PREDICTING THE EFFECTIVENESS OF

CHEMICAL-PROTECTIVE CLOTHING: MODEL

AND TEST METHOD DEVELOPMENT

PREDICTING THE EFFECTIVENESS OF CHEMICAL-PROTECTIVE CLOTHING
MODEL AND TEST METHOD DEVELOPMENT

by

Abhoyjit S. Bhown
Elizabeth F. Philpot
Donald P. Segers
Gary D. Sides
Ralph B. Spafford

Southern Research Institute
Birmingham, Alabama 35255

Contract No. 68-03-3113

Project Officer

Michael D. Royer
Releases Control Branch
Hazardous Waste Engineering Research Laboratory
Edison, New Jersey 08837

DISCLAIMER

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

As part of the Premanufacture Notification (PMN) program, which is mandated by the Toxic Substances Control Act (TSCA), EPA's Office of Toxic Substances evaluates the potential hazards posed by the manufacture of new chemicals. In support of the PMN program, the current work was undertaken to develop improved methodologies for assessing the effectiveness of chemical protective clothing for preventing harmful exposures to new chemical substances.

Francis T. Mayo, Director
Water Engineering Research Laboratory

iii

ABSTRACT

A predictive model and test method were developed for determining the chemical resistance of protective polymeric gloves exposed to liquid organic chemicals (solvents). The prediction of permeation through protective gloves by solvents was emphasized.

Several theoretical models and test methods applicable to estimating permeation-related properties were identified during a literature review and were evaluated in light of permeation tests performed during this study. The models and test methods chosen were based on theories of the solution thermodynamics of polymer/solvent systems and the diffusion of solvents in polymers (as opposed to being based on empirical approaches). These models and test methods were further developed to estimate the solubility, S, and the diffusion coefficient, D, for a solvent in a glove polymer. Given S and D, the permeation of a glove by a solvent can be predicted for various exposure conditions using analytical or numerical solutions to Fick's laws.

The model developed for estimating solubility is based on Universal Quasichemical Functional-group Activity Coefficient for Polymers (UNIFAP) theory, which is an extension of the Universal Quasichemical Functional-group Activity Coefficient (UNIFAC) method for predicting phase equilibria. The model recommended for estimating diffusion coefficients versus concentration is the Paul model, which is based on free-volume theory. The predictive test method developed is a liquid-immersion adsorption/desorption method that provides estimates of S and D. The models and test method chosen were incorporated into an algorithm for evaluating protective gloves recommended (in Premanufacture Notification [PMN] submittals to EPA) for use with new chemicals.

Finally, limited confirmation of the developed models and test method was secured by comparing estimated values of S and D with reported experimental data and by using the estimated values to predict instantaneous permeation rates, breakthrough times, and steady-state permeation rates for comparison with experimental permeation data.

This report was submitted in fulfillment of Contract No. 68-03-3113 by Southern Research Institute under the sponsorship of the U.S. Environmental Protection Agency. The study was conducted under subcontract with JRB Associates, McLean, Virginia 22102. This report covers the period January 1985 to September 1985, and work was completed as of September 1985.

CONTENTS

TABLES

TABLES

FIGURES

(continued)

ACKNOWLEDGMENTS

LABORATORY NOTEBOOKS

The work described in this report is documented in the following Institute laboratory notebooks: D0107, D0220, D0265 and D0301.

SECTION 1

INTRODUCTION

Section 5 of the Toxic Substances Control Act (Public Law 94-469) requires prospective manufacturers of new chemicals to submit Premanufacture Notifications (PMNs), which are reviewed by the U.S. Environmental Protection Agency's Office of Toxic Substances (OTS). PMN submittals often propose specific chemical-protective clothing to limit the dermal exposure of workers to toxic chemicals. Because OTS has only 90 days to complete each PMN review and because testing by the manufacturer must be kept to a minimum, the development of reliable models for predicting the performance of protective clothing is desirable. Thus, the purpose of Task I under the contract was to develop predictive models applicable to the evaluation of the chemical resistance of protective clothing exposed to liquid organic chemicals.

No matter how sophisticated the models developed under this contract or in future efforts, it is likely that there may often be insufficient data available to allow a given model to make predictions as accurate as those requested in the statement of work for the contract (±50% for permeation rate and ±20% for breakthrough time). Thus, predictive test methods are also needed that will allow the estimation of the permeation of chemical-protective clothing under expected exposure conditions. The purpose of Task II of the contract was to develop such methods (either by recommending the use of existing test methods or by developing new ones).

The completion of Tasks I and II, as defined above, would have been impossible within the six-month period allowed for the performance of the technical effort without guidelines to limit the scope of the effort. The primary guidelines developed for the current work were:

- This work emphasized the prediction of permeation through polymeric barrier materials, especially protective gloves.

- Predictive models or test methods that would have required significantly more experimental data or effort to execute than permeation tests were eliminated from further consideration.

- The models (and test methods) developed were based as much as possible on theory (as opposed to empirical approaches).

- The technical effort emphasized the development of algorithms or approaches rather than computer programs.

Each of these guidelines is discussed briefly below.

Permeation through polymeric barrier materials. The dermal exposure of workers who are wearing protective clothing to toxic organic liquids may occur primarily by two mechanisms: permeation and penetration. Penetration is a physical process that involves the macroscopic flow or transport of liquid through openings in the protective material. These openings may be natural (for example, the open structure in fabrics), or they may be caused by wear (due to, for example, abrasion or punctures) or by chemical degradation. Because penetration cannot be readily modeled and because ASTM methods exist or are currently being developed to measure the resistance of protective materials to penetration, the current work emphasized permeation, that is, the diffusion of chemicals through materials.

Simple predictive models and test methods. If a predictive model requires data that are not commonly available or easy to determine experimentally, then the model would be of little practical value. In other words, if permeation tests were simpler to complete (that is, less time-consuming, safer, less expensive, and so forth) than experiments to generate the data needed to use a given model, then it is likely that most manufacturers would choose instead to perform permeation tests. The same general statements may be made in the comparison of predictive test methods with permeation tests.

Theoretical basis of models and test methods. Because the contract required quantitative predictions (for example, breakthrough times and permeation rates) rather than qualitative predictions (such as good, fair, poor, and so forth), it was necessary to base the predictive models and test methods developed as much as possible on theory, that is, on the development of rigorous mathematical expressions. Given a mathematical expression for permeation rate versus time, it is simple to calculate, for example, a breakthrough time (given its definition) or the cumulative permeation at a given time. With an empirical approach, however, the transformation from one measure of protection (such as breakthrough time) to another (for example, steady-state permeation rate) is usually not possible.

Emphasis on algorithms. Prior to the development of "user-friendly" computer programs (which will be required for utilization of the predictive models in the PMN review process), algorithms or approaches to predicting permeation using models or test methods must be developed. After these algorithms have been defined, the programming effort is relatively simple. Thus, although some programming was completed, this work emphasized the development of algorithms.

After the guidelines outlined above were developed, the work was completed in essentially the same order presented in this report. First, a review of the existing literature on predictive models and test methods, as well as diffusion theory, was conducted. This review included collecting information on chemical-protective-clothing formulations, studying chemical-resistance literature published by manufacturers of protective clothing, evaluating chemical-protective information published in scientific journals and reports, and obtaining solubility and diffusivity data for polymers used to formulate

protective clothing. (As shown by the discussion beginning on page 23, solubility and diffusivity data allow permeation to be predicted.)

Following the literature review, a general approach to the development of predictive models and test methods was formulated. This approach incorporated the guidelines presented above as well as considered information collected during the literature review.

After the formulation of a general approach to the study, predictive models for the determination of solubilities were developed. This work was conducted concurrently with the selection and evaluation of predictive models for determining diffusivities (that is, diffusion coefficients). Also, test methods that resulted in solubility and diffusivity data were evaluated.

Once the work described above was completed, algorithms for the evaluation of protective polymeric barriers (such as gloves) were outlined. These algorithms comprise the predictive model developed under the contract. At this stage of the work, the distinction between predictive models and predictive test methods became unimportant. That is, the predictive algorithms functioned on the basis of the data available, whether from a model or from a test.

After the predictive model (a set of algorithms) was developed, it was used to make a limited number of predictions of breakthrough times and permeation-rate curves, and these predictions were compared to experimental data and manufacturers' recommendations.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Models that have been developed for the prediction of the permeation of organic compounds through protective-glove polymers have often been based on empirical approaches with little emphasis on diffusion theory. The current work has demonstrated that predictive models and predictive test methods that yield diffusion coefficients and solubilities may be used to estimate permeation data such as breakthrough times (for a given definition), steady-state permeation rates, and permeation-rate curves. These fundamental parameters may be estimated using the theoretical models or the simple test methods described in this report. Only relatively simple diffusion theory and mathematical methods are required to calculate permeation data from diffusion coefficients and solubilities. These permeation data may then be used to estimate the protection afforded by polymeric gloves recommended in PMN submittals.

This work has shown the potential of theoretical methods for estimating solubilities and diffusion coefficients of organic compounds in polymers used in the manufacture of chemical-protective gloves. Theoretical models for predicting these fundamental parameters are especially useful for new chemicals because the models require only limited physicochemical data, such as density and viscosity as a function of temperature. For example, a model based on UNIFAP theory needs only the densities of the organic compound and the polymer at the temperature of interest to estimate the solubility of the compound in the polymer (given, of course, the structure of the polymer and of the organic compound and other limited information).

Because even limited physicochemical data may not be available for the organic compound and polymeric glove of interest, it may frequently be necessary to conduct experiments to determine the resistance of the glove to permeation. The traditional method of determining the chemical resistance of a protective-glove material is to conduct a permeation test. However, such tests generally require the initial purchase of expensive analytical instrumentation, such as gas chromatographs, and they must be performed by well-trained technical personnel. The current research effort has resulted in the application of a simple liquid-immersion test to the determination of data that can be used to estimate solubilities and diffusion coefficients for organic compounds in protective-glove polymers. This test method requires only the purchase of a simple and relatively inexpensive analytical balance. Also, personnel with limited technical backgrounds can easily perform immersion tests.

The liquid-immersion test described in this report may be used to estimate permeation-rate curves (and, thus, parameters such as breakthrough times) even when the identity and composition of the polymeric glove material and the identity of the organic liquid are unknown. This predictive test method would prove especially useful if a manufacturer recommends a protective glove based on a proprietary polymer formulation. It could also be used for evaluating

4

protective gloves with complex formulations that could not be modeled using theoretical methods or when the physicochemical data necessary to use theoretical methods are unavailable.

The work described in this report was a feasibility study. Although models and test methods for the prediction of permeation data are presented, the brief confirmation studies described were conducted only for unsupported glove formulations. There is a need to extend the research effort to a wider range of protective-glove formulations and organic chemicals. For example, neither the theoretical models nor the immersion test can currently generate data sufficient to allow the quantitative prediction of permeation rates for organic chemicals through PVC-based protective gloves.

Most of the limited confirmation work conducted under this contract was performed "manually." That is, although computers were used to model polymer/ solvent systems, to perform curve fits of experimental data, and to predict permeation-rate data, the computer programs written were not integrated into a single software package and they were not made "user friendly." Thus, work under the confirmation task was tedious and time-consuming. For this reason, it was not possible to evaluate all of the experimental immersion and permeation data obtained under this contract, and the Paul model was used to predict diffusion coefficients for only two polymer/solvent systems.

The limited development of integrated computer software during the current feasibility study should not be considered unusual, particularly because this study emphasized the identification and preliminary investigation of predictive models and test methods. Thus, much of the effort consisted of reviewing the literature and completing mathematical derivations.

Any continued research effort based on the work described here, however, should begin with the consolidation of the programs written into a single software package. This package should also include the predictive algorithms outlined in Section 8 of this report. Thus, future confirmation work should, to a large extent, begin to resemble the preparation and evaluation of PMN-submittal-review software.

The predictive algorithms described in Section 8 emphasize diffusion theory; thus, time-dependent permeation (or immersion) data are necessary to confirm the algorithms. Because of the general lack of such data in the chemical-resistance literature, the initial confirmation work under a future contract should emphasize the use of the experimental data presented in the separate data volume accompanying this report. However, additional time-dependent permeation and immersion test data should be generated for a variety of polymeric glove materials and organic chemicals.

It may also be possible to use semiquantitative data bases such as those represented by manufacturers' chemical-resistance brochures or permeation databases to assist in the confirmation of predictive algorithms. However, such semiquantitative data bases should not strongly influence the development of predictive algorithms, because these data bases often contain information on the chemical-resistance of protective gloves of unknown origin and parameters such as breakthrough times may not be properly defined.

Future efforts to continue the work described here should include the identification and use of computerized data bases of physicochemical data that are needed to make predictions of diffusion coefficients and solubilities [using, for example, the Paul model or Universal Quasichemical Functional-group Activity Coefficients for Polymers (UNIFAP) theory]. Also, work should include addressing the limitations of the UNIFAP theory and the modified Paul model described in this report. In addition, the consideration of other theoretical models should be encouraged.

Perhaps the major recommendation to result from the current study is that there should continue to be a strong emphasis on the development of predictive algorithms that are based as much as possible on the rigorous interpretation of diffusion theory. This approach will allow permeation-rate and cumulative-permeation curves to be calculated as desired; other permeation-related parameters (for example, breakthrough times) can be determined from these curves. It should be noted that rigorous predictive algorithms can always be modified to yield simple correlations; however, the extension of an algorithm based on empirical correlations to the calculation of quantitative data is often difficult if not impossible.

SECTION 3

LITERATURE REVIEW

A literature review was conducted to develop a broad-based understanding of the current state of knowledge concerning chemical-protective clothing and to collect permeation data that could be used to evaluate predictive models and test methods. The review included collecting and evaluating information about chemical-protective-glove formulations, chemical-resistance data for gloves, and solubility and diffusivity data for polymers commonly used in fabricating protective clothing. In addition, the fundamentals of diffusion theory were reviewed, and information on predictive models and test methods was collected and evaluated.

The information collected during the literature review was obtained from a number of sources, including journal articles, manufacturers' literature, Government reports, and discussions with experts on diffusion in polymers and protective clothing.

The key information collected during the literature review was summarized in the monthly and quarterly reports prepared under this contract, and most of this information is repeated in this report. In addition, copies of about 70 articles of particular relevance were provided to EPA during the contract period.

One of the early key findings of the literature survey was that almost all of the published chemical-resistance data concerns polymeric gloves. Thus, because of the need for experimental data with which to evaluate predictive models and test methods, the emphasis throughout the remainder of the contract was placed on gloves.

CHEMICAL-PROTECTIVE GLOVES

The development of predictive permeation models (Task I) and test methods (Task II) depended on an understanding of chemical-protective gloves. Thus, a survey was conducted to identify glove manufacturers, construction and manufacturing processes used by them, and glove styles and formulations. The information obtained in the survey was based on the experience of Institute staff in the manufacture of protective gloves, on manufacturers' literature, and on references such as Waterman (1) and Blackley (2).

The information obtained in the survey of protective-glove literature showed that seven glove formulations account for almost all of the commercial market. These are poly(vinyl chloride), natural rubber, neoprene rubber, nitrile rubber, butyl rubber, poly(vinyl alcohol), and polyethylene. Six glove styles are in general use; these are unsupported, coated interlock, coated jersey, coated flannel, inner flocked, and thin, unsupported disposable. Also, the manufacturing processes and construction methods used vary greatly

depending on the glove style. There are approximately 35 manufacturers of chemical-protective gloves in the United States.

The development of predictive models and, to some extent, the development of test methods are made difficult by the large number of glove manufacturers and the variety of construction and manufacturing processes used by them. Also, polymeric gloves are not "pure" polymers, but they include other components such as fillers, plasticizers, stabilizers, pigments, and antioxidants (for example, see Tables 1 and 2). The identities and amounts of these additives in a given formulation will often have a major impact on the rate of permeation of chemicals through the glove. This is particularly true for poly(vinyl chloride) gloves, which often contain a higher percentage of additives, especially plasticizers, than the PVC resins used to form the · gloves. PVC gloves have the largest share of the market in chemical-protective gloves.

Even gloves that are formulated for the same application, but that are made by different manufacturers, often have very different chemical-protective properties. For example, Williams (3) reported a variation of a factor of three in the breakthrough times obtained for the permeation of carbon tetrachloride through PVC gloves of the same thickness and formulated for the same purpose, but made by three different manufacturers.

After a review of glove styles, construction methods, manufacturing processes, and formulations, it was concluded that unsupported natural-rubber gloves would be the simplest for which to begin the development of predictive permeation models and test methods primarily because of the "purity" of the typical formulation for such gloves. Thus, much of the modeling effort during the remainder of the contract emphasized natural rubber.

It should be noted that the validity of the PMN approval, whether based on a predictive model or on test data, may be nullified in the event a manufacturer elects to make a change in the formulation of a glove. This change may be dictated by economic considerations or by the availability of materials, and the change may affect the permeability of the glove with respect to the chemical against which it is supposed to provide protection. For this reason, once PMN approval is granted, it should be made specific for a given glove formulation from a specific glove manufacturer (both recommended, of course, by the prospective manufacturer of the new chemical).

CHEMICAL-RESISTANCE DATA

After the development of a predictive model (or predictive test method), its applicability must be confirmed by comparing predictions such as breakthrough times (for a given definition), steady-state permeation rates, and permeation-rate-versus-time data with experimental chemical-resistance data of the same type. Thus, the existing chemical-resistance literature was searched for such quantitative data.

TABLE 1.   TYPICAL FORMULATIONS FOR NATURAL-RUBBER, NEOPRENE-RUBBER,
AND NITRILE-RUBBER CHEMICAL-PROTECTIVE GLOVES[a,b]

Component	Natural rubber		Neoprene rubber		Nitrile rubber	
	Uns	Sup	Uns	Sup	Uns	Sup
Latex	93.3	83.5	83.0	80.5	93.8[c]	91.0[c]
Plasticizer	0	4.0	4.0	4.0	0	0
Zinc oxide	0.9	1.6	4.2	4.0	0	2.5
Clay	0	0-5	4.0	4.0	0	0
Color pigments	1.4	1.5	1.5	2.0	1.5	1.5
Antioxidant	1.0	0.8	0.8	0.8	1.0	1.0
Sulfur	1.0	0.8	0.8	1.0	0.2	0
Potassium hydroxide	0.5	0.5	0.1	0.1	0	1.0
Butyl zimate	0	0	0.8	0.5	0.5	1.0
Other accelerators	1.4	1.6	0	2.0	2.5	1.0
Ammoniated casein	0.5	0.5	0.3	0.5	0.5	0.2
Thickener	0	0.08	0.5	0.1	0.5	0.4
Wetting agents	0	0.08	0	0.5	0	0.5
Bactericide	0.02	0.02	0	0	0	0

[a]The numbers in the table are in units of weight percent. "Uns" means
unsupported; "Sup" means supported.

