of potassium chloride and 2 gms of lactic acid per liter of distilled water.*

2.4 In this case, *Permeation* is a process by which a harmful liquid penetrates protective clothing materials on the molecular level. Permeation involves (1) the sorption of molecules of the liquid into the contacted (outside) surface of a protective clothing material, (2) the diffusion of the sorbed molecules through the material, and (3) the desorption of the molecules from the opposite (inside) surface of the material. Permeation is not the bulk flow of liquid through pores or holes in a material.

***Source:** Shohl, *Mineral Metabolism*, Reinhold Publishing, p. 90, 1939.

2.5 *Breakthrough Time* is the elapsed time between initial contact of harmful liquid with the outside surface of a protective clothing material and the time at which the permeating liquid can be detected at the inside surface of the material.

2.6 *Steady State Permeation* is denoted by a linear increase in harmful liquid concentration in the perspiration simulant as a function of time. This definition is valid only when the concentration of harmful liquid in the perspiration simulant is considerably less than the saturation concentration (<20%).

2.7 *Harmful Liquid Detection* is the quantitative detection of permeating harmful liquid in the perspiration simulant. Any analytical technique capable of identifying and measuring the harmful species at concentrations of 1-10 ppm is satisfactory for this purpose.

2.8 *Ambient Temperature* is considered to be 21 ±3°C (70 ±5°F).

3.0 Test Specimen

3.1 Each protective clothing material specimen to be tested shall be a rectangle at least 4.6 cm (1.8 in.) on a side.

3.2 Each specimen may consist of either a single layer or a composite of multiple layers which is representative of an actual protective clothing construction with all layers arranged in proper order. In each test, the specimen's normal outer surface shall contact the harmful liquid.

3.3 If a proposed design of an item of protective clothing specifies different materials or thicknesses of materials at different locations, specimens from each location shall be tested.

3.4 If a proposed design has stitched-through or other type seams, additional specimens containing these seams shall be tested.

4.0 Number of Tests

4.1 Three specimens shall be tested for each material, composite, or area (in the case of a heterogeneous design).

5.0 Test Apparatus

5.1 The harmful liquid permeation test apparatus shall consist of a two-chambered cell for contacting a material specimen with the harmful liquid on the specimen's outside surface and either a perspiration simulant or distilled water on the specimen's inside surface.

5.1.1 The test cell, as shown in Figure B-6, shall consist of two glass pipe reducer elbows* nominally sized to 5.1 cm (2-in.) diameter by 2.5 cm (1-in.) diameter with the small-diameter sections joined horizontally by aluminum flanges.

5.1.2 A stainless steel clothing material specimen holder** shall be positioned between the aluminum flanges as shown. When the specimen holder and specimen are in place, the test cell is divided into two chambers.

5.1.2.1 The specimen holder shall be designed, as shown in Figure B-7, to expose approximately a 2.5 cm (1-in.) diameter specimen to the test liquids.

5.1.2.2 In the configuration shown, the specimen holder will accept and retain a material specimen in either a relaxed or a strained condition.

5.1.3 Teflon gaskets shall be used in all joints.

5.1.4 Stainless steel discs** shall be used as covers for the top openings of each chamber.

5.1.4.1 Holes shall be provided in each cover as necessary to provide for stirring, heating, cooling, temperature measurement and sample withdrawal.

5.1.4.2 Samples of the perspiration simulant can be withdrawn either continuously by pump or as discrete samples by syringe.

5.2 A thickness gauge, capable of measuring thickness to the nearest 0.1 mm (or nearest 0.001 in.), as specified in Federal Standard 191, Method 5030.2, shall be provided to determine the thickness of each material specimen.

6.0 Test Procedure

6.1 Each material specimen shall be pre-conditioned for a minimum of 24 hours by exposure to a temperature of 21 ±3°C (70 ±5°F) and a relative humidity of 50 ±5%.

6.2 The thickness of each conditioned specimen shall be measured to the nearest 0.01 mm (or nearest 0.001 in.) and recorded.

6.3 The first specimen to be tested shall be mounted in the material specimen holder and the test apparatus assembled as shown in Figure B-6.

6.3.1 If the specimen is to be tested in a relaxed condition, it shall be mounted in the specimen holder with normal tautness.