[b]See, for example, Waterman (1) and Blackley (2).

[c]Nitrile gloves are prepared from a copolymer of about 40% acrylonitrile
and about 60% butadiene.

TABLE 2. TYPICAL FORMULATIONS FOR POLY(VINYL CHLORIDE) CHEMICAL-PROTECTIVE GLOVES[a]

General Purpose

Component	Weight %
High-molecular-weight PVC resins	42-52
Phthalate-type plasticizers	42-53
Filler	0-5
Pigment	0.2
Heat stabilizer	0-2.6

Solvent Resistant

Component	Weight %
High-molecular-weight PVC resins	42-52
Butyl benzylphthalate; polyglycol benzoates	23-39
Polyester plasticizer	15-26
Filler	0-5
Pigment	0.2
Heat stabilizer	1.0-2.5

Low Temperature

Component	Weight %
High-molecular-weight PVC resins	43-46
Phthalate-type plasticizers	35-46
Adipate-type plasticizers	7-14
Filler	0-2
Pigment	0.2
Heat stabilizers	1.2-2.3

[a]See, for example, Waterman (1) and Blackley (2).

Manufacturers' Brochures

Manufacturers of chemical-protective gloves generally provide chemical-resistance tables in their marketing brochures. These tables usually include no permeation data but only recommendations such as excellent, good, fair, poor, and not recommended. Often, no criteria for these ratings are given, and thus, they are of little value in making or confirming quantitative predictions.

Two exceptions to the qualitative data generally presented by manufacturers of gloves are those provided by North Hand Protection (Siebe North, Inc.) and by Edmont (Becton Dickinson and Company). Both the North and Edmont brochures include measured breakthrough times. However, most details concerning the permeation-test methods used to generate the data are not included in the North and Edmont literature. For example, the North brochure defines breakthrough time as "the elapsed time between initial contact of the liquid chemical with the outside surface of the glove and the time at which the chemical can be detected at the inside surface of the glove by means of the analytical technique." However, neither North nor Edmont include analytical detection limits for any of the chemicals in their literature.

North also gives the maximum permeation rates observed during tests of unspecified duration. The Edmont literature categorizes the maximum permeation rate during a six-hour test as none detected, excellent, very good, and so forth. Each qualitative maximum permeation rate reported by Edmont is defined in terms of an order-of-magnitude quantitative range; for example, a maximum permeation rate categorized as "good" means that the maximum rate observed was in the range of 1.5 to 15 $mg/(m^2 \cdot sec)$.

There is no way to relate the breakthrough times and maximum permeation-rate data reported for North and Edmont gloves to fundamental parameters such as solubilities and diffusion coefficients, which are needed to predict quantitative permeation data under a variety of exposure conditions. It should be noted also that both North and Edmont recommend strongly that users conduct their own permeation (and degradation) tests to determine the suitability of a given protective glove for a specific application.

Data similar to those provided by North and Edmont are also available from the Pioneer Industrial Products Division of Brunswick Corporation. These data (as well as those of North and Edmont) are included in the second edition of a two-volume document entitled "Guidelines for the Selection of Chemical Protective Clothing" (4). The Pioneer data given in that report include percentage weight change and percentage volume change as a function of time for polymeric glove samples immersed in organic liquids. The thickness of each glove sample is also presented in the report. However, neither the initial weights nor the initial volumes of the samples are given; thus, the weight-change and volume-change data cannot be used to calculate solubilities in units of concentration (for example, g/cm^3).

Government Reports

A number of reports published under Government contract were reviewed. These included the two-volume document entitled "Guidelines for the Selection of Chemical Protective Clothing" (5), which was originally published by Arthur D. Little, Inc., under the auspices of the EPA and the American Conference of Government Industrial Hygienists. Although the original document included no quantitative data on the permeation of polymeric materials, a revised version that includes breakthrough times and steady-state permeation-rate data collected from a number of sources was issued recently (4). Tables of immersion data (including percentage weight changes and percentage volume changes as a function of time) and diffusion coefficients have also been added to the document. Almost all of the diffusion coefficients reported are, however, for chemical-protective materials for which the manufacturers are unknown.

The document referenced above also includes an overview of considerations involved in the selection of chemical-protective clothing, a review of simple permeation theory, and a list of ASTM methods currently used to evaluate protective clothing. In addition, a summary of manufacturers' recommendations and 280 references are presented.

SRI International recently published a report entitled "Studies to Support PMN Review: Effectiveness of Protective Gloves" (6). The report includes a brief introduction to simple permeation theory. It also presents tables and figures that attempt to show a correlation between separation of solvent* and polymer in solubility space and permeability coefficient. Observed correlations were good to poor. Thus, the predictive value of such correlations is questionable. Also, little correlation between separation in solubility space and diffusion coefficient was observed.

One of the primary points made in the SRI International report is that little permeation data that can be used in evaluating models currently exist. Also, much of the data that do exist is of questionable value. For example, breakthrough times reported for various glove/solvent combinations are of limited use in the calculation of diffusion coefficients, because these times depend on the sensitivity of the analytical methods employed. Also, on the basis of simple diffusion theory, the so-called lag times rather than breakthrough times should be used to calculate diffusion coefficients; the SRI International report stated that diffusion coefficients based on breakthrough times may be in error by as much as a factor of ten.

The SRI International report also includes estimates of diffusion coefficients for various glove/solvent combinations. It also contains permeability coefficients for glove/solvent combinations that were based on reported steady-state permeation rates. Each steady-state permeation rate was divided by the vapor pressure of the solvent at saturation and multiplied by

---

*The word "solvent" is often used in this report as a substitute for the phrase "liquid organic chemical."

12

the thickness of the glove polymer to yield an estimate of the permeability coefficient. The SRI International report also includes brief discussions of solubility parameters and how to calculate them; in addition, it contains 55 references.

Another document reviewed under the current contract was a draft copy of a monograph being prepared by NIOSH (7). This monograph, which summarizes a computerized data base, includes breakthrough times and steady-state permeation data collected from a variety of sources. Although this report will represent an impressive collection of information when it is published, it does not contain all the data necessary (for example, diffusion coefficients and solubilities) to evaluate a model that must make quantitative predictions, such as permeation rate versus time. As illustrated by the discussion below, the primary reason such data (for example, analytical detection limits) are not included in the monograph is that these data are generally not available.

Journal Articles

Journal articles were collected that describe experiments in which protective gloves were exposed to various solvents and other chemicals. Table 3 gives a summary of the types of data contained in these articles that specifically address glove permeation. These articles and the data included in them are believed to be representative of the information on the permeation of protective gloves that has been reported in the scientific literature.

Unfortunately, much of the information reported in the articles referenced in Table 3 demonstrates a lack of appreciation of permeation theory by the authors. Also, extracting useful data from the literature is often made difficult by the careless use of terminology; for example, the terms "permeation rate" and "cumulative permeation" are frequently used interchangeably even though the significance of the two types of data and the theories used to interpret the data differ considerably. Thus, most of the data reported in the literature are of limited value in the validation of either predictive models or test methods.

The most significant data that can be generated to allow the validation of models and simple test methods are the permeation rate* (J) or the cumulative permeation (Q) as a function of time. Unfortunately, little of these data exists for protective gloves. Most of the data that exist are in the form of breakthrough times, which are dependent on analytical sensitivity and which provide insufficient information to characterize fully the permeation being studied.

A significant amount of the permeation data and interpretation of these data is based on misunderstandings of simple permeation theory. For example, the so-called normalized breakthrough time (t_j/ℓ^2 or t_q/ℓ^2) and the product $Q \cdot \ell$ listed in Table 3 have no basis, even in simple theory. Yet the concept of

---

*The correct terminology is permeation flux; however, the use of "rate" in place of "flux" is widespread.

TABLE 3. TYPES OF DATA REPORTED IN TWENTY-FIVE JOURNAL ARTICLES DESCRIBING GLOVE-PERMEATION EXPERIMENTS

Data reported	References
Permeation rate (J) versus time	3, 8
Cumulative permeation (Q) versus time	9-20
Lag time (t_L)	8
Steady-state permeation rate (J_∞)	3, 8, 11, 13, 19, 21, 22
Permeation rate (J) at selected times	23, 24
Cumulative permeation (Q) at selected times	12, 20, 25, 26
Ratios of products of cumulative permeation (Q) and polymer thickness (ℓ)	27
Weight or volume changes at a given time	8-10, 20, 28
Breakthrough times (t_j) based on permeation rate	3, 8, 13, 22, 23
Breakthrough times (t_q) based on cumulative permeation	3, 8-12, 14, 19-21
Normalized breakthrough times $(t_j/\ell^2$ or $t_q/\ell^2)$	8-11, 20
Diffusion coefficients (calculated incorrectly)	11, 14
Other	13[a], 15[b], 16[c], 18[c], 28[d], 29[e], 30[f], 31[g]

[a] Time at which the permeation rate is equal to one-half the steady-state rate.

[b] Percent equilibrium.

[c] Distribution of nitrosamines between solvent, glove, and receiving fluid.

[d] Percent loss of solvent through glove; percent change in length; other physical effects.

[e] Droplet test data (generated using a so-called splash test).

[f] Diffusion coefficient and solubility (incorrectly labeled solubility coefficient) versus vapor concentration.

[g] Physiological symptoms versus time in glove-permeation tests using human subjects.

normalized breakthrough time is widely used, and such data are frequently reported.

On first examination, there appears to be a significant (though not extensive) body of data in the open literature on the permeation of protective-glove materials by chemicals. For example, Table 4 lists 19 references for studies of the permeation of natural-rubber-based gloves by 67 compounds. An examination of the articles referenced in the table, however, revealed that very little of the data (which represent about 130 permeation experiments) would be of significant value in evaluating quantitative predictive models or test methods for natural-rubber gloves. For example, the permeation data for only three chemicals (pentachlorophenol, dimethyl sulfoxide, and benzene) in three references listed in the table meet the following simple criteria:

- That a permeation-related property (for example, permeation rate, cumulative permeation, weight change, or volume change) be reported as a function of time.

- That the glove be clearly identified (that is, the glove manufacturer, type, catalog number, and thickness should be reported).

Even more revealing is that of more than 2000 glove/chemical-permeation experiments found in 23 references, only about 52 of these experiments meet the two criteria listed above.

A more extensive survey of the type described above was beyond the scope of this contract. The limited survey results presented here are only intended to demonstrate the lack of data suitable for evaluating quantitative, predictive models or test methods.

Not all glove-permeation data in the literature are worthless for evaluating predictive models. The data that exist are useful for comparing trends in a homologous series of compounds or for a single compound in a series of glove materials. Also, some of the data are sufficient to allow the evaluation of models and test methods that are intended to identify gross glove/chemical incompatibilities.

PERMEATION DATA FOR POLYMERS

Because little time-dependent permeation-related data were found to exist for polymeric glove samples, the literature was reviewed to obtain such data for polymers commonly used in the manufacture of protective gloves. Approximately 118 journal articles were reviewed; of these, only 17 contained data of potential use in the present study (32-48). These data included solubilities, diffusion coefficients, and permeabilities (the product of the diffusion coefficient and the solubility). The most relevant of the solubility and diffusion-coefficient data in the journal articles referenced (as well as in a report by ADL (49)) are presented in Tables 5 and 6.

TABLE 4. CHEMICALS FOR WHICH PERMEATION DATA
FOR NATURAL-RUBBER GLOVES EXIST
IN THE SCIENTIFIC LITERATURE

Compound	Reference
Acetone	14, 15, 18, 22, 27, 28
Acrylonitrile	25
Allyl glycidyl ether	28
Aniline	15, 27
Aroclor	10
Benzene	15, 20[a], 22, 29, 30
Butyl acetate	22
n-Butanol	15
Carbon tetrachloride	15, 22, 29
p-Chloroaniline	14
Chloroform	15, 22
m-Cresol	22
Cyclohexane	22
1,2-Dibromo-3-chloropropane	25
1,2-Dibromoethane	8
Dichloromethane	14, 18
Dimethyl formamide	15, 27
Dimethyl sulfoxide	12[a], 15, 22
Dioxane	15, 22
Epichlorohydrin	8
Ethanol	14, 15, 18, 22
Ethylene dibromide	25
Ethylene dichloride	22
Ethylene glycol	22
Ethylene glycol dinitrate	31
Freon TF	22
n-Hexane	15
Isoamyl acetate	22
Methanol	15, 22
Methylene bis(2-chloroaniline)	14
Methylene chloride	15, 22
4,4'-Methylene dianiline	14
Methyl ethyl ketone	15, 22
Methyl iodide	15
Nitric acid, inhibited red fuming	23
Nitroglycerin	31
N-Nitrosobutyl methylamine	18
N-Nitrosodibutylamine	16, 17
N-Nitrosodiethylamine	16-18
N-Nitrosodimethylamine	16-18
N-Nitrosodipropylamine	16-18
N-Nitrosoethyl methylamine	18
N-Nitrosomethyl pentylamine	16
N-Nitrosopiperidine	16, 17

(continued)

16

TABLE 4 (continued)

Compound	Reference
N-Nitropyrrolidine	16, 17
N-Nitrosodi-sec-butylamine	18
Pentachlorophenol	11[a]
Pentane	22
Perchloroethylene	8, 15
Phenol	9, 15, 22
Phenyl glycidyl ether	28
2-Propanol	15
Pyridine	15, 22
1,1,2,2-Tetrachloroethane	15
Tetrachloroethane	22
Tetrahydrofuran	15, 22
Toluene	15, 22, 28
p-Toluidine	14
Trichlorobenzene	10
1,1,1-Trichloroethane	22, 28
1,1,2-Trichloroethane	15
Trichloroethylene	8, 22
Trifluoroethanol	22
Unsymmetrical dimethylhydrazine	23
Water	28
Water, tritiated	14, 15, 18
Xylene	22

[a]Only these reference/chemical combinations meet the acceptance criteria listed on page 15.

TABLE 5. SOLUBILITIES[a] OF SELECTED ORGANIC
LIQUIDS IN POLYMERS

Polymer	Organic liquid	Reference	Solubility, cm^3/cm^3	Temp., K
Butyl rubber	Benzene	49	0.662	295
	1,1-Dimethylhydrazine	49	0.138	295
	Epichlorohydrin	49	0.044	295
	Ethylenimine	49	0.169	295
	2-Nitropropane	49	0.021	295
	Trichloroethylene	49	1.46	295
Natural rubber	Acetone	48	0.125	297
	Benzene	49	3.91	295
	Benzyl alcohol	48	0.147	297
	n-Butanol	48	0.114	297
	t-Butanol	48	0.391	303
	Carbon tetrachloride	48	5.21	297
	Cyclohexane	48	3.67	297
	Cyclohexanone	48	3.55	297
	Diethyl carbonate	48	0.770	297
	Ethanol	48	0.0050	297
	Ethyl acetate	48	0.755	297
	2-Ethyl-1-butanol	48	0.319	297
	Ethylenimine	49	0.169	295
	n-Heptane	48	2.33	297
	n-Hexane	48	2.03	297

(continued)

18

TABLE 5 (continued)

Polymer	Organic liquid	Reference	Solubility, cm^3/cm^3	Temp., K
	Isopropanol	48	0.0406	297
	Methanol	48	0.0020	297
	Methyl ethyl ketone	48	0.642	297
	n-Pentanol	48	0.142	297
	t-Pentanol	48	0.479	297
	n-Propanol	48	0.110	297
	n-Propyl acetate	48	1.47	297
	Tetrachloroethylene	48	4.29	297
	Tetralin	48	4.53	297
	Toluene	48	4.13	297
	Trichloroethylene	48	5.13	297
Neoprene rubber	Benzene	40	2.98	298
			3.75	328
			4.12	355
		49	3.91	295
	Carbon tetrachloride	40	3.44	298
			3.69	328
			3.41	355
	Diisobutylene	40	0.25	298
			0.47	328
			0.57	355
	1,1-Dimethylhydrazine	49	0.664	295
	Epichlorohydrin	49	0.455	295
	Ethyl acetate	40	1.20	298
			1.16	328
			1.27	355
	Methanol	40	0.04	298
			0.26	328

(continued)

19

TABLE 5 (continued)

Polymer	Organic liquid	Reference	Solubility. cm^3/cm^3	Temp. K
	Methyl ethyl ketone	40	1.42	298
			1.52	328
			2.02	355
	2-Nitropropane	49	0.289	295
	Trichloroethylene	49	0.993	295
Nitrile rubber	1.1-Dimethylhydrazine	49	0.631	295
	Epichlorohydrin	49	0.241	295
	2-Nitropropane	49	0.717	295
	Trichloroethylene	49	1.46	295
Polyethylene	Benzene	35,36	0.0343	298
			0.0350	303
			0.0355	308
		49	0.295	295
	Epichlorohydrin	49	0.092	295
	n-Heptane	35,36	0.0542	298
			0.0535	303
			0.0524	308
	n-Hexane	35,36	0.0264	298
			0.0276	303
			0.0290	308
	2-Nitropropane	49	0.065	295
	Trichloroethylene	49	0.039	295
Poly(vinyl alcohol)	Benzene	49	0.035	295
	Trichloroethylene	49	0.028	295

[a]The solubilities reported are in units of cm^3 of organic liquid per cm^3 of unswollen polymer. The densities of the organic liquids. which can be found in chemical reference-data handbooks. may be used to convert the solubilities given to units of g/cm^3.

TABLE 6. DIFFUSION COEFFICIENTS FOR SELECTED ORGANIC
LIQUIDS IN NATURAL RUBBER[a]

Organic liquid	10^3 x Concentration.[b] moles/cm^3	10^6 x Diffusion coefficient, cm^2/sec	Reference[c]
Benzene	43.1	2.37	45
Carbon tetrachloride	54.0	1.67	45
		2.01	47
Cyclohexane	35.9	1.80	45
		1.78	46
Cyclohexanone	26.0	0.66	45
		0.74	47
n-Heptane	15.9	3.07	45
n-Hexane	15.0	4.06	45
Isooctane	11.8	2.73	45
		1.95	47
Methyl ethyl ketone	6.91	4.09	45
Methyl isobutyl ketone	12.3	1.67	45
Tetralin	32.4	0.82	45
Toluene	40.2	2.36	45
		2.75	47
o-Xylene	36.7	1.78	45

[a]The data were obtained at 303 K.

[b]The concentrations reported are in units of moles of organic liquid per cm^3 of unswollen polymer. (These data represent solubility data in addition to those given in Table 5). Each reported diffusion coefficient was experimentally determined at the corresponding concentration.

[c]The column labeled "D_m x 10^4" in Table 1 of Reference 47 should be labeled "D_m x 10^6".

Of some interest also are solubility data reported by Curry and McKinley (44) for acetone and benzene in natural rubber as a function of the partial pressure of the vapor to which the polymer was exposed. This reference includes expressions for the concentration dependence of the diffusion coefficients of acetone and benzene in natural rubber. (The data are not presented here because the primary interest under the current effort is the exposure of polymers to organic liquids rather than to vapors.)

Another article of interest was authored by Fujita (50). It included a review of diffusion theory as well as data originally published by Hayes and Park (51) that demonstrate the concentration dependence of the diffusion coefficient for benzene in natural rubber. (These data are included in Figure 5 in this report.)

DIFFUSION THEORY

During the literature survey, diffusion theory was reviewed to ensure that the critique of literature data and that proposed models and test methods were based on the correct interpretation of theory. Several well-recognized references were consulted (52-54). A brief summary of simple diffusion theory is presented below.

Fick's Laws

In general the permeation of polymeric gloves by an organic liquid may be described by Fick's laws of diffusion:

$$j = -D \partial C / \partial x \qquad (1)$$

$$\partial C / \partial t = \partial (D \partial C / \partial x) / \partial x \qquad (2)$$

where j is the flux through a plane perpendicular to the x axis, D is the diffusion coefficient, and C is the concentration of the solvent in the polymer.

To solve Equations 1 or 2 for quantities such as permeation rate, J, versus time or concentration versus time and position in the polymer, it is necessary to specify initial conditions (for example, $C(x,0)=0$) and boundary conditions (for example, $C(0,t) = S$ and $C(\ell,t)=0$). After the initial and boundary conditions are specified (and, usually, after other simplifying assumptions are made), the differential equations may be solved to yield the desired analytical solutions. Alternatively, numerical methods may be used to "solve" the equations.

Permeation

The simplest theory that describes the permeation of a polymeric glove by a solvent requires that the following assumptions be made:

- Diffusion obeys Fick's laws.

- Diffusion occurs in only one dimension.

- The diffusion coefficient, D, is independent of the solvent concentration in the polymer.

- The initial concentration of the solvent throughout the polymer sample is zero.

- The solvent has a finite solubility, S, in the polymer, and this solubility is attained instantly at the surface of the polymer in contact with the solvent.

- The concentration of the solvent on the challenge side of the polymeric glove sample is much greater than that in the receiving fluid (gas or liquid) on the opposite side of the sample throughout the measurement.

- The thickness of the polymer is constant; that is, negligible swelling occurs as the solvent dissolves in the polymer.

- The temperature of the test apparatus and the polymeric sample remains constant throughout the experiment.

- The solvent does not react with the polymer or alter its physical properties.

Almost all of the interpretation of permeation data for protective gloves reported in journal articles is based on these assumptions.

If the assumptions above are true (and often one or more are not), then the time-dependent diffusion equation, Equation 2, may be solved to yield:

$$J = (DS/\ell)\left\{1 + \sum_{m=1}^{\infty} 2 \cdot \cos(\pi m) \cdot \exp(-m^2 \pi^2 Dt/\ell^2)\right\} \tag{3}$$

where J is the permeation rate at a given time ($g/cm^2 \cdot sec$), D is the diffusion coefficient (cm^2/sec), S is the solubility of the organic liquid in the polymer (g/cm^3), ℓ is the polymer thickness (cm), and t is the time (sec).

If the glove-permeation experiment is designed to measure J versus t, then a relatively simple computer program may be used to determine D and S from such data. These are the fundamental parameters that are needed to understand permeation through polymeric gloves and to make quantitative predictions of permeation behavior under a variety of glove-use conditions that differ from those used in the permeation test.

If the cumulative quantity of solvent that permeates the glove being tested is determined as a function of time, then the parameters D and S may be calculated by fitting the following equation to these data:

$$Q = (DS/\ell)\left\{t - \ell^2/6D - (2\ell^2/\pi^2 D) \sum_{m=1}^{\infty} [(-1)^m \exp(-m^2\pi^2 Dt)/\ell^2]/m^2\right\} \quad (4)$$

If Q-versus-t or J-versus-t data were generated and reported routinely, then the fundamental parameters D and S could be determined. And these data could be used for the evaluation of predictive models and test methods.

Because Equations 1 through 4 look complicated and require the use a computer program, albeit very simple, to determine D and S, workers who evaluate protective gloves usually seek approximations that may be useful for comparing permeation data. One approach to determining the parameters D and S without the aid of a computer is to transform Equation 3, using a method suggested by Holstein (55), to yield the so-called early-time approximation:

$$\ln(J \cdot t^{1/2}) = \ln[2S(D/\pi)^{1/2}] - \ell^2/4Dt \quad (5)$$

If this equation is used, a plot of $\ln(J \cdot t^{1/2})$ versus $1/t$ yields a straight line with a slope equal to $-\ell^2/4D$ and a y-intercept equal to $\ln[2S(D/\pi)^{1/2}]$. Thus, in this manner, D and S can be determined graphically.

At long times, Equation 3 reduces to the so-called steady-state approximation:

$$J_\infty = DS/\ell \quad (6)$$

where J_∞ is the steady-state permeation rate. Thus, in tests where steady-state permeation is achieved, researchers have only to calculate the product DS (also known as the permeability) to compare the relative effectiveness of different types of protective gloves.

Although the calculations are simple, the determination of steady-state permeation rates is of limited value because no time-dependent information is obtained. Also, because of the breakdown of the assumptions listed above, steady-state permeation may never be achieved for a given glove/solvent combination. In addition, knowing the permeation rate for a given glove polymer may be of much more significance at early times, as the protection afforded by the glove begins to fail, than at long times when the steady-state permeation rate may be far above that which results in acceptable exposure levels.

Steady-state permeation rates (or frequently, a detector signal proportional to J_∞) are often multiplied by glove thickness (ℓ) to yield a result which is directly proportional to the product DS (see Equation 6). Thus, a comparison of $J_\infty \cdot \ell$ values for various gloves enables their ability to protect against permeation by a solvent at steady state to be compared. Unfortunately, even this simple normalization has been incorrectly applied. For example, Sansone and Tewari (27) multiplied cumulative-permeation (Q) data rather than steady-state permeation-rate (J_∞) data times glove thickness (ℓ) in an ill-founded attempt to correct for the effect of sample thickness in their study of gloves obtained from several manufacturers.

Another useful approximation may be obtained by reducing Equation 4 for long times to:

$$Q_\infty = (DS/\ell)\left\{t - \ell^2/6D\right\} \tag{7}$$

If cumulative-permeation data obtained at long times (more correctly, when steady-state permeation is achieved) are extrapolated to zero cumulative permeation, then Equation 7 reduces to:

$$0 = (DS/\ell)\left\{t_L - \ell^2/6D\right\} \tag{8}$$

where t_L is the so-called lag time. And,

$$t_L = \ell^2/6D \tag{9}$$

Thus, if the lag time is determined, then the diffusion coefficient D may be calculated.

The misinterpretation of Equations 8 and 9 has resulted in two major errors in the literature:

- Confusion of the lag time with breakthrough time.

- "Normalizing" breakthrough-time data by dividing by ℓ^2.

Researchers often use an experimental method and analytical technique to determine the time at which the permeation rate (J) or the cumulative permeation (Q) exceeds a given value, usually the analytical detection limit. And, as stated above, they frequently and incorrectly equate the breakthrough time with lag time.

Mathematically, the breakthrough times generally used (t_q and t_j below) are defined by the equations:

$$Q_b = (DS/\ell)\left\{t_q - \ell^2/6D - (2\ell^2/\pi^2 D)\sum_{m=1}^{\infty}[(-1)^m \exp(-m^2\pi^2 Dt_q)/\ell^2]/m^2\right\} \tag{10}$$

and

$$J_b = (DS/\ell)\left\{1 + \sum_{m=1}^{\infty} 2\cdot\cos(\pi m)\cdot\exp(-m^2\pi^2 Dt_j/\ell^2)\right\} \tag{11}$$

where t_q is the time at which the cumulative permeation equals Q_b and t_j is the time at which the permeation rate equals J_b. As may be seen, the breakthrough time derived from either Equation 10 or 11 differs considerably from the lag time defined by Equation 9. Also, dividing breakthrough times by ℓ^2 to yield so-called normalized breakthrough times has no basis in diffusion theory, but rather results from mistakenly equating lag time and breakthrough time.

ASTM Method F739-81, which is entitled "Standard Test Method for Resistance of Protective Clothing to Permeation by Hazardous Liquid Chemicals," recommends reporting breakthrough times. However, the breakthrough times reported are usually dependent on the sensitivity of the analytical method used, and values for D and S cannot be determined from breakthrough times alone. The ASTM method

also recommends reporting the steady-state permeation rate, which can be used to estimate the product DS. In addition, it recommends reporting a graph of cumulative-permeation-versus-time data, which, if reported correctly, could be used to determine D and S if the assumptions listed on pages 22 and 23 remain valid throughout a given experiment. Also, more sophisticated theories than describe above could be used to analyze the data when, for example, D is concentration dependent. Unfortunately, most testing laboratories using ASTM Method F739-81 do not report either J-versus-t or Q-versus-t data.

Absorption and Desorption

Other data reported in the literature include the percentage weight gain at a specific time (usually 24 hr) for a polymer sample immersed in an organic liquid. Simple diffusion theory may be used to show that the weight gain as a function of time for a thin planar sample of a polymer immersed in a liquid is given by the equation:

$$M_t/M_\infty = 1 - (8/\pi^2) \sum_{m=0}^{\infty} (2m+1)^{-2} \exp(-D(2m+1)^2\pi^2t/\ell^2) \tag{12}$$

where M_t is the net weight gained at time t and M_∞ is the net weight gained at long times (at equilibrium). (S may be calculated from the value determined for M_∞.) However, the weight gain at a single time does not yield enough information to allow the calculation of D and S.

The weight gained per unit volume at 24 hr (or at another fixed time) by a polymer sample immersed in an organic liquid is often considered to be the solubility, S. However, most researchers who study the absorption of organic liquids by protective gloves fail to prove that equilibrium is actually achieved. That is, they do not determine the weight gained as a function of time to show that equilibrium has been achieved. Thus, the weight gain of the polymer at 24 hr cannot be assumed to equal the value of S.

The weight gained by a given polymer sample when it is immersed in an organic liquid may not reach an equilibrium. In fact, weight loss caused by the leaching of additives from the polymer is not unusual (8,28). Thus, the effective value of S when the polymer sample is first immersed in the liquid may differ considerably from the effective value of S at long times.

After a polymer sample immersed in a solvent has reached equilibrium, it may be removed from the solvent and blotted to remove excess solvent, and then its weight may be monitored as a function of time. The desorption of the solvent from the polymer sample as a function of time is also described by Equation 12, except that M_t is now defined as the cumulative weight loss at time t. As for absorption, the values of D and M_∞ (proportional to S) may be determined by fitting the M_t-versus-t data to Equation 12.

As in permeation studies, approximations are often useful in absorption/desorption studies. One such approximation (52), derived from

Equation 12, is that the time, $t_{1/2}$, for which $M_t/M_\infty = 1/2$ is approximately given by

$$t_{1/2} = -(\ell^2/\pi^2 D) \ln\{(\pi^2/16)-(1/9)(\pi^2/16)^9\} \qquad (13)$$

with an error of about 0.001%. Thus,

$$D = 0.049 \; \ell^2/t_{1/2} \qquad (14)$$

and if the half-time of a sorption process is experimentally determined, the diffusion coefficient (concentration independent) can be readily calculated.

Unfortunately, polymer swelling and concentration-dependent diffusion coefficients are common for many polymer/solvent systems. The application of Equations 12 and 14 to absorption/desorption data for nonideal systems yields an apparent diffusion coefficient averaged over the concentration range corresponding to the particular experiment. This apparent diffusion coefficient is often a good approximation to the integral diffusion coefficient, D_{int}, given by

$$D_{int} = (1/C_0) \int_0^{C_0} DdC \qquad (15)$$

where 0 to C_0 is the concentration range existing in the polymer sheet during the absorption/desorption experiment. If the apparent diffusion coefficient is approximately the same as the integral diffusion coefficient, then it can be used (along with a value for S) to predict permeation-rate data for exposure conditions similar to those in the sorption experiment.

The common practice in presenting data from absorption or desorption experiments is to plot the ratio M_t/M_∞ against the quantity $t^{1/2}/\ell$, where M_t is the amount of a given solvent absorbed in or desorbed from a given polymer sample for a time t from the start of the experiment, M_∞ is the equilibrium weight gain of the polymer in the immersion experiment (related to the measured solubility of the liquid in the polymer), and ℓ is the thickness of the polymeric glove sample. The resulting curve is called the reduced absorption or desorption curve. The initial portion of these reduced curves is normally linear, that is, the amount absorbed or desorbed is directly proportional to the square root of time. This is true regardless of the relationship between the diffusion coefficient and concentration, assuming Fickian behavior (see the paragraph below).

As discussed by Fujita (50) and by Crank (52), an apparent diffusion coefficient can be calculated from the initial slope of the reduced absorption or desorption curve according to the equation:

$$D = (\pi/16)I^2 \qquad (16)$$

where I is the slope of the initial (linear) portion of the reduced sorption curve.

It should be noted that experimental curves of absorption and desorption data for a liquid/polymer system can often demonstrate the nature of the diffusion of the organic chemical in the test polymer (50,52). If the reduced absorption-versus-time curve is equivalent to the reduced desorption-versus-time curve, the diffusion is Fickian and the diffusion coefficient is concentration independent. If a simple hysteresis is observed, then the diffusion may still by classified as Fickian, but the diffusion coefficient is concentration dependent. If the absorption curve shows an inflection point and the absorption and desorption curves intersect, then the diffusion is non-Fickian or anomalous. Non-Fickian behavior has been attributed to time-dependent effects on diffusion. For a given polymer at temperatures above its glass-transition temperature, Fickian behavior is usually observed, while at temperatures below its glass-transition temperature, non-Fickian behavior is generally observed.

Numerical Methods

The equations presented above are analytical solutions that may be obtained if the diffusion processes being studied are ideal. Often one or more of the assumptions made fail. For example, the diffusion coefficient is often dependent on the concentration of the organic compound in the polymer. Equation 2 must then be written as:

$$\partial C/\partial t = \partial(D(C)\partial C/\partial x)/\partial x \qquad (17)$$

Usually the functional dependence of D on C is not known. For such cases, numerical methods may be used to determine the empirical dependence of D on C from, for example, permeation-rate-versus-time data.

Because even very "simple" deviations from the assumptions given previously may result in differential equations that cannot be solved analytically, it becomes necessary to rely on numerical methods. As more sophisticated predictive models and test methods are developed, there will be an increasing need to use such techniques.

Applications

As stated previously, the approach to the development of predictive models and test methods in this work involved the development of rigorous mathematical expressions (or the use of numerical methods). These expressions may then be used to make whatever calculations are necessary to demonstrate that a given glove provides the desired protection against permeation. For example, Equation 10 may be used to solve for the breakthrough time corresponding to a given cumulative amount of an organic compound in the receiving fluid in a closed-loop-mode permeation test. Also, Equation 11 may be used to solve for the breakthrough time corresponding to a given concentration of an organic compound in the receiving fluid in the open-loop mode (if the flow rate of the receiving fluid is known). Equation 6 may be used to determine the steady-state permeation rate.

Obviously, if such quantitative data can be determined, then qualitative permeation ratings can be established based on ranges such as those used by Edmont in the definition of their permeation ratings.

PREDICTIVE MODELS

Very few attempts appear to have been made to predict quantitatively the permeation of polymeric gloves by organic compounds. Most modeling efforts have been qualitative and empirical in approach. And they usually involve only the consideration of solubility and not diffusivity.

Attempts have been made by a number of researchers (8-10) to correlate weight or volume changes in glove materials at a fixed time after the immersion of test samples in a chemical with normalized breakthrough times. These correlations have yielded poor results at best. The primary reasons for the poor correlations observed are:

- The type of experimental data reported in the literature is generally not sufficient to demonstrate correlations.

- Normalized breakthrough times (t_i/ℓ^2 or t_q/ℓ^2) are based on a misinterpretation of permeation theory.

- Glove materials may lose weight or shrink in volume in contrast to expectations of weight gains or volume increases on immersion in an organic liquid.

- Equilibrium may not be reached at 24 hr or at any other fixed time during the immersion test.

The permeation literature includes numerous attempts to correlate permeation-related observations, such as percentage weight gain on immersion, with solubility parameters. The solubility parameter for an organic compound (or polymer) is defined as the square root of its cohesive energy density (which is the energy of vaporization per cubic centimeter); extensive tables of solubility parameters exist (for example, Reference 56). Solubility parameters may be related to solubility by the Flory interaction parameter (see Section 4). Two compounds (or a compound and a polymer) are thought to be miscible if there is a close match in their respective solubility parameters. Also, they are generally considered to be immiscible if their solubility parameters differ greatly.

As an example, Haxo, Nelson, and Miedema (57) presented plots of maximum percentage weight gain on immersion of polymer samples in various organic liquids as a function of solubility parameter. In their work, they indeed found examples of organic liquids that resulted in large weight gains for a given polymer sample and that had about the same solubility parameter as the polymer. However, they also identified other compounds whose solubility parameters approximately matched that of the polymer, but there were little or no weight gains observed for polymer samples immersed in these organic liquids (see Figure 4 in Reference 57).