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*A Pyrex glass pipe reducer elbow, Corning Glass catalogue No. P-1251, or its equivalent, is satisfactory for this purpose.

**Type 316 stainless steel, or its equivalent, is satisfactory for this purpose.

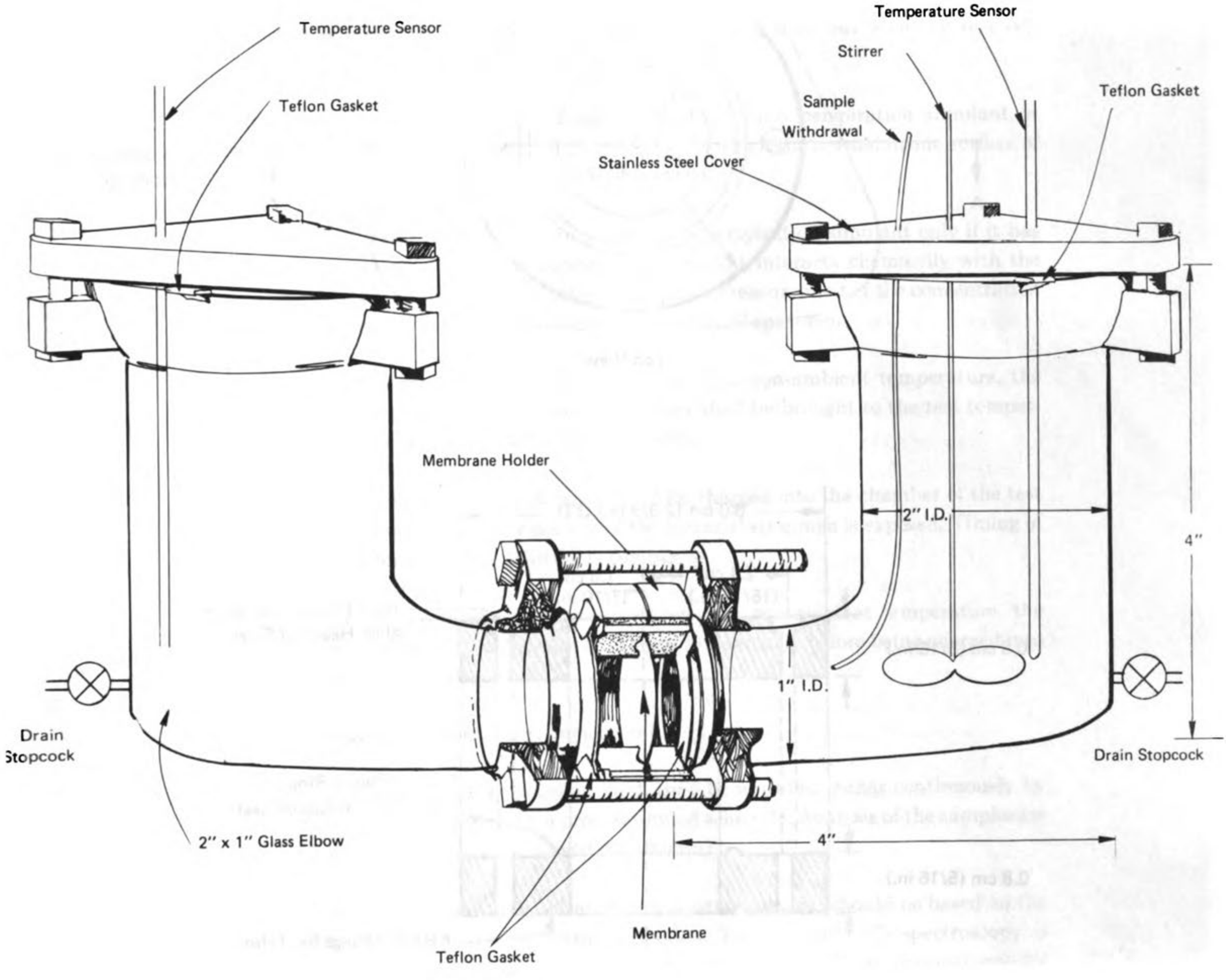
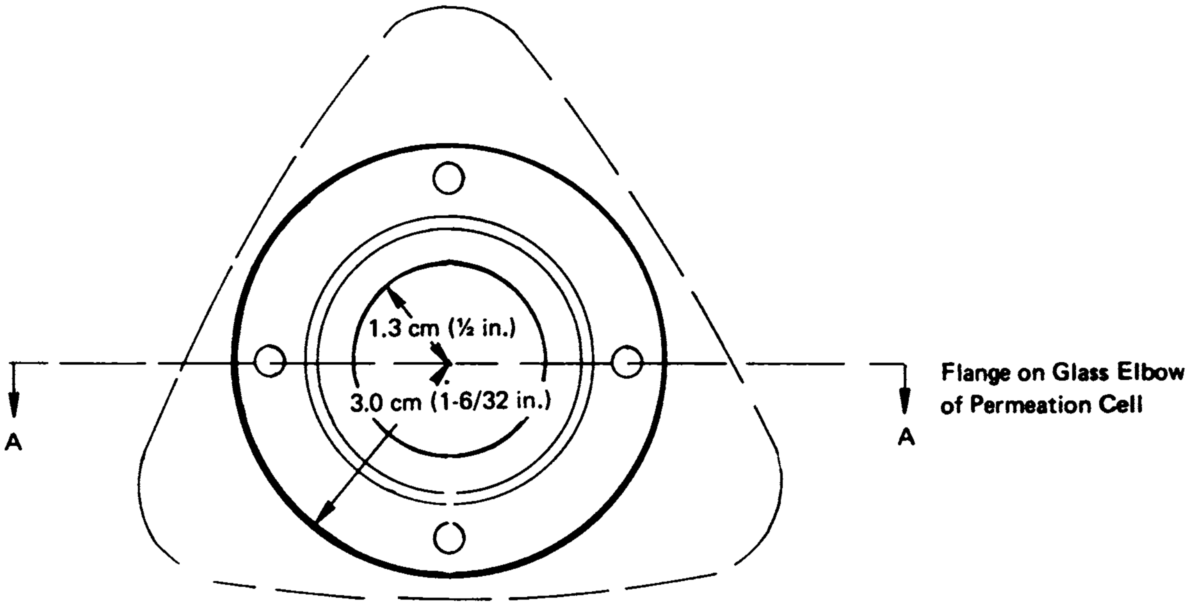
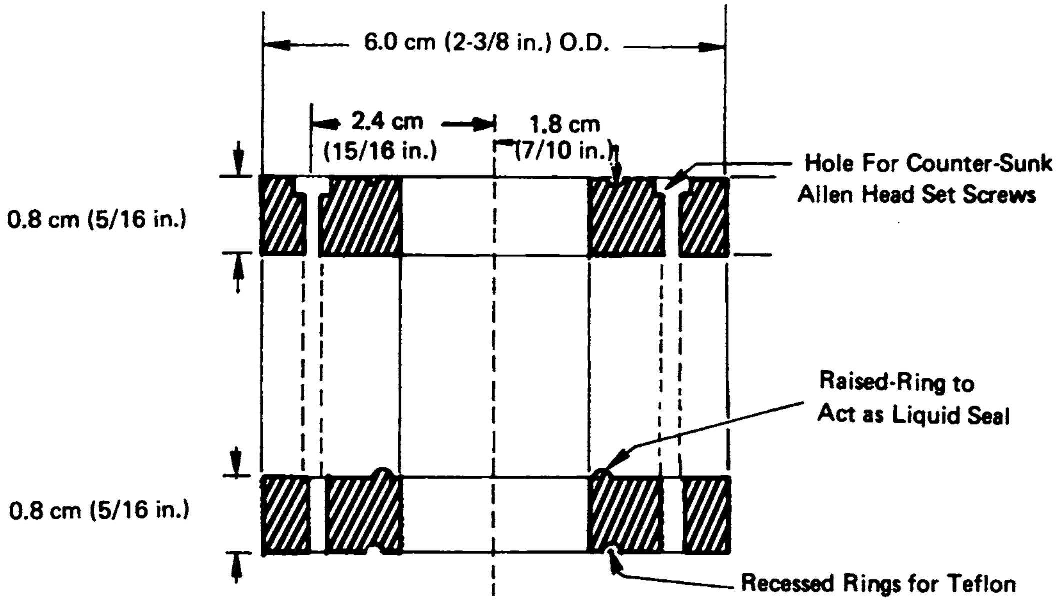


FIGURE B-6 SKETCH OF PERMEATION CELL



(Top View)



(Cross-Section A—A)

FIGURE B-7 MATERIAL SPECIMEN HOLDER

6.3.2 If the specimen is to be tested in a strained condition, it shall be pulled to the desired extension by a tensile testing machine, such as an *Instron* or its equivalent, and mounted in the specimen holder while still under strain.