As described previously, SRI International (6) found that correlations between the permeability coefficient and the separation in solubility space of the solvent and the polymer (effectively, the difference in solubility

29

parameters) ranged from good to poor. Even worse results were obtained in the current work in attempts to correlate solubility and separation in solubility space (see Section 5).

Very few researchers concerned with protective clothing have considered the effect of diffusivity (that is, the diffusion coefficient) on permeation. However, the diffusion coefficient may strongly affect observed permeation rates (or parameters such as breakthrough times) because it appears not only as a multiplier in, for example, Equation 3 but also in the exponential terms. In addition, the diffusion coefficient is often strongly coupled to the concentration of the organic compound in the polymer. That is, as the concentration of the compound in the polymer increases (or decreases), the diffusion coefficient may change significantly (44,50,51).

Correlations of the type referenced above may be of some value for screening gross incompatibilities between gloves and organic liquids. However, if a model is to be generally useful, then it must be capable of quantitative predictions of data such as permeation rate as a function of time.

Several models were identified during the literature search for estimating solubilities and diffusivities. Discussions of these models are presented in Sections 5 and 6 of this report.

PREDICTIVE TEST METHODS

During the first three months of the contract referenced above, written descriptions of test methods were collected from several sources, including the American Society for Testing and Materials (ASTM), the International Organization for Standardization (abbreviated ISO), the British Standards Institute, and the US Army. The test methods and types of data reported in journal articles and in reports by other contractors and Government agencies (for example, Arthur D. Little, Inc.; NIOSH; and SRI International) were also reviewed critically.

In general, the permeation-test methods in use are satisfactory. However, they are not universal. That is, extensive analytical methods development is often necessary when applying a given test method to the measurement of the permeation of a specific permeant (solvent or other liquid chemical). Thus, the adaptation of permeation test methods currently in use to evaluate protective gloves is usually quite expensive, time-consuming, and complex.

For the reasons given above, the efforts on Task II emphasized the identification of potential test methods that would be more universal than those currently in use and that would allow the prediction of permeation rate versus time. It should be noted that there are currently no test methods that attempt to use simple experimental procedures to predict permeation rate versus time.

Summary of Test Methods

The existing standard test methods for evaluating chemical protective clothing were recently compiled in Arthur D. Little's "Guidelines for the Selection of Chemical Protective Clothing" (4,5). This compilation was based on an earlier list in the ADL report entitled "Development of Performance Criteria for Protective Clothing Used Against Carcinogenic Liquids" (49). With the exception of the stress-crazing test and the transparency test, which are specific for the evaluation of rigid plastics, all of the test methods listed and discussed in these reports are applicable to the evaluation of protective gloves. (The fabric and textile tests included in ADL's compilation are considered applicable to the evaluation of fabric-supported gloves.)

An updated list of standard test methods that includes those given in the two ADL reports, proposed ASTM test methods, British and ISO test methods, and the Army's standard test methods for evaluating the resistance of protective clothing to·permeation by chemical-warfare agents is given in Table 7. All of the test methods listed in Table 7 except the ISO and British standards were reviewed. Copies of the ISO and British standards were ordered but were not received during the contract period. Brief descriptions of all of the methods reviewed are given in Appendix A.

The test methods listed in Table 7 can be divided into two broad categories according to the glove properties that are being evaluated: chemical resistance of the gloves and mechanical properties of the gloves. The glove properties included in the chemical-resistance category are permeation resistance, penetration resistance, degradation resistance, and swelling and solubility. The glove properties included in the mechanical-properties category are tear resistance and strength, cut resistance, puncture resistance, abrasion resistance, flexibility, ozone resistance, and UV resistance. (Ozone resistance and UV resistance are technically chemical-degradation tests, but they are not grouped in the chemical-resistance category because the tests do not measure degradation caused by the liquid chemicals that the gloves were developed to resist.)

Evaluation of Test Methods

Although both categories of tests are necessary, the primary purpose of chemical-protective gloves is to prevent the exposure of workers to hazardous liquid chemicals. Thus, the chemical-resistance category was considered more important to this work than the mechanical-properties category. Within the chemical-resistance category, the importance of the tests (in descending order) was considered to be as follows: permeation resistance, penetration resistance, degradation resistance, and swelling and solubility. This ranking of the tests is consistent with a recent survey of the members of ASTM Subcommittee F23.30 on Chemical Resistance that rated the priority of subcommittee objectives and projects. Listed in descending order, these were: permeation, penetration, degradation, decontamination, standard chemicals, splash, and particles.

Of the existing or proposed standard methods for evaluating chemical-protective gloves, the most definitive is the permeation-resistance test. The permeation resistance of a glove dictates the ultimate choice of the type

31

TABLE 7.   STANDARD TEST METHODS FOR THE EVALUATION
OF CHEMICAL-PROTECTIVE MATERIALS

Glove property	Test method	Title
Permeation resistance	ASTM Method F739-81	Resistance of protective clothing materials to permeation by hazardous liquid chemicals
	ASTM Draft Test Method F739-8X (Revision of ASTM F739-81)	Resistance of protective clothing materials to permeation by liquids or gases
	British standard test Method BS 4724:1971	Resistance of air-impermeable clothing materials to penetration by harmful liquids
	Draft ISO Method 6529 (Identical to BS 4724)	Protective clothing resistance to penetration by dangerous liquid chemicals
	ISO Method 6530	Clothing for limited protection against dangerous liquid chemicals—resistance to penetration—marking
	CRDC-SP-84010	Laboratory methods for evaluating protective clothing systems against chemical agents
Penetration resistance	ASTM Draft Test Method F903	Resistance of protective clothing materials to penetration by liquids
Degradation resistance	ASTM Draft Test Method Fxxx	Test method for evaluating protective clothing materials for resistance to degradation by liquid chemicals
Swelling and solubility	ASTM Method D471-79	Rubber property—effect of liquids

(continued)

TABLE 7 (continued)

Glove property	Test method	Title
	ISO Method 2025	Lined industrial rubber boots with general purpose oil resistance
Tear resistance and strength	ASTM Method D751-79	Standard methods of testing coated fabrics
	ASTM Method D412-83	Rubber properties in tension
	ASTM D1682-64 (Fed. 191A-5102)	Breaking load and elongation of textile fabrics
	ASTM D2261-83	Tearing strength of woven fabrics by the tongue (single rip) method (constant-rate-of-extension tensile testing machine)
Cut resistance	ASTM Draft Test Method Fxxx	Resistance to cut
Puncture resistance	ASTM Draft Test Method Fxxx	Resistance to puncture
Abrasion resistance	ASTM Method D4157-82 (Replaces ASTM D1175-71)	Abrasion resistance of textile fabrics (oscillatory cylinder method)
Flexibility	ASTM D1388-64	Stiffness of fabrics
Ozone resistance	ASTM Method D3041-79	Coated fabrics--ozone cracking in a chamber
Ozone resistance	ASTM Method D1149-81	Rubber deterioration--surface ozone cracking in a chamber (flat specimen)
UV resistance	ASTM Method G26-83 (Combination of two previous methods--G26 and G27)	Operating light-exposure apparatus (xenon-arc type) with and without water for exposure of nonmetallic materials

of chemical-protective glove material to be used in a given application. Penetration resistance is a manufacturing quality-control problem that is independent of the identity of the solvent or chemical in contact with the gloves. Resistance to chemical degradation is a materials-compatibility problem; that is, the selection of a glove material should be made only from a list of materials that have already been screened for compatibility with the chemical of interest.

All of the standard permeation tests are based on a partition-cell method in which the glove material to be evaluated is mounted in a test cell so that the cell is divided or partitioned into two chambers by the sample. One side of the test sample is exposed to a liquid-challenge chemical, and the amount of the chemical that permeates through the sample into an appropriate collecting fluid (either gas or liquid) is monitored as a function of time.

ASTM Method F739-81, which is typically cited as the standard permeation-test method, is rather general in scope. The major emphasis of the method is the designation of a specific test cell to use in conducting the tests. No specific analytical methods are recommended in the ASTM method, because the analytical method must be chosen specifically for each chemical or class of chemicals to be tested. Typical analytical methods that have been used include gas, liquid, and ion chromatography; UV and IR spectrophotometry; the use of radioactive isotopes; and wet chemical methods.

The current draft ASTM Method F739-8X contains two major additions to Method F739-81--modification of the test method to allow gas or vapor challenges of the test material and provision for using alternative test cells that have been found to be equivalent to the ASTM reference cell. (A standard method for experimentally determining the equivalency of test cells is currently under development by ASTM Committee F23.) Otherwise, the revised method is identical to Method F739-81.

Unlike ASTM Method F739-81, the methods given in CRDC-SP-84010 (58) are very specific. The methods specify test-cell design, test procedures, and analytical methods for permeation tests using chemical-warfare agents. Criteria for interpreting the test results are also given; these criteria can be specified because both the physicochemical and physiological properties of CW agents are known and well defined. Thus, the methods given in CRDC-SP-84010 are not generally applicable to the evaluation of chemical-protective gloves against a wide variety of organic liquids.

The major disadvantages of the standard permeation tests are the specificity of the analytical method for the challenge chemical and the frequent requirement for relatively complex and expensive analytical instrumentation. A general, relatively inexpensive test method or a "universal" analytical instrument is desirable for the routine experimental determination of the resistance of gloves to permeation.

In Section 6 of this report are proposed gravimetric absorption/desorption procedures for determining the solubility, S, and the diffusion coefficient, D, of a solvent in a glove sample. Data such as the steady-state permeation rate and lag time (which is inversely proportional to D) as well as the permeation

rate and cumulative permeation as a function of time can be predicted once D and S are known. Although a method based on such absorption/desorption procedures may be more time-consuming than a direct permeation test and may require sophisticated mathematical computation, the method would be general, relatively simple, and inexpensive in terms of the analytical instrumentation (the only requirement being a sensitive balance or a calibrated quartz spring and cathetometer) and technical training required.

SECTION 4

GENERAL APPROACH TO THE DEVELOPMENT OF
PREDICTIVE MODELS AND TEST METHODS

As a result of the literature review and the requirements of the PMN review process, the decision was made to base the development of models and test methods on the separate and independent prediction of the diffusion coefficient, D, and the solubility, S. The coupling of D and S through the concentration dependence of the diffusion coefficient would be considered as well. Once D and S are determined, then predictions of quantities such as breakthrough times, cumulative permeation, and maximum permeation rate can be based on analytical or numerical solutions of Fick's laws of diffusion. (Diffusion that does not appear to obey Fick's laws, that is, anomalous diffusion, is also possible. Such anomalous or non-Fickian diffusion was not specifically considered in this work.)

The prediction of D and S may be based on theory (for example, the use of solution thermodynamics to determine S) or on simple test methods capable of yielding D and S (for example, the use of immersion tests). The development of predictive models in this work was based on the independent determination of D and S. Two theoretical methods for the prediction of solubilities were evaluated, and these methods are described in Section 5 of this report. Two approaches for the prediction of diffusion coefficients based on free-volume theory were identified and also evaluated; these approaches are outlined in Section 6 of this report.

As with theoretical models, the primary emphasis in the selection of test methods was in the independent (if necessary) determination of estimates of solubilities and diffusion coefficients. In addition, the test methods developed emphasized simplicity, low cost, and the desire to use relatively untrained technical personnel to perform the tests. In conjunction with the development of predictive test methods, there was a need to conduct some permeation tests in order to have reliable time-dependent data to verify both test methods and predictive models.

After the selection of specific approaches to the prediction of D and S, these approaches were evaluated by comparing predicted D and S values to values published in the chemical literature.

Once the methods for the prediction of D and S were selected and evaluated, simple diffusion theory (such as that described in Section 3) was used to predict permeation-rate-versus-time curves. Then parameters such as breakthrough times and steady-state permeation rates were determined from these curves. The results obtained were first compared to manufacturers' chemical-resistance and degradation-rating tables. These predictions were then compared to the available experimental data.

In this initial approach, simple diffusion theory was employed. In the future, as examples of failures of the predictive ability of the models and

test methods are identified, the diffusion theory (as well as that used to predict D and S) can be increased in sophistication as necessary to reduce the frequency of the failures. The availability of physicochemical data for organic liquids and polymers must be considered.

Throughout the development of the predictive model, the emphasis was on the development of algorithms as opposed to "user-friendly" computer programs. Some programming was necessary to ease, for example, the calculations required to estimate diffusion coefficients and to make possible calculations that required numerical methods.

SECTION 5

PREDICTIVE MODELS FOR SOLUBILITY

This section of the report describes two approaches evaluated for the estimation of the solubility of an organic compound in a polymer. These were Flory-Huggins theory and UNIFAP theory.

FLORY-HUGGINS THEORY

Discussion of the Theory

The thermodynamics of solutions is difficult to quantify in many cases· however, many theories have been developed which accurately predict the behavior of particular systems. Solution equilibrium depends on the Gibbs energy of mixing, which consists of an enthalpy term and an entropy term. The regular-solution theory of Scatchard and Hildebrand ($\underline{59}$) has been successfully used to characterize various nonpolar solutions where the components are of similar molecular size. This theory assumes that the Gibbs free energy of mixing depends only on the enthalpy of mixing, that is, the entropy of mixing is zero (assuming no volume change on mixing). In conjunction with the development of this theory, Hildebrand introduced the concept and the use of solubility parameters. In reference to polymer solutions, Flory ($\underline{60}$) and Huggins ($\underline{61-63}$) took an alternative approach and initially assumed that the enthalpy of mixing is zero for solutions of small molecules and long-chain molecules; solutions of this type are termed athermal solutions.

The Flory-Huggins equation (derived using statistical mechanics) for an athermal solution of a solvent and a polymer is

$$\ln a_1 = \ln \phi_1 + (1 - \overline{v}_1 / \overline{v}_2) \phi_2 \qquad (18)$$

where a_1 is the activity of the solvent, ϕ_1 is the volume fraction of the solvent, and ϕ_2 is the volume fraction of the polymer. The parameter $\overline{v}_1$ is the partial molar (or molal) volume of the solvent (cm^3/mole), and $\overline{v}_2$ is the partial molar (or molal) volume of the polymer (cm^3/mole). Generally, it is assumed that the partial molar volumes, $\overline{v}_1$ and $\overline{v}_2$, are equal to the molar volumes, v_1 and v_2, of the pure components.

Although Flory-Huggins theory first demonstrated the importance of the entropy term for solutions of components differing in size, experimentation showed that the enthalpy of mixing was still important for many systems. Therefore, Flory and Huggins expanded their theory to include the enthalpy of mixing, which they related to the difference in solubility parameters of the solution components (binary systems). Flory-Huggins theory was the-first "complete" theory for polymer solutions.

If a term to account for the enthalpy of mixing, deviations from complete randomness of mixing, and other factors is added to Equation 18, the Flory-Huggins equation may be written as follows:

$$\ln a_1 = \ln \phi_1 + (1-v_1/v_2)\phi_2 + \chi\phi_2^2 \qquad (19)$$

where χ is the Flory interaction parameter for the polymer/solvent system. The Flory interaction parameter can be related to Hildebrand's solubility parameters by the following equation:

$$\chi = (v_1/RT)(\delta_1-\delta_2)^2 \qquad (20)$$

where R is the universal gas constant (cal/K·mole), T is the absolute temperature (K), δ_1 is the solubility parameter of the solvent [(cal/cm^3)$^{1/2}$], and δ_2 is the solubility parameter of the polymer [(cal/cm^3)$^{1/2}$]. Flory-Huggins theory will account for polymer swelling; however, Equation 18 was derived assuming no volume change on mixing, which may not hold for highly swelling systems.

If we assume that $(1-v_1/v_2) = 1$ for high-molecular-weight polymers and given that $\phi_1+\phi_2 = 1$, Equation 19 becomes:

$$\ln a_1 = \ln \phi_1 + (1-\phi_1) + \chi(1-\phi_1)^2 \qquad (21)$$

Huggins (63) has shown that if χ is larger than a critical value given by:

$$\chi_c = (1/2)\left[1 + (\overline{v}_1/\overline{v}_2)^{1/2}\right]^2 \qquad (22)$$

then the calculated curve for activity, a_1, versus the mole fraction of polymer, x_2, (or versus ϕ_2 or C_2, where C_2 equals the concentration of the polymer in the solution in moles/cm^3) exhibits a minimum and a maximum, indicating a phase separation. Examination of Equation 22 shows that the limiting value of χ_c is 0.5 for high-molecular-weight polymers. Thus, for polymer/solvent systems, a phase separation (that is, a finite solubility) can be expected when $\chi > 0.5$. (When $\chi < 0.5$, the solvent and the polymer will be miscible in all proportions if the theory is applicable. At values of $\chi=0.5$, the behavior will be uncertain.)

For the case when a phase separation occurs, $a_1=1$, and Equation 21 reduces to:

$$0 = \ln \phi_1 + (1-\phi_1) + \chi(1-\phi_1)^2 \qquad (23)$$

The concentration of the solvent, C_1, in moles/cm^3 of unswollen polymer is related to ϕ_1 by the following equation:

$$C_1 = [\phi_1/(1-\phi_1)]/\nu_1 \qquad (24)$$

Thus, if χ is known, ϕ_1 can be calculated using Equation 23 and an iterative computation on a computer. The concentration C_1, which can be calculated using Equation 24, will equal the solubility of the solvent in the polymer.

As discussed above, the Flory interaction parameter, χ, for nonpolar systems can be calculated using Hildebrand's solubility parameters. A refinement of solubility theory involves the use of three-dimensional solubility parameters where δ is given by

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (25)$$

where δ_d is for dispersion forces, δ_p is for polar effects, and δ_h is for hydrogen bonding. The use of three-dimensional solubility parameters in the calculation of χ should make Flory-Huggins theory more applicable for polar systems.