6.3.3 If the permeation test is to be carried out at a non-ambient temperature, the assembled test cell shall be immersed to approximately 5.1 cm (2.0 in.) of the top covers in a water bath at the test temperature and allowed to equilibrate at the test temperature. The permeation test shall be carried out with the test cell immersed in the water bath.

6.4 After assembly of the test apparatus, 100cm^3 of either a perspiration simulant or distilled water shall be charged into the chamber to which the normal inside surface of material specimen is exposed.

6.4.1 Distilled water shall be used in place of the perspiration simulant only if it has been determined that the perspiration simulant interacts chemically with the harmful liquid under test or prevents accurate measurement of the concentration of the harmful liquid as it permeates the material specimen.

6.4.2 If the permeation test is to be carried out at a non-ambient temperature, the perspiration simulant or the distilled water shall be brought to the test temperature before being charged into the test cell.

6.5 Without delay, 100cm^3 of harmful liquid shall be charged into the chamber of the test cell to which the normal outside surface of the material specimen is exposed. Timing of the test is to begin when this addition is completed.

6.5.1 If the permeation test is to be carried out at a non-ambient temperature, the harmful liquid shall be brought to the test temperature before being charged into the test cell.

6.6 Stirring of each liquid shall begin immediately.

6.7 Sampling of the perspiration simulant shall then be initiated, either continuously by pump or discretely by syringe, on a predetermined schedule. Analysis of the samples for harmful liquid content shall be carried out promptly.

6.7.1 The method chosen for perspiration simulant withdrawal should be based on the technique selected for analytical detection. For example, UV spectroscopy is often used for continuous analysis of a sample stream while gas chromatography requires the analyses of discrete samples.

6.7.2 Samples which are withdrawn and analyzed on a continuous basis shall be returned to the test cell directly after analysis to maintain proper volume of the perspiration simulant.

6.7.3 Samples which are withdrawn and analyzed as discrete samples shall be replaced by an equivalent volume of fresh perspiration simulant at the test temperature to maintain proper volume of the perspiration simulant.

6.8 A record shall be kept of the concentration of harmful liquid found in the perspiration simulant and the time which has elapsed between the initial liquid contact with the material specimen and withdrawal of each sample.

6.9 Sampling shall be discontinued and the test terminated after a steady-state permeation rate has been established.

6.10 After the first material specimen has been tested, the test cell shall be disassembled, thoroughly cleaned, and prepared for another test.

6.11 Additional material specimens shall be tested until three specimens per condition, as outlined in paragraph 4.0, have been tested.

7.0 Report of Test Results

7.1 For each material specimen tested, a report shall be prepared which describes the concentration of harmful liquid found in each sample of perspiration simulant as a function of elapsed time after initial liquid contact with the material specimen. This report shall be prepared in graphical form as concentration versus time as shown in Figure B-8. The concentrations shall be reported to the nearest ppm.

7.1.1 The concentrations of harmful liquid found in samples of the perspiration simulant which were withdrawn and analyzed on a continuous basis represent the harmful liquid that has actually permeated the material specimen and should be reported directly.

7.1.2 The concentrations of harmful liquid found in samples of the perspiration simulant which were withdrawn and analyzed as discrete samples must be corrected to account for the dilution effects of fresh perspiration simulant which was added throughout the test to maintain proper volume. The corrected concentration shall be reported.