The Flory interaction parameter depends on the difference in Hildebrand's solubility parameters (Equation 20). However, there is some disagreement over the calculation of the "difference" in solubility parameters when three-dimensional solubility parameters are used. For example, Bomberger and coworkers (6) reported a so-called "separation in solubility space," A, for various solvents in polymeric glove materials. They stated that the A values which they reported were calculated by Henriksen (64) or by themselves using the following equation:

$$A = [(\delta_d^p - \delta_d^\ell)^2 + (\delta_p^p - \delta_p^\ell)^2 + (\delta_h^p - \delta_h^\ell)^2]^{1/2} \qquad (26)$$

where the p and ℓ superscripts refer respectively to the polymer and the liquid solvent. Even though Equation 26 is often used (56) to define A, the equation actually used by Henriksen is:

$$A' = [4(\delta_d^p - \delta_d^\ell)^2 + (\delta_p^p - \delta_p^\ell)^2 + (\delta_h^p - \delta_h^\ell)^2]^{1/2} \qquad (27)$$

where the factor of 4 is added to provide a spherical interaction volume.

Hansen and Beerbower (65) have suggested another method for calculating the "difference" in solubility parameters. They state that δ_p and δ_h are not really separable and, therefore, the following equation should be used:

$$A'' = [(\delta_d^p - \delta_d^\ell)^2 + 0.250(\tau^p - \tau^\ell)^2]^{1/2} \qquad (28)$$

where $\tau = (\delta_p^2 + \delta_h^2)^{1/2}$.

Calculation of Solubilities

Table 8 contains A, A', and A'' values calculated using Equations 26, 27, and 28, respectively, for a given set of solvents and natural rubber. These values were calculated using three-dimensional solubility parameters reported

TABLE 8. VALUES OF A, A', AND A" FOR SELECTED
SOLVENTS AND NATURAL RUBBER[a]

Solvent	A, $(cal/cm^3)^{1/2}$	A', $(cal/cm^3)^{1/2}$	A", $(cal/cm^3)^{1/2}$
Methanol	9.1	9.5	4.7
Ethanol	7.0	7.3	3.6
Isopropanol	5.1	5.6	2.8
n-Butanol	4.7	5.2	2.6
n-Pentanol	3.7	4.3	2.1
Benzyl alcohol	3.8	3.8	1.9
n-Propanol	5.6	6.0	3.0
Acetone	4.3	5.0	1.9
2-Ethyl-1-butanol	3.5	4.2	2.1
t-Pentanol	5.2	6.6	3.1
Diethyl carbonate	1.1	1.9	0.91
Methyl ethyl ketone	3.7	4.3	1.4
Ethyl acetate	2.1	3.1	1.3
n-Propyl acetate	3.7	5.2	2.3
n-Hexane	4.0	5.0	2.5
n-Heptane	3.9	4.7	2.4
Tetralin	2.2	2.4	1.1
Cyclohexane	3.6	3.9	1.9
Cyclohexanone	2.3	2.4	0.35
Toluene	2.5	2.5	1.2
Tetrachloroethylene	3.1	3.1	0.31
Carbon tetrachloride	3.4	3.4	1.7
Trichloroethylene	1.0	1.1	0.38

[a]The separation in solubility space A was calculated using Equation 26.
A' and A" were calculated using Equations 27 and 28, respectively.

by Hansen and Beerbower or by Barton (56). In most cases, the A and A' values in Table 8 are the same or very close, but significant differences are still observed for a couple of the solvents. Large variations are observed when the A" values are compared to the A and A' values.

Equation 20 [written $\chi = (v_1/RT)A^2$] and the A, A', and A" values given in Table 8 were used to calculate χ, χ', and χ'' values, respectively, at 298 K to be used in Equation 23. This latter equation was then solved for ϕ_1, ϕ_1', and ϕ_1'' values from which C_1, C_1', and C_1'' values were calculated using Equation 24. The prime superscript indicates that A' was used in the calculations, and the double-prime superscript indicates that A" was used in the calculations. The results of these calculations are given in Table 9. This table also includes solubilities (specified by C_{exp}) directly calculated from experimental volume-fraction data reported by Paul and coworkers (48).

Comparison of the C_1, C_1', and C_1'' values in Table 9 shows that C_1 and C_1' are generally similar, while C_1'' is considerably greater. Comparison of the calculated values with the literature values can be made by visual inspection of Figures 1, 2, and 3, which present C_1, C_1', and C_1'', respectively, versus C_{exp}. The solid line in each plot represents C_1 equal to C_{exp} for all possible values of C_{exp}. The dashed lines define the range of possible calculated values which fall within one order of magnitude greater than or less than the experimental values. Figures 1, 2, and 3 all have approximately the same number of calculated values within the dashed lines. The C_1 and C_1' values are generally smaller than the corresponding C_{exp} values, while the C_1'' values are generally larger. Overall, the C_1 and C_1' values are better than the C_1'' values for the less soluble solvents, but the C_1 and C_1' values become more scattered for the more soluble solvents. The C_1'' values appear to be better for the soluble solvents. The prediction of miscibility in all proportions or "infinite solubility" occurs more often for the C_1'' values, indicating that the C_1'' values could possibly be used to screen out highly soluble solvents when evaluating natural rubber as a protective-glove material.

An example of the dependence of the estimated solubility on the technique used to calculate the separation in solubility space is given by the values listed in Table 9 for the solubility of t-pentanol in natural rubber: 0.0000223, 0.00000110, and 0.000929 moles/cm³. As another example, the use of Equations 26 and 27 resulted in relatively low solubilities (0.000699 and 0.000308 moles/cm³, respectively) for methyl ethyl ketone in natural rubber. However, the use of Equation 28 resulted in the prediction that methyl ethyl ketone and natural rubber should be miscible in all proportions.

For the entire data set in Table 9, Equation 26 resulted in solubilities in error by factors from 1.5 to 280 and a linear-regression correlation coefficient of 0.15 (when compared to the experimental solubilities

TABLE 9   SOLUBILITIES CALCULATED FOR VARIOUS SOLVENTS IN
NATURAL RUBBER[a] (BASED ON FLORY-HUGGINS THEORY
AND SOLUBILITY PARAMETERS)

Solvent	Literature solubility[b] $10^5 \times C_{exp}$	Calculated solubility[c,d] $10^5 \times C_1$	$10^5 \times C_1'$	$10^5 \times C_1''$
Methanol	4.92	3.21	1.88	392
Ethanol	8.59	5.37	3.21	394
Isopropanol	52.8	18.7	9.21	604
n-Butanol	125	14.3	6.99	475
n-Pentanol	130	34.5	13.7	724
Benzyl alcohol	142	35.0	35.0	2630
n-Propanol	146	9.33	5.25	439
Acetone	169	64.2	26.7	--
2-Ethyl-1-butanol	259	28.1	8.48	483
t-Pentanol	437	2.23	0.110	92.9
Diethyl carbonate	636	--	858	--
Methyl ethyl ketone	713	69.9	30.8	--
Ethyl acetate	766	1400	151	--
n-Propyl acetate	1270	28.4	1.74	363
n-Hexane	1540	8.57	1.15	152
n-Heptane	1580	5.71	1.00	135
Tetralin	3330	266	157	--
Cyclohexane	3380	39.7	25.9	1380
Cyclohexanone	3410	489	429	--
Toluene	3870	299	284	--
Tetrachloroethylene	4240	136	127	--
Carbon tetrachloride	5370	94.8	88.9	--
Trichloroethylene	5690	--	--	--

[a]The concentrations (solubilities) reported are in units of
moles/cm^3 of unswollen polymer at 298 K.

[b]These values are calculated from the experimental volume-fraction data
given in Reference 48

[c]These values are calculated using Flory-Huggins theory. The term C_1 means
that Equation 26 was used to calculate the separation in solubility
space. C_1' corresponds to Equation 27, and C_1'' corresponds to Equation 28.

[d]The symbol "--" means that no solubility could be calculated, because
these systems are predicted to be miscible in all proportions.
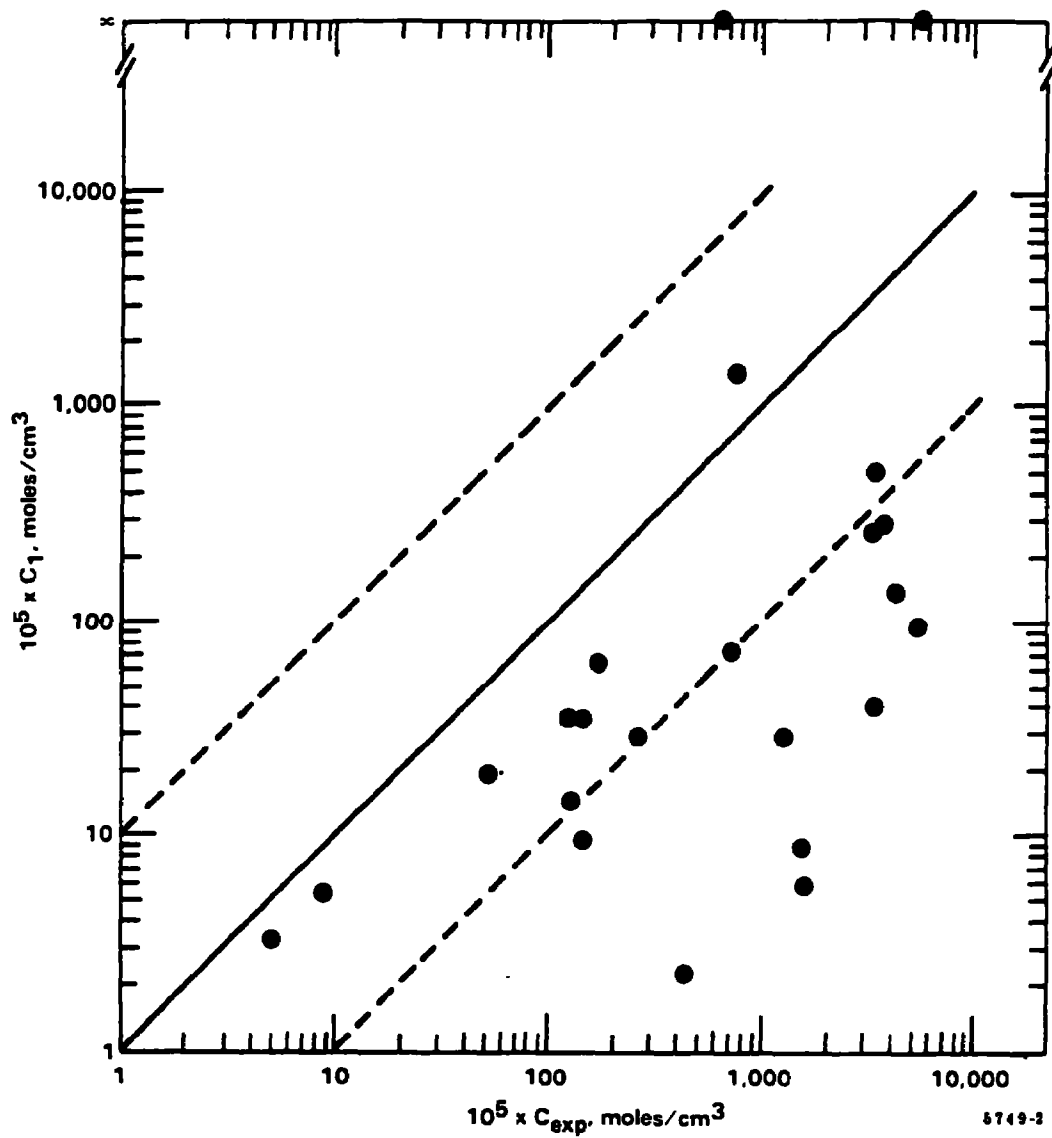
Figure 1. Comparison of solubilities calculated using Flory-Huggins theory, C_1, with experimental solubilities, C_{exp}.
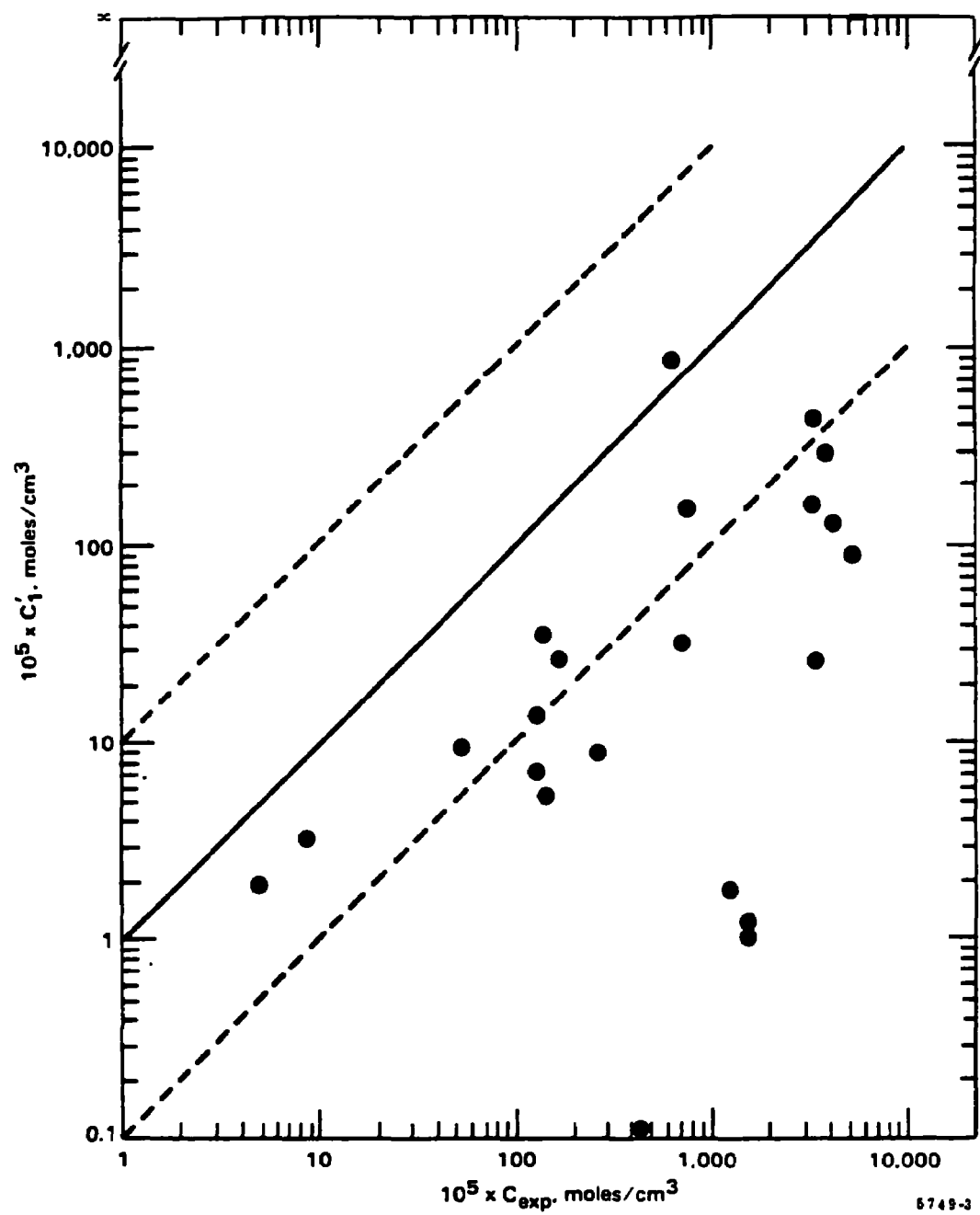
Figure 2. Comparison of solubilities calculated using Flory-Huggins theory, C'_1, with experimental solubilities, C_{exp}
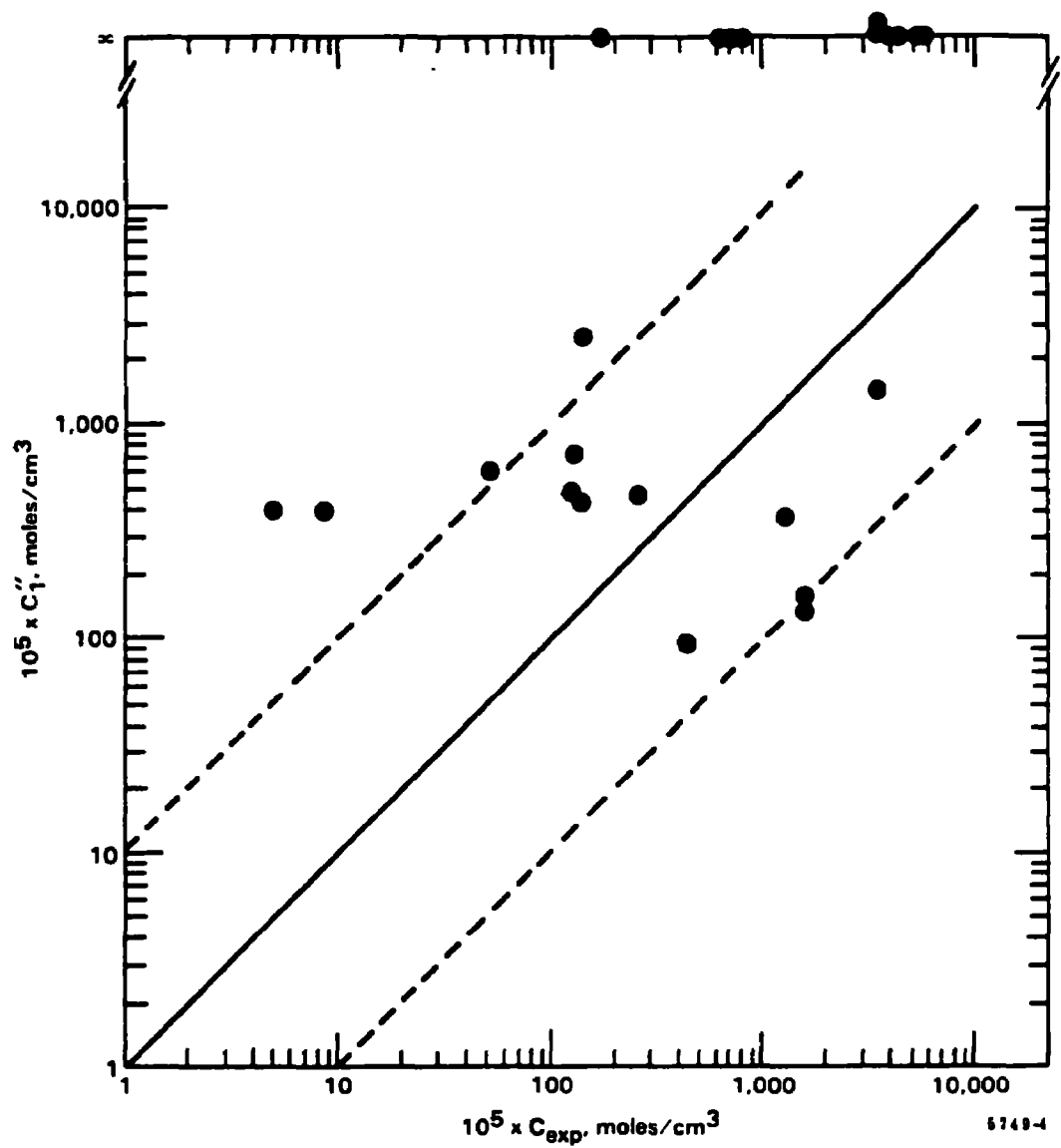
Figure 3. Comparison of solubilities calculated using Flory-Huggins theory, C''_1, with experimental solubilities, C_{exp}

included in.the table). Equation 27 resulted in solubilities in error by factors from 1.3 to 4000 and a correlation coefficient of 0.23. Equation 28 resulted in solubilities in error by factors from 1.9 to 80 and a correlation coefficient of 0.073.

Because of the poor correlation of the calculated solubilities with the experimental solubilities, the development of a method based on Flory-Huggins theory and solubility parameters for the estimation of solubilities was not pursued further.

UNIFAP THEORY

Discussion of the Theory

The UNIFAP equations, like the Flory-Huggins equation, model liquids as being in a solid-like or quasicrystalline state. In other words, both approaches are based on lattice theories. These theories propose that molecules of a liquid are fixed in an ordered arrangement and that the behavior of the liquid depends on the molecules' interactions with their neighbors. If the molecules show no preference in the selection of their neighbors, then a completely random mixture exists, that is, ideal conditions are present. However, this rarely occurs, and Guggenheim proposed in his quasichemical theory of liquid mixtures to correct for this nonideality (66). He described the behavior of nonrandom systems with equally sized molecules. Flory and Huggins independently used lattice theory to predict the behavior of mixtures whose molecules varied in size but were chemically similar (66,67). Their work resulted in a relatively simple one-parameter equation. However, because of the strong dependence of the Flory interaction parameter on composition and several assumptions made in the derivation of the Flory-Huggins equation, it does not give a good quantitative description of solubility.

Wilson extended Flory and Huggins' work by examining the interactions between different molecules (68). His semiempirical approach is based on the local composition concept, which assumes that a liquid is not homogeneous on a molecular level. Therefore, the energies of interactions are significant and must be taken into account. Wilson accounted for molecular interactions by including two adjustable parameters for each pair of molecules in his equation.

Abrams and Prausnitz's universal quasichemical equation, UNIQUAC (universal quasichemical activity coefficients), uses local area fractions instead of local mole fractions as used in the Wilson equation (68). UNIQUAC provides no major improvements over the Wilson equation for predicting the behavior of completely miscible vapor/liquid systems, but it allows a prediction of the behavior of liquid/liquid systems, even liquid/liquid systems with more than two components. As in the Wilson equation, UNIQUAC uses only two adjustable parameters for each pair of molecules, and with several specific assumptions, the UNIQUAC equation reduces to the Flory-Huggins equation or any of the well-known equations derived from Guggenheim's work.

47

Fredenslund et al. (69,70) combined UNIQUAC with the solution-of-groups concept that a physical property can be predicted by summing the effects of the functional groups (that is, the structural units) comprising the compound. The resulting model, UNIFAC (UNIQUAC Functional-group Activity Coefficients), contains two adjustable parameters per pair of functional groups instead of containing two adjustable parameters per pair of molecules as in UNIQUAC. Compared to UNIQUAC, this significantly reduces the number of interaction parameters required to apply the model, because the number of possible functional groups is much smaller than the number of existing compounds. Furthermore, this allows a quantitative description of the behavior of systems for which no experimental data are available but that contain functional groups whose energies of interaction have been experimentally determined. However, this extrapolation technique holds only if the behavior of any given group is not affected by the presence of the other groups within the molecule. Often this assumption is not true; thus, UNIFAC is an approximate method.

As in the Flory-Huggins equation, the UNIFAC equation used to calculate the liquid-phase activity coefficient for a given component consists of an entropy term or a combinatorial part, resulting from the differences in the size and shape of the functional groups in the mixture, and an enthalpy term or residual part, resulting from the interaction energies between the functional groups.

The combinatorial part of the UNIFAC equation is calculated from the functional-group parameters known as normalized van der Waals group volumes and interaction surface areas. These parameters are determined independently from pure component, atomic and molecular structure data (70).

The residual part of the UNIFAC equation depends on the "concentrations" of the functional groups and the interactions between the groups. Therefore, the solution-of-groups concept plays an important part in calculating this term. In addition, the residual term resembles the Wilson equation written in terms of area and segment fractions.

The group-interaction parameters, a_{nm}, in the residual part of the model characterize the energy of interactions between the functional groups n and m. They have the units of Kelvin, and for interactions between a given pair of functional groups, there exist two distinct parameters (that is, $a_{nm} \neq a_{mn}$). These parameters are determined empirically from experimental vapor/liquid equilibrium data. An extensive compilation of such data are available on magnetic tape from the University of Dortmund (Dortmund, West Germany); the Dortmund data base contains vapor/liquid equilibrium data for systems meeting the following requirements (70): the pressure is less than 15 atm, and the components only consist of water or organic compounds with a normal boiling point higher than 273 K. Fortunately, tables of group-interaction parameters are available in the literature (71-73).

As more phase-equilibrium data for vapor/liquid systems become available, it is possible to estimate previously missing interaction parameters and to improve the estimation of the parameters that were based on very limited data (71).

The UNIFAC model has two significant advantages: It is very simple because the interaction parameters are not very strong functions of temperature and pressure within the range of applicability; it is also very flexible and, thus, very easily applied to a large number of systems because UNIFAC parameters are available for a large number of different functional groups.

Overall, UNIFAC has been proven to predict satisfactorily activity coefficients in a large number of systems. However, UNIFAC does have limitations (74). It can only be applied when:

- The pressure is no more than a few atmospheres.

- All components are well below their critical points.

- The temperature of interest is in the range of .300 to 425 K (80 to 300 °F).

- No noncondensables or electrolytes are contained in the system.

- No immiscible liquids are contained in the system.

- No polymers are contained in the system.

- Only components that contain ten or less different UNIFAC functional groups are present.

Oishi and Prausnitz (75) extended UNIFAC to the calculation of solvent activities in polymer solutions, and they referred to the modified theory as UNIFAP (UNIFAC for polymer systems). They began by working in terms of activities rather than activity coefficients; they felt mole fractions were "awkward units" of concentration for polymer solutions because of the much larger molecular weight of the polymer versus the solvent. In addition, they added another contribution term to the model to take into account the changes in free volume caused by mixing the solvent and the polymer. Thus, the activity of the solvent is determined by

$$\ln a_1 = \ln a_1^c + \ln a_1^r + \ln a_1^{fv} \qquad (29)$$

where a_1^c is the combinatorial activity (an entropy term), a_1^r is the residual activity (an enthalpy term), and a_1^{fv} is the free-volume activity.

The equations necessary to apply the UNIFAP model are tedious. An excellent summary of the equations and an illustrative calculation are given in Reference 75. A copy of the UNIFAP software package written by Oishi and Prausnitz, which is based on the equations given in Reference 75, is available from the Friends of Chemical Engineering (University of California, Berkeley, CA).

In general, the UNIFAP (UNIFAC for polymer systems) model has been proven to predict activities satisfactorily for polymer/solvent systems (75,76). However, as in the case of UNIFAC, the independence of the interaction parameters to changes in temperature and to the effects of other functional groups contained in the system may not always be a valid assumption. Thus,

49

accounting for such effects in the determination of the group-interaction parameters would greatly improve the reliability of UNIFAP in predicting solubility (76).

Calculation of Solubilities

The UNIFAP software obtained from the Friends of Chemical Engineering yields activities at specific volume fractions. The UNIFAP software was modified slightly to determine activities for various solvent volume fractions. The modified software allows the determination of the volume fraction of the solvent that yields an activity of one (that is, $a_1=1$). Therefore, the solubility of the solvent in a polymer can be determined.

Using the modified UNIFAP program, solubilities, C_{uni}, for various solvents in natural rubber at 298 K were calculated. In general, the temperature of the system, the densities of the solvent and the polymer, and the functional groups comprising the solvent and the polymer were the only required inputs of this method. From these inputs, a solvent volume fraction was generated at the saturation condition (that is, for $a_1=1$). Finally, this volume fraction, ϕ_1, was converted to solubility, C_{uni}, in units of moles/cm^3 of unswollen polymer by using the following equation:

$$C_{uni} = [\phi_1/(1-\phi_1)]/v_1 \tag{30}$$

where v_1 is the molar volume of the solvent.

The data used in the UNIFAP calculations of solubilities are listed in Table 10. The UNIFAP results and experimental solubilities, C_{exp}, reported by Paul et al. (48) are given in Table 11. In addition, the calculated values and the experimental values are compared graphically in Figure 4. Several types of regressions were performed on the data, but a linear regression provided the best fit with a correlation coefficient, r, equal to 0.92. The equation given in Figure 4 indicates that solubilities calculated using the UNIFAP model are generally less than experimental values by about a factor of two (except for very low solubilities and solubilities that indicate miscibility in all proportions). Future work using UNIFAP should address this systematic error.

As shown by the results in Table 11, the equilibrium solubilities for some polymer/solvent combinations (for example, acetone or n-pentanol in natural rubber) can be described accurately by the UNIFAP model. However, solubilities for many of the systems given can only be determined within a factor of five. This error probably results from inaccuracies in the group-interaction parameters in the data base used in performing the calculations or the breakdown of some of the assumptions on which UNIFAP is based.

50

TABLE 10. SOLVENT DATA USED IN UNIFAP CALCULATIONS

Solvent	Molecular weight, g/mole	Density,[a] g/cm^3	Functional groups[b]
Acetone	58.08	0.788	1 CH_3, 1 CH_3CO
Benzyl alcohol	108.1	1.05	5 ACH, 1 $ACCH_2$, 1 OH
n-Butanol	74.12	0.810	1 CH_3, 1 CH_2, 1 OH
t-Butanol	74.12	0.786	3 CH_3, 1 C, 1 OH
Carbon tetrachloride	153.8	1.59	1 CCl_4
Cyclohexane	84.16	0.778	6 CH_2
Cyclohexanone	98.14	0.948	5 CH_2, 1 CH_2CO
Diethyl carbonate	118.3	0.976	2 CH_3, 1 CH_2O, 1 CH_2COO
Ethanol	46.06	0.816	1 CH_3, 1 CH_2, 1 OH
Ethyl acetate	88.10	0.902	1 CH_3, 1 CH_2, 1 CH_3COO
2-Ethyl-1-butanol	102.2	0.833	2 CH_3, 3 CH_2, 1 CH, 1 OH
n-Heptane	100.2	0.684	2 CH_3, 5 CH_2
n-Hexane	86.17	0.660	2 CH_3, 4 CH_2
Isopropanol	60.09	0.785	2 CH_3, 1 CH, 1 OH
Methanol	32.04	0.792	1 CH_3OH
Methyl ethyl ketone	72.10	0.805	1 CH_3, 1 CH_2, 1 CH_3CO
n-Pentanol	88.15	0.815	1 CH_3, 4 CH_2, 1 OH
t-Pentanol	88.15	0.808	3 CH_3, 1 CH_2, 1 C, 1 OH
n-Propanol	60.09	0.805	1 CH_3, 2 CH_2, 1 OH
n-Propyl acetate	102.1	0.836	1 CH_3, 2 CH_2, 1 CH_3COO
Tetrachloroethylene	165.9	1.62	1 C=C, 4 Cl(C=C)

(continued)

TABLE 10 (continued)

Solvent	Molecular weight, g/mole	Density,[a] g/cm^3	Functional groups[b]
Tetralin	132.2	0.970	4 CH_2, 4 ACH, 2 AC
Toluene	92.13	0.866	5 ACH, 1 $ACCH_3$
Trichloroethylene	131.4	1.46	1 CH=C, 3 Cl(C=C)

[a]These are the densities at 298 K.

[b]The symbol AC designates an aromatic carbon.

TABLE 11. SOLUBILITIES CALCULATED FOR VARIOUS SOLVENTS IN NATURAL
RUBBER[a,b] (BASED ON "VAPOR/LIQUID" UNIFAP THEORY)

Solvent	10^5 x C_{uni}, moles/cm^3	10^5 x C_{exp}, moles/cm^3
Methanol	26.5	4.92
Ethanol	42.4	8.59
Isopropanol	81.6	52.8
n-Butanol	93.3	125
n-Pentanol	103	130
Benzyl alcohol	27.5	142
n-Propanol	100	146
Acetone	185	169
2-Ethyl-1-butanol	114	259
t-Butanol	81.5	414
t-Pentanol	96.9	437
Diethyl carbonate	202	636
Methyl ethyl ketone	271	713
Ethyl acetate	411	766
n-Propyl acetate	581	1270
n-Hexane	*	1540
n-Heptane	*	1580
Tetralin	*	3330

(continued)

TABLE 11 (continued)

Solvent	$10^5 \times C_{uni}$, moles/cm^3	$10^5 \times C_{exp}$, moles/cm^3
Cyclohexane	*	3380
Cyclohexanone	*	3410
Toluene	*	3870
Tetrachloroethylene	*	4240
Carbon tetrachloride	*	5370
Trichloroethylene	*	5690

[a]The UNIFAP calculations of the solubilities at 298 K were performed using group-interaction parameters estimated by fitting vapor/liquid phase equilibrium data to the UNIFAC equations.

[b]The symbol "*" indicates that an activity of one was achieved only for a solvent volume fraction equal to one. Thus, the polymer and the solvent are predicted to be miscible in all proportions.
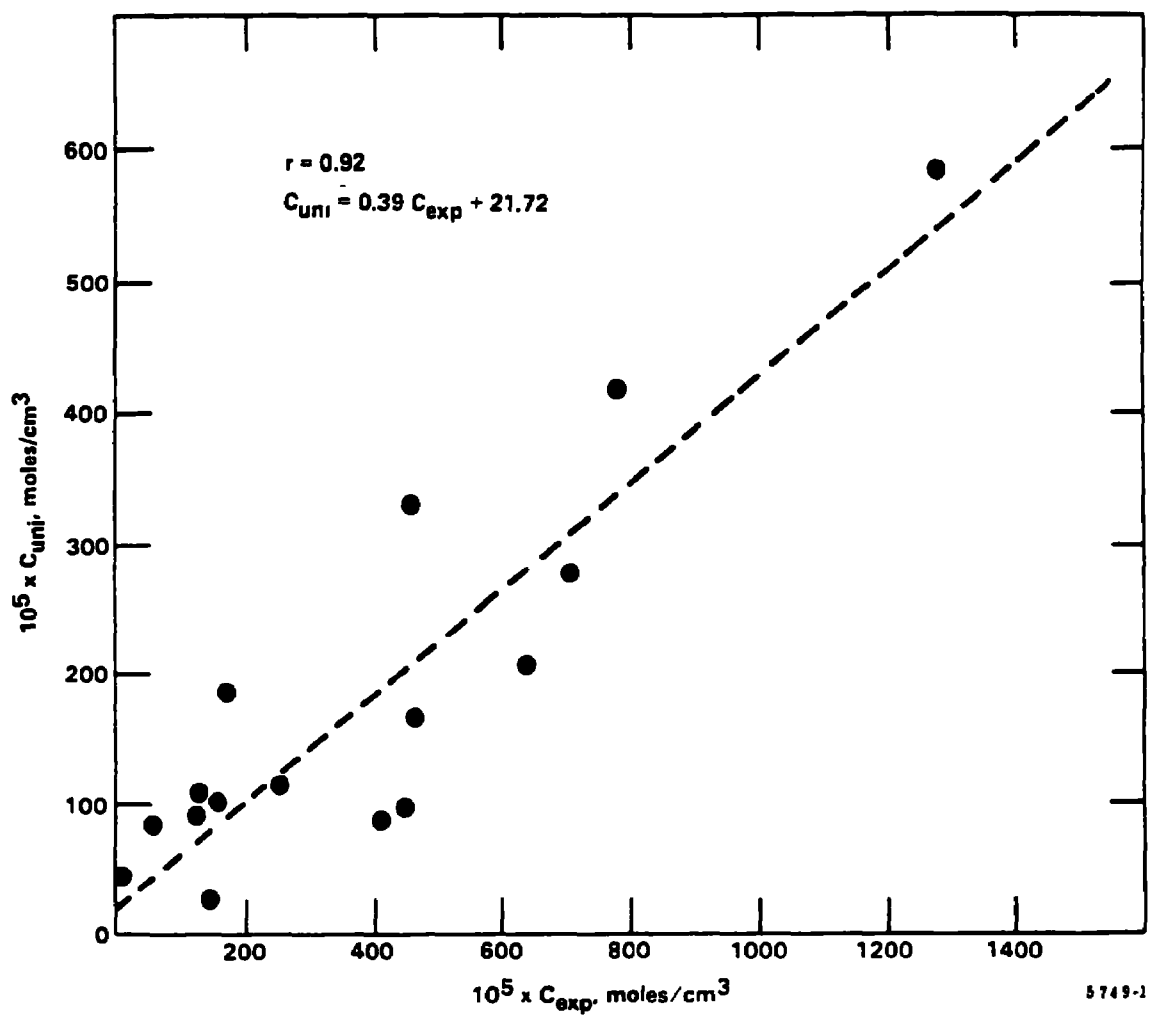
Figure 4. Comparison of solubilities calculated using vapor/liquid UNIFAP, C_{uni}, with experimental solubilities, C_{exp}.

55

It should be noted that the error in the UNIFAP results given here is most significant in comparison to very small and very large experimental solubilities. In fact, at extremely large solubilities, an activity of one (which is indicative of reaching equilibrium and, thus, defines the solubility) is achieved only for a solvent volume fraction equal to one. Thus, at large solvent concentrations, UNIFAP predicts a greater solubility than is actually observed experimentally. This phenomenon is expected because the UNIFAP calculations do not take into account the amount of crosslinking in a polymer, which may limit the swelling of the polymer. Rather than being a limitation, if the UNIFAP model yields an activity of one only at a solvent volume fraction of one, then the solvent and the polymer may be miscible in all proportions; that is, only one phase may exist. Therefore, the polymer probably would not be suitable as a protective barrier material for the solvent. (Nonetheless, future modifications of UNIFAP theory should consider the degree of crosslinking.)