7.1.2.1 For each discrete sample, a corrected concentration shall be calculated by the following formula:

$$C_n = c_n + \frac{V_s}{V_p} \sum_{i=1}^{n-1} c_i$$

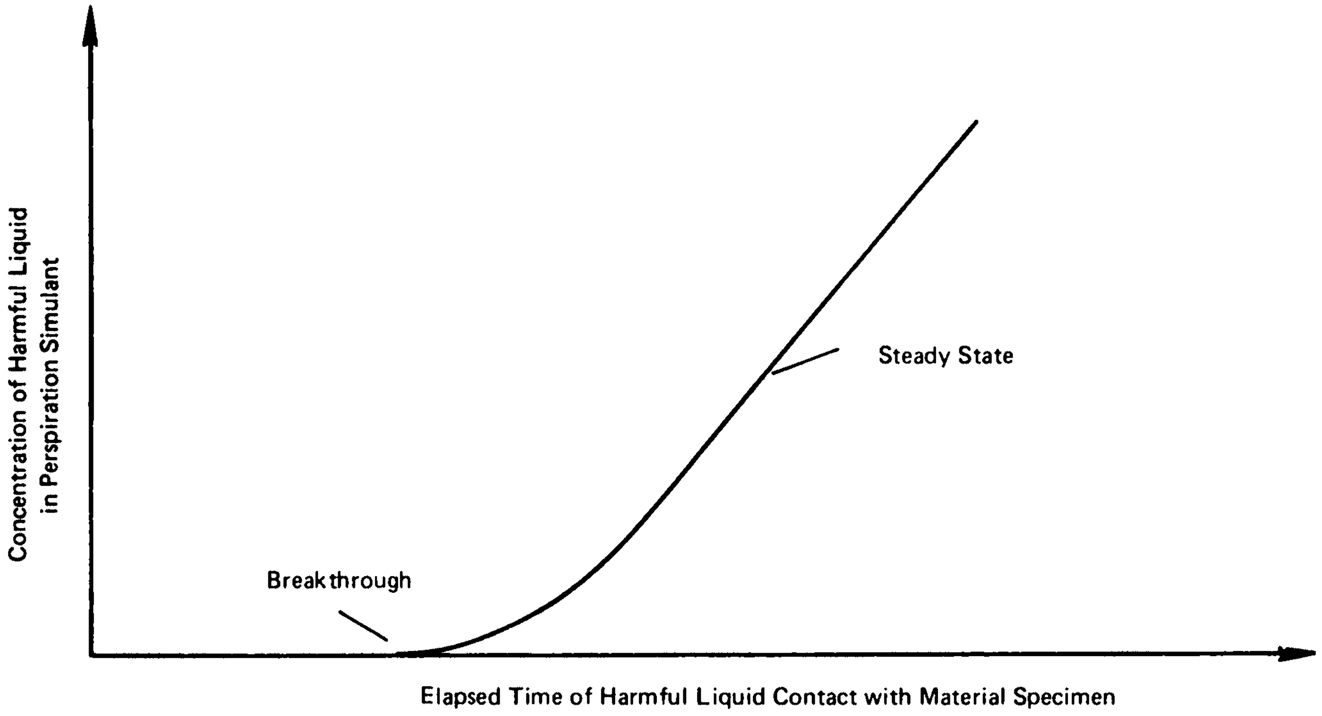


FIGURE B-8 TYPICAL HARMFUL LIQUID PERMEATION THROUGH AN ELASTOMERIC MATERIAL where

i = an indexing number assigned to each discrete sample taken, starting with $i = 1$ for the first sample.

c_i = the concentration of harmful liquid found in discrete sample number i.

n = the number of the most recent discrete sample taken.

c_n = the concentration of harmful liquid found in discrete sample number n.

C_n = the corrected concentration of harmful liquid in the perspiration simulant at the time of discrete sample number n.

V_s = the volume of each discrete sample taken, usually 2cc.

V_p = the volume of perspiration simulant in the test cell, usually 100cc.

7.1.2.2 Note that when $n = 1$, the value of the summation is zero.

7.2 The thickness of each material specimen shall be reported to the nearest 0.01 mm (or nearest 0.001 in.). The average thickness of the specimens tested for each material type shall also be calculated and reported.

7.3 The breakthrough time for each material specimen shall be identified from the previously prepared graphical presentation of harmful liquid concentration versus elapsed time. The location of this parameter is illustrated in Figure B-8. An average breakthrough time of the specimens tested for each material type shall also be calculated and reported.

7.4 The steady-state flux of permeating harmful liquid shall be calculated and reported for each material specimen. This calculation shall be based on the value of the slope of the curve depicting harmful liquid concentration versus elapsed time. The value of the slope of the curve shall be taken in the linear region denoting steady-state permeation as shown in Figure B-8. In addition, an average steady-state flux for each material type shall be calculated and reported.