As discussed above, the group-interaction parameters are assumed to be independent of temperature and independent of the other groups within the given molecule. However, these group-interaction parameters may not be constant, and determinations of the dependence of these parameters on composition, pressure, and temperature need to be made (76). Furthermore, the data base currently being used is a table of group-interaction parameters obtained by fitting experimental vapor/liquid phase-equilibrium data to the UNIFAC equations. Theoretically, the parameters and equations used for the prediction of a vapor/liquid system's behavior at equilibrium also can be used for the prediction of a liquid/liquid system's behavior at equilibrium (77). And it has been shown that group-interaction parameters determined from vapor/liquid equilibrium data typically give a deviation of approximately 9 mole% (78) when used to determine equilibrium in liquid/liquid systems. However, using a UNIFAC interaction-parameter table obtained from liquid/liquid equilibrium data rather than vapor/liquid data would be expected to yield better results.

Magnussen, Rasmussen, and Fredenslund (78) presented a data base of UNIFAC group-interaction parameters for predicting liquid/liquid equilibrium behavior in 1981. These parameters were estimated by fitting experimental liquid/liquid equilibrium data measured between 283 and 313 K to the UNIFAC equations. A data base for the UNIFAP software that included these group-interaction parameters was set up. This data base was a combination of the previously listed vapor/liquid interaction parameters and the "new" liquid/liquid interaction parameters. This combination was necessary because only a limited set of reliable experimental phase-equilibrium data exists for liquid/liquid systems. If only this small liquid/liquid data base were used to calculate group-interaction parameters, then there would be an insufficient set of them. That is, predictions could be made for only a limited number of polymer/solvent systems.

Solubilities calculated for several polymer/solvent systems using this combined data base and the experimental solubilities, C_{exp}, reported by Paul et al. (48) are compared in Table 12. Several solubility predictions for individual systems were in closer agreement using liquid/liquid interaction parameters than when using vapor/liquid interaction parameters. For example, Paul experimentally determined a solubility equal to 125×10^{-5} moles/cm^3 for

TABLE 12. SOLUBILITIES CALCULATED FOR VARIOUS SOLVENTS IN NATURAL
RUBBER[a,b] (BASED ON "LIQUID/LIQUID" UNIFAP THEORY)

Solvent	10^5 x C_{uni}, moles/cm^3	10^5 x C_{exp}, moles/cm^3
Methanol	30.8	4.92
Ethanol	58.8	8.59
Isopropanol	110	52.8
n-Butanol	124	125
n-Pentanol	135	130
Benzyl alcohol	101	142
n-Propanol	138	146
Acetone	76.3	169
2-Ethyl-1-butanol	138	259
t-Butanol	105	414
t-Pentanol	197	437
Diethyl carbonate	93.0	636
Methyl ethyl ketone	101	713
Ethyl acetate	*	766
n-Propyl acetate	*	1270
n-Hexane	*	1540
n-Heptane	*	1580
Tetralin	*	3330

(continued)

TABLE 12 (continued)

Solvent	10^5 x C_{uni}, moles/cm^3	10^5 x C_{exp}, moles/cm^3
Cyclohexane	*	3380
Cyclohexanone	*	3410
Toluene	*	3870
Tetrachloroethylene	259	4240
Carbon tetrachloride	128	5370
Trichloroethylene	310	5690

[a]The UNIFAP calculations of the solubilities at 298 K were performed using group-interaction parameters estimated by fitting vapor/liquid and liquid/liquid phase-equilibrium data to the UNIFAC equations.

[b]The symbol "*" indicates that an activity of one was achieved only for a solvent volume fraction equal to one. Thus, the polymer and the solvent are predicted to be miscible in all proportions.

n-butanol in natural rubber. Using UNIFAP, solubilities were found to be 124×10^{-5} moles/cm^3 and 93.3×10^{-5} moles/cm^3 using liquid/liquid and vapor/liquid interaction parameters, respectively. However, using liquid/liquid parameters to calculate solubilities, several solvents previously determined to be totally miscible with natural rubber (using vapor/liquid parameters) were predicted to show phase separation (that is, an activity of one was obtained at a solvent volume fraction less than one). In addition, some of the predicted solubilities were low by factors as large as 42 in comparison to experimental solubilities. Also, several types of regressions were performed on the comparison of the calculated values and the experimental values, but no satisfactory correlation resulted. Therefore, it is suggested that the vapor/liquid interaction-parameter data base instead of the liquid/liquid parameter data base be used to calculate solubilities until more thermodynamically consistent liquid/liquid equilibrium data are available.

It should be noted that the selection of functional groups comprising a compound is sometimes somewhat arbitrary because the set of functional groups for which interaction parameters are available is limited. Therefore, a "best guess" of the functional groups used to construct the compound must be made. It may be possible to construct a given compound from two or more "best-guess" sets of functional groups. And the two sets of functional groups may yield very different predicted solubilities using UNIFAP. For example, using liquid/liquid interaction parameters and the functional groups 2 CH$_3$, 1 CH$_2$O, and 1 CH$_2$COO for diethyl carbonate generated an activity of one only for a solvent volume fraction equal to one; that is, no finite solubility could be predicted. However, using liquid/liquid interaction parameters and the functional groups 2 CH$_3$, 1 CH$_2$, 1 CH$_2$O, and 1 COO for diethyl carbonate generated a UNIFAP solubility equal to 93.0×10^{-5} moles/cm^3 of unswollen polymer. To eliminate such "arbitrary" choices of functional groups, the set of functional groups for which interaction parameters are available needs to be expanded.

As previously discussed, the UNIFAP model generally provides a good estimate of solubilities for many polymer/solvent systems. With improvements in estimating the values of the group-interaction parameters and in standardizing the process of selection (or definition) of the functional groups comprising the compounds, the reliability of this method will probably improve significantly.

The UNIFAP software also needs to be extended to predict the behavior of ternary and other larger systems to account for the presence of plasticizers and various other additives in glove formulations. (Because the UNIFAP model works with only functional groups, the model can describe the behavior of ternary or larger systems; however, the software to perform calculations for such systems has not yet been developed.) Furthermore, the UNIFAP model needs to take into account the possibility of the polymer being crosslinked. Currently, the model is limited to only uncrosslinked polymers. (As stated previously, this limitation accounts for the predictions of total miscibility given in Table 11 for some of the solvents in crosslinked natural rubber even though experimental solubilities less than "infinity" have been reported.)

SECTION 6

PREDICTIVE MODELS FOR THE DIFFUSION COEFFICIENT

Predicting the permeation rate of a solvent through a polymeric membrane involves solving the governing mass transport equations. If the simple diffusion theory presented in Section 3 is applicable, it is necessary only to solve Fick's first and second laws with the appropriate boundary and initial conditions. An important term appearing in Fick's laws is the diffusion coefficient. Numerous theories and correlations are reported in the literature for predicting the diffusion coefficient, D, of various substances under various conditions (79). For solvent diffusion in polymers, however, no single theory has yet been universally accepted. One of the more widely used approaches to predicting diffusion coefficients is based on free-volume theory.

Free-volume theory depends on a concept in which solvent diffusion is related to "holes" or "free volume" which exists throughout the polymer bulk. Free volume is defined as the volume in a polymer bulk not occupied by polymer molecules themselves. Because of random molecular motion, individual free-volume elements are constantly being collapsed and recreated, but the total free volume does not change as a result of this motion. If it is assumed that solvent diffusion occurs due to the random motion of solvent molecules through the free volume, then relationships can be derived to predict the diffusion coefficient. Also, because the solvent molecules will occupy the free volume as they diffuse into the polymer, free-volume theories can generally account for concentration-dependent diffusion coefficients. This capability is especially important in polymer/solvent systems.

Two diffusion theories based on free-volume concepts are discussed below. The two do not constitute the entire set of free-volume theories, but are meant to be representative of them. The first of the two theories discussed was developed by Vrentas and Duda (80-82) and is more complex than the second, which was developed by Paul (83). Because of the relative simplicity of the Paul model, its application was emphasized in the current work, the goal of which was to demonstrate the feasibility of the development of predictive models.

VRENTAS-DUDA MODEL

The Vrentas-Duda model can predict diffusion coefficients over a majority of the possible solvent volume-fraction range. Because the model uses specific information about the polymer/solvent system at small solvent volume fractions, it is especially accurate at very small solvent volume fractions ($\phi_i < 0.1$). At very large volume fractions ($\phi_i > 0.9$), free-volume concepts are no longer valid and, therefore, the Vrentas-Duda model is inaccurate. At intermediate volume fractions, the model is able to predict diffusion coefficients fairly accurately.

A major drawback to the Vrentas-Duda model, however, is the large amount of experimental data necessary to compute the diffusion coefficient, D. The data needed include:

- Ratio of the number of surface sites for the polymer segments to the number of surface sites for the solvent. (This can be estimated from molecular dimensions.)

- Energy interchange parameter. (This can be derived from enthalpy of dilution data for the mixture.)

- Entropy interchange parameter. (This can be derived from reduced, residual chemical-potential data near zero polymer segment fraction. The reduced, residual chemical-potential data are derived from chemical-potential-versus-temperature data. Polymer segment fraction refers to a parameter defined using specific volume and other characteristic data.)

- Viscosity of the solvent as a function of temperature.

- Viscosity of the polymer as a function of temperature and molecular weight.

- Specific volume of the solvent and the polymer at 0 K.

- Polymer glass-transition temperature as a function of molecular weight.

- Diffusion coefficient of the solvent in the polymer near zero solvent concentration.

- Solvent and polymer molecular weights.

A very complex series of calculations is required to estimate D using the Vrentas-Duda model. Because of the rather extensive set of required data, some of which may often be difficult to obtain, and because of the complexity of the calculations, the Vrentas-Duda model was considered less satisfactory than the Paul model for initial attempts to predict D.

PAUL MODEL

The Paul model (83) for predicting diffusion coefficients is also based on free-volume theory. One advantage of this model over the Vrentas-Duda model, however, is the relatively small amount of data needed to calculate the diffusion coefficient. These data include:

- Viscosity of the solvent as a function of temperature.

- Density (or specific volume) of the solvent as a function of temperature.

- Density (or specific volume) of the solvent and the polymer at the temperature of interest and at absolute zero (0 K).

- Critical volume of the solvent (see Appendix B).

- Molecular weight of the solvent and the polymer.

- Solvent chemical potential as a function of solvent volume fraction. [These data can be derived from UNIFAP data (see Appendix B)].

Given the data listed above and the following assumptions (which represent a modification of Paul's model), diffusion coefficients can be calculated.

- The average solvent molecular velocity is proportional to $T^{1/2}$.

- The free volume is randomly distributed among all units of mass in the solution.

- The only volume which is not freely distributed is the molecular volume and the interstitial volume associated with a random packing of the molecules. (The molecular volume and the associated interstitial volume is approximated by the volume at 0 K.)

- Polymer segments have a negligible chance of refilling a void space compared to a solvent molecule. (This assumption makes the Paul model less accurate for solvent volume fractions less than 0.1).

- The polymer self-diffusion coefficient is negligible.

- The excess volume of mixing is zero at all concentrations.

- The polymer is nonglassy and, thus, above its glass transition temperature.

A detailed derivation of the modified Paul model is given in Appendix B. A computer program written to perform the necessary calculations is also included in this appendix.

The concentration-dependence of the diffusion coefficient for benzene in natural rubber at 298 K, calculated using the modified Paul model; is illustrated in Figure 5. Similar data for n-heptane in natural rubber at 298 K are shown in Figure 6. The input data used to perform these calculations are given i Appendix B. (The UNIFAP calculations that were necessary used the vapor/liquid data base.)
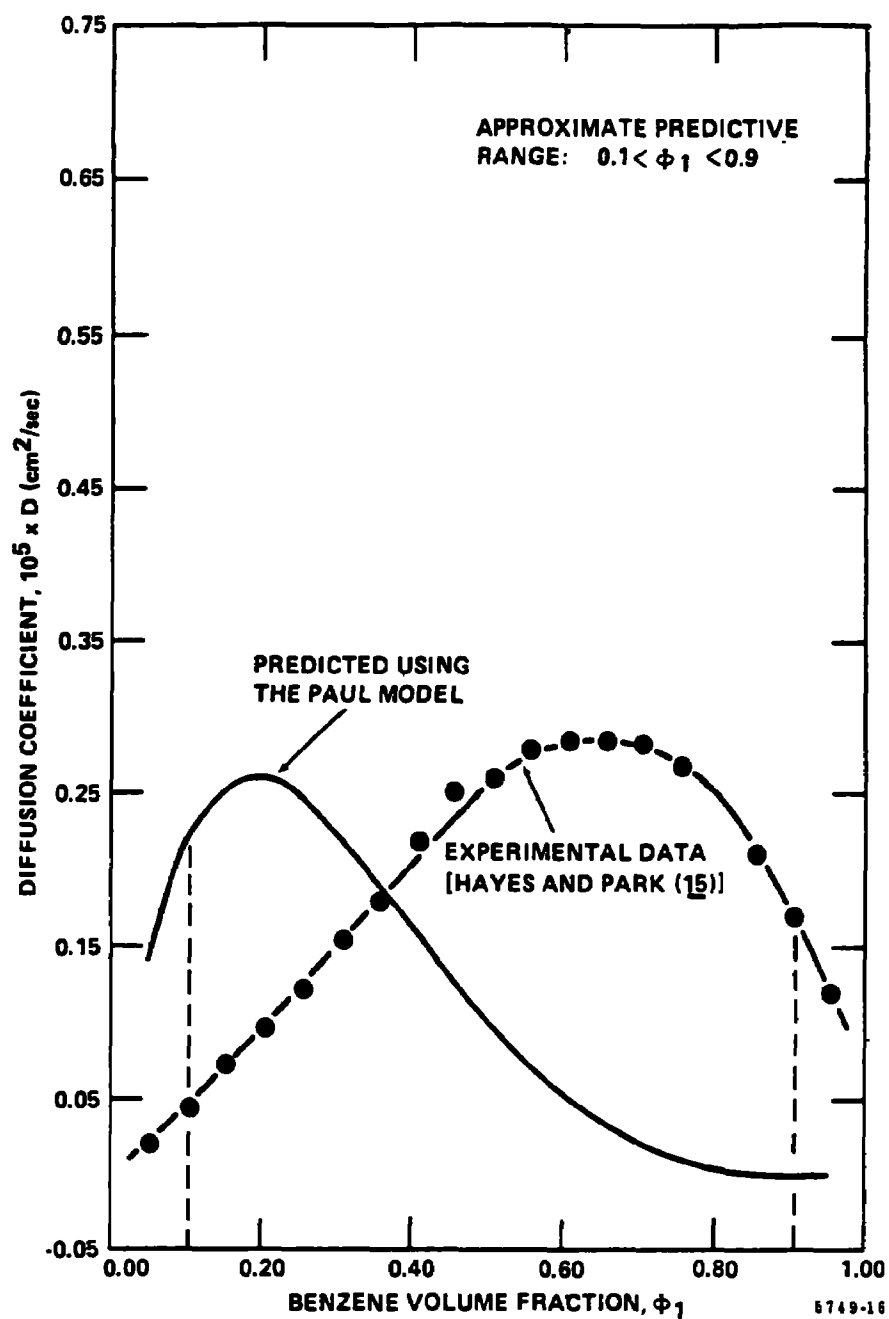
Figure 5. Diffusion coefficient of benzene in natural rubber as a function of volume fraction.
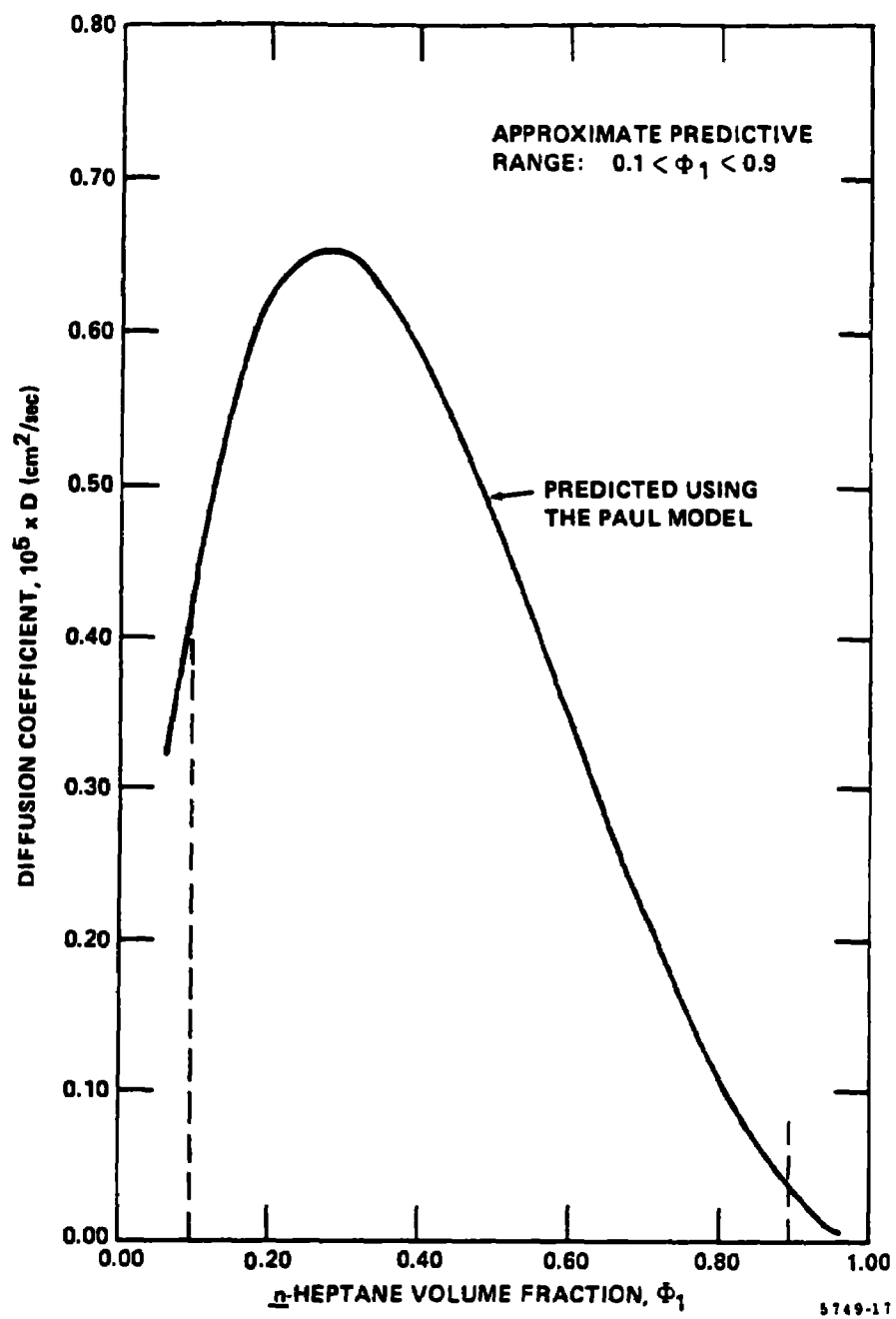
Figure 6. Diffusion coefficient of n-heptane in natural rubber as a function of volume fraction

Figure 5 also shows an experimental curve reported by Hayes and Park (51) for benzene in natural rubber at 298 K. The maximum value of D reported is close to the value predicted by the modified Paul model. However, the volume fraction at which the maximum occurs is not in agreement; the theoretical curve ·appears to be shifted to the left. No plausible explanation has yet been developed for this disagreement.