7.4.1 For each material specimen, the steady-state flux shall be calculated by the following formula:

$$J = (mw_p a)\left(\frac{1}{A}\right)$$

where

m = the slope of the curve depicting concentration of harmful liquid versus elapsed time, in ppm/hr.

w_p = the weight of 100cc of perspiration simulant in gm.

a = a conversion factor equal to gm/10^6 gm/ppm (grams of harmful liquid per 10^6 grams of perspiration simulant per ppm of harmful liquid).

A = the area of the material specimen contacted by perspiration simulant in cm^2.

J = steady-state flux in gm/cm^2/hr.

APPENDIX C
A CORRECTION FOR DECOMPOSING COMPOUNDS

β-Propiolactone (BPL) rapidly decomposes when in solution with water. Since the permeation test protocol involves the collection of BPL as aqueous samples, this decomposition must be accounted for in interpreting the results of chromatographic analysis of each sample. Corrected concentrations (non-decomposed) can be found through the mathematical treatment described below:

A. MATERIAL BALANCE

The principle of conservation of mass applies to all mass transport processes. This principle is stated by the expression:

rate of mass input = rate of mass output + rate of mass accumulation.

In performing a material balance on the downstream chamber of our permeation test cell, the suspected carcinogen permeating the material specimen is considered to be the mass input while the carcinogen collected in the downstream chamber is considered to be the mass accumulation. The mass output is represented by any loss of carcinogen from the downstream chamber by a mechanism such as chemical degradation. In order to calculate the rate of mass input (i.e., the rate of permeation) for β-propiolactone, the rate of degradation must be established. Analytically measured downstream concentrations provided data for the rate of mass accumulation.

B. β-Propiolactone Degradation

The first step in establishing the rate of β-propiolactone degradation was to prepare aqueous solutions of several known initial concentrations and monitor the β-propiolactone concentrations as a function of time. The data were then plotted as measured concentration divided by initial concentration versus time. This permitted identification of both the type of degradation reaction and the associated reaction rate constant. By this technique the reaction was found to follow first-order kinetics and could be represented by equation (1)

$$\text{rate of mass output} = \frac{dC_{\beta,r}}{dt} = kC_\beta \qquad (1)$$

where:

C_β is the measured concentration;

t is time;

k is the reaction rate constant; and,

$dC_{\beta,r}/dt$ is the rate of mass output due to the degradation reaction.

From the slope of the plotted data, k was found to equal 0.0023 min.^{-1}

C. STEADY-STATE PERMEATION

Under conditions of steady-state permeation, the rate of mass input to the downstream chamber of the permeation test cell is constant. The rate of mass accumulation is measured by GC analyses of the downstream solution. Mathematically, the rate of accumulation can be described as

$$\frac{dC_{\beta,a}}{dt}*.$$

By substituting these rate expressions into the general material balance and combining the result with equation (1), equations (2) and (3) are obtained:

$$\text{Rate of mass input (P)} = \frac{dC_{\beta,r}}{dt} + \frac{dC_{\beta,a}}{dt} \tag{2}$$

$$P = kC_\beta + \frac{dC_\beta}{dt} \tag{3}$$

where P is in units of ppm/min.

Equation (3) is a first order differential equation best solved by using the integrating factor $e^{\int kdt}$ Multiplying equation (3) by the factor yields:

$$Pe^{\int kdt} = e^{\int kdt}\ kC_\beta + e^{\int kdt}\ \frac{dC_\beta}{dt} \tag{4}$$

Simplification of equation (4) results in:

$$\frac{Pe^{kt}}{k} = C_\beta e^{kt} + A \tag{5}$$

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* The subscript "a" is used to differentiate this rate expression from the previous similar rate expression used for the degradation reaction.

where A is a constant of integration found by substituting the initial condition $C_\beta = 0$ at $t = 0$ into equation (5). Thus $A = -P/k$ and equation (5) can be rewritten as:

$$P = \frac{kC_\beta}{(1-e^{-kt})} \qquad (6)$$

Substitution of the calculated value for k and a measured value for C_β at a time t in equation (6) provides the corrected permeation rate, P, at time t. The raw data from the chromatographic analyses in this test series were reduced in this manner before presentation in Tables 18 and 24. As expected, the corrections were most apparent for the longest permeation times.

APPENDIX D
REFERENCES (TO TEXT)

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