D.R. Paul (45) reported experimental diffusion coefficients for benzene and n-heptane in natural rubber of 2.37×10^{-6} cm^2/sec and 3.07×10^{-6} cm^2/sec, respectively, at 303 K; the diffusion coefficient for benzene was determined at a volume fraction of 0.8, and the diffusion coefficient for n-heptane was determined at a volume fraction of 0.7. The modified Paul model predicts that the diffusion coefficients are 2.72×10^{-8} cm^2/sec for benzene and 2.71×10^{-6} cm^2/sec for n-heptane at volume fraction of 0.8 and 0.7, respectively. Comparison of D.R. Paul's reported diffusion coefficients with those calculated using the modified Paul model suggests that the model has only limited applicability. However, much more extensive evaluations of the Paul model must be made before discarding it in favor of more sophisticated models.

The predicted D-versus-ϕ_1 curves in Figures 5 and 6 exhibit a maximum, a phenomenon observed experimentally by others (51,81,84,85). The curves also suggest that the solvent diffusion coefficient approaches zero as the solvent volume fraction approaches one. Because free-volume theory requires a considerable amount of polymer-polymer contact, this result is not surprising. Below a minimum polymer volume fraction, the concept of free-volume within a polymer bulk is no longer valid (81). For small polymer volume fractions, theories for dilute and infinitely dilute polymer concentrations are valid. Berry and Fox (86) report that the minimum polymer mass fraction, which may be related to volume fraction, for which free-volume calculations are acceptable is given by:

$$w_2 = 4/(1 + 0.2 \ MW_2^{1/2}) \tag{31}$$

where MW_2 is the molecular weight of the polymer. For natural rubber, the polymer molecular weight is approximately 68,100, assuming a degree of polymerization of 1000. Thus, the minimum polymer mass fraction for which free-volume calculations are valid for natural rubber is about 0.08.

On first examination, use of the modified Paul model appears to be a limited approach to predicting diffusion coefficients. However, because only benzene/natural-rubber predictions were checked with D-versus-ϕ_1 experimental data, no firm conclusions can yet be drawn. Future work should include extensive checking of the model against experimental data. Because of the relatively small amount of experimental data reported in the literature, the thorough confirmation of the model will be difficult without experimentally determining diffusion-coefficient data for a series of solvents in a variety of polymers. An alternative is to use diffusion-coefficient data calculated with the Paul model and solubility data to calculate permeation-rate-versus-time

65

curves (see Section 7). By comparing these data to experimental permeation-rate curves, the Paul model could be indirectly confirmed or refuted. Criteria such as defined breakthrough times, lag times, and steady-state permeation rates calculated from the predicted permeation-rate curves could also be compared to experimental data to indirectly confirm the modified Paul model.

SECTION 7

PREDICTIVE TEST METHODS FOR SOLUBILITY AND
THE DIFFUSION COEFFICIENT

Under Task II of the contract, two potential predictive test methods that could be used to estimate the solubility and diffusion coefficient of an organic liquid in a polymeric glove material were investigated. Permeation tests for selected glove/solvent combinations were also conducted to generate data that could be used to demonstrate the validity of the predictive methods studied.

SELECTION OF PREDICTIVE TEST METHODS

As discussed in Section 3 of this report, the most accurate, precise, and reliable method for "predicting" the permeation rate of an organic liquid through a glove material as a function of time is a direct permeation test, such as ASTM Method F739. However, the apparatus that is needed to perform permeation tests may be costly and conceptually complex; thus, such tests must usually be performed by well-trained chemical professionals. The major components of a permeation-test system include a permeation test cell; a gas or liquid stream or reservoir to collect the solvent after it permeates through the test sample; a sophisticated, sensitive, and usually expensive analytical instrument for quantifying the solvent, and possibly a temperature-control system. For these reasons, it is desirable to develop alternative predictive test methods that are simpler and less expensive than direct permeation tests and that can be performed by personnel with less technical training than is normally required for permeation testing.

The first step in the selection of alternative methods was a review of the existing standard test methods for evaluating chemical-protective clothing. The test methods reviewed were described in Section 3 and in Appendix A of this report. As stated previously, these methods can be divided into two broad categories: chemical-resistance tests and mechanical-properties tests. The glove properties included in the chemical-resistance category are permeation resistance, penetration resistance, degradation resistance, and swelling and solubility. The glove properties included in the mechanical-properties category were tear resistance and strength, cut resistance, puncture resistance, abrasion resistance, flexibility, ozone resistance, and UV resistance. However, no existing standard test method other than the direct permeation test was identified that would yield solubilities and diffusion coefficients of organic liquids in polymeric glove materials.

A review of experimental methods described in the scientific literature, however, revealed that absorption and desorption methods have been developed and used extensively for many years by academic and industrial researchers to study the diffusion of permanent gases and organic vapors in polymer films (see, for example, Reference 50). In addition, exact analytical solutions of Fick's laws that describe absorption and desorption have been developed. On

the basis of this experience, two test methods for evaluation and development were selected; these were a saturated-vapor absorption/desorption method and a liquid-immersion absorption/desorption method. Each of the methods is a gravimetric procedure that was expected to yield both the solubility, S, and the diffusion coefficient, D, of a solvent in a polymeric glove sample in a single experiment. Although these methods may be more time-consuming than direct permeation tests and may require relatively sophisticated mathematical computation, they are experimentally quite simple. Thus, the analytical instrumentation required is relatively inexpensive and unsophisticated, and personnel with only a minimum of technical training can conduct the tests.

IMMERSION ABSORPTION/DESORPTION TESTS

Description of the Test

In the immersion test, the weight of an organic liquid absorbed by a polymer sample totally immersed in the liquid was measured as a function of time with an analytical balance. To begin the test, the dimensions of a polymeric glove sample were measured, and the sample was weighed accurately and immersed in the organic liquid. After a specified time, the sample was removed from the liquid, the excess liquid was blotted from the exposed surfaces of the glove sample, and the sample was weighed. The sample was then reimmersed in the liquid and reweighed following the same procedure at specified intervals. The weighing and reimmersion procedure was repeated until a constant weight was attained. After equilibrium absorption or saturation was reached, the cumulative desorption of the organic chemical from the glove material was determined by monitoring the weight loss of the saturated sample as a function of time with an analytical balance.

Determination of Solubilities and Diffusion Coefficients

The solubility, S, of the organic liquid in the polymeric glove material was determined by dividing the equilibrium weight gain of the glove sample during the immersion test by its unswollen volume. The diffusion coefficient, D, was estimated from the time-dependent absorption and desorption data by an approximate method described by Crank (52) and by numerically fitting Equation 12 to the entire absorption or desorption curve. These two methods are described briefly below. (A more extensive discussion of these data-reduction techniques was presented in Section 2 of this report.)

Direct Curve Fit--

The absorption or desorption of a substance into or from a planar sample (if edge effects are negligible) can be described by the equation:

$$M_t/M_\infty = 1 - (8/\pi^2) \sum_{m=0}^{\infty} (2m+1)^{-2} \exp(-D(2m+1)^2 \pi^2 t/\ell^2) \qquad (12)$$

where t is the time (sec), M_t is the cumulative absorption or desorption (g) at time t, M_∞ is the cumulative absorption or desorption (g) at infinite time

(effectively, after equilibrium has been reached), D is the diffusion coefficient (cm^2/sec), and ℓ is the thickness of the sheet (cm). This equation is applicable to the liquid immersion test if the diffusion is effectively one dimensional (thin samples) and the diffusion coefficient is concentration independent. Experimental time-dependent absorption or desorption data can be fit, with the aid of a computer, to Equation 12 using nonlinear curve-fitting techniques to yield the diffusion coefficient.

Initial Rates of Absorption and Desorption--

As stated previously in Section 3, the common practice (50) in presenting data from absorption or desorption experiments is to plot the ratio M_t/M_∞ against the quantity $t^{1/2}/\ell$, where M_t is the cumulative amount of a given solvent absorbed in or desorbed from a given polymer sample at time t from the start of the absorption or desorption experiment. M_∞ is the equilibrium weight gain of the polymer in the immersion experiment (related to the solubility of the liquid in the polymer), and ℓ is the thickness of the original, unswollen polymer sample. The resulting curve is called the reduced absorption or desorption curve.

As discussed by Fujita (50) and by Crank (52), an apparent diffusion coefficient can be calculated from the initial slope of the reduced absorption or desorption curve according to the equation:

$$D = (\pi/16)I^2 \qquad (16)$$

where D is the apparent diffusion coefficient and I is the slope of the initial (linear) portion of the reduced sorption curve. In this report, D and I are denoted D_a and I_a, respectively, for an absorption experiment and D_d and I_d, respectively, for a desorption experiment.

Test Samples

Liquid-immersion absorption and desorption tests were conducted using five protective-glove materials and four solvents. The glove materials used were butyl rubber, natural rubber, neoprene rubber, nitrile rubber, and poly(vinyl chloride). All of the gloves were unsupported. The solvents used were acetone, cyclohexane, isopropanol, and toluene. The natural-, neoprene-, and nitrile-rubber gloves were manufactured by the Edmont Company and were obtained from a local supplier. The PVC gloves were manufactured by the Pioneer Company, and the butyl-rubber gloves were made by the Norton Company; both of these types of gloves were obtained from the stockroom at the Institute. The manufacturer, supplier, and style number of each glove used in the immersion and desorption tests are given in Table 13. The solvents used in the measurements were reagent-grade chemicals obtained from the Institute stockroom. Two brands of solvents were used during the test program-- Mallinckrodt (Paris, KY) and EM Science (Cherry Hill, NJ).

The glove materials used in the tests were considered representative of a variety of commercially available, unsupported protective gloves in common use. The chemicals used in the tests were selected because they are common, nontoxic solvents that encompass several chemical functional groups.

69

TABLE 13. IDENTIFICATION OF GLOVE MATERIALS USED IN LIQUID-IMMERSION
ABSORPTION AND DESORPTION TESTS

Glove	Manufacturer	Style No.	Nominal thickness, mil	Source
Butyl rubber	Siebe Norton, Inc. N. Charleston, SC	B-224	25	SRI stockroom
Poly(vinyl chloride)	Pioneer Industrial Products Co. Willard, OH	V-5 Quixam	5	SRI stockroom
Neoprene rubber	Edmont Coshocton, OH	29-875	19	Southern Safety Products, Inc. Birmingham, AL
Natural rubber	Edmont Coshocton, OH	26-680	21	Southern Safety Products, Inc. Birmingham, AL
Nitrile rubber	Edmont Coshocton, OH	37-165	22	Southern Safety Products, Inc. Birmingham, AL

Absorption tests were conducted with each glove material with each solvent. However, because of the low solubility of some of the solvents in some of the gloves, the duration of some of the immersion tests, and the apparent extraction of some component of the PVC gloves (as discussed in the next section), desorption tests were conducted with only ten of the glove/solvent combinations. All of the tests were performed as simply as possible using common laboratory equipment. Also, all of the tests were purposely conducted at ambient temperature and relative humidity in the laboratory with no provision for temperature or humidity control to keep the test requirements as simple as possible.

Each glove sample tested was a flat, circular sample punched from a protective glove with an arch punch. The diameter of each sample was 1-3/8 in. The nominal thickness of each glove material except PVC was approximately 20 mil (0.0508 cm). The nominal thickness of the PVC gloves was 5 mil (0.0127 cm). The diameter of each glove sample was measured with a stainless steel ruler calibrated in units of 0.01 in. (0.0254 cm). The thickness of each glove sample was measured with a Starrett dial gauge that was capable of measuring accurately a thickness of less than 0.2 mil (0.000508 cm). Five thickness measurements were made uniformly over the surface of each glove sample. Each reported sample thickness was the average of the five measurements.

Test Procedure

In the absorption tests, each glove sample was weighed to the nearest 0.0001 g on a top-loading Sartorius analytical balance. The weighed glove sample was then immersed in approximately 50 mL of a given solvent in a wide-mouth, screw-cap jar. At timed intervals, the sample was removed from the jar, quickly and lightly blotted between two sheets of ashless filter paper, placed in a tared, wide-mouth weighing bottle, and weighed on the analytical balance. After some weighings, the diameter and thickness of the test sample were also measured. The sample was then reimmersed in the solvent in the jar. The weighing and reimmersion at timed intervals was continued until a constant weight was observed. For some tests, a constant weight was not attained, even after three weeks.

The desorption tests were run with samples that had reached equilibrium solubility (that is, attained a constant weight) in a given solvent. In the desorption tests, a solvent-saturated sample was removed from the solvent, quickly and lightly blotted between two sheets of ashless filter paper, and mounted on a tared wire tripod (constructed from 18-gauge copper wire) on the pan of the analytical balance. The tripod-mounted sample was left on the balance pan for the remainder of the desorption test, and the weight of the sample was monitored and recorded as a function of time at ambient temperature and relative humidity. The glass sliding doors on the side and top of the weighing chamber on the balance were left slightly open. A low airflow was maintained through the chamber by means of an aspirator pump connected to the opening in the door on the top of the weighing chamber.

71

The raw data collected in the tests were sample weights as a function of absorption time or desorption time. The data were analyzed as described above.

Immersion Test Results

The immersion absorption and desorption tests that were conducted during the study are listed in Table 14. Three main types of sorption behavior were observed:

- Each PVC sample lost weight from immersion in each solvent. Such weight loss indicates the extraction of some component of the PVC formulation (probably a plasticizer) by the solvent.

- The neoprene-, nitrile-, butyl-, and natural-rubber glove samples each showed small weight gains over a long period (several days) with two of the four solvents.

- The neoprene-, nitrile-, butyl-, and natural-rubber glove samples each showed large, rapid weight gains over a period of hours with the other two of the four solvents.

Desorption tests were conducted with the eight glove/solvent combinations that exhibited large, rapid solvent uptake by the glove sample during the immersion tests and with two glove/solvent combinations that exhibited small, slow uptake—natural-rubber/acetone and neoprene-rubber/acetone.

The data obtained in the liquid-immersion absorption tests are summarized in Table 15. The table includes for each test the average initial dimensions of each glove, the range of test conditions (temperature and relative humidity), the average initial weight of each glove, and the average weight gain at equilibrium saturation for each glove/solvent combination. A summary of these data for each glove/solvent absorption test conducted are presented in Table 26 in Appendix D.

The time-dependent absorption and desorption data for each glove/solvent combination tested are given in the data tables included as a separate volume with this report. Absorption and desorption curves for selected tests are plotted as reduced sorption curves and given in Appendix D (see Figures 11 through 18).

Solubilities—

According to the principles on which the immersion test is based, the weight gain of the glove sample at long times (that is, at equilibrium) should yield the solubility of the solvent in the polymer. Estimated solubilities (in g/cm^3 of unswollen polymer) obtained in this work are included in Table 16. A comparison of the average solubilities (in $moles/cm^3$) determined in this work for the four solvents used versus solubilities calculated from the data of Paul et al. (48) is given below for natural rubber:

TABLE 14. SUMMARY OF THE TYPES OF LIQUID-IMMERSION TESTS CONDUCTED

Glove	Solvent	Absorption	Desorption[a]
Butyl rubber	Acetone	X	
	Cyclohexane	X	X
	Isopropanol	X	
	Toluene	X	X
Natural rubber	Acetone	X	X
	Cyclohexane	X	X
	Isopropanol	X	
	Toluene	X	X
Neoprene rubber	Acetone	X	X
	Cyclohexane	X	X
	Isopropanol	X	
	Toluene	X	X
Nitrile rubber	Acetone	X	X
	Cyclohexane	X	
	Isopropanol	X	
	Toluene	X	X
Poly(vinyl chloride)	Acetone	X	
	Cyclohexane	X	
	Isopropanol	X	
	Toluene	X	

[a]Desorption tests were conducted for solvent/glove combinations that achieved equilibrium during absorption tests.

TABLE 15. SUMMARY OF AVERAGE LIQUID-IMMERSION ABSORPTION TEST DATA

Glove	Solvent	Initial diameter, cm.	Initial thickness, cm.	Initial weight, g	Maximum weight gain, g	Temperature range, °F	R.H. range, %
Butyl rubber	Acetone	3.53	0.0597	0.6604	0.0268	70-79	63-86
	Cyclohexane	3.53	0.0582	0.6455	1.5491	67-78	55-75
	Isopropanol	3.53	0.0592	0.6555	0.0024	70-79	63-86
	Toluene	3.56	0.0587	0.6484	1.0264	67-78	55-74
Natural rubber	Acetone	3.56	0.0632	0.6323	0.0958	69-79	51-88
	Cyclohexane	3.56	0.0660	0.6612	1.7633	69-78	51-80
	Isopropanol	3.56	0.0655	0.6486	0.0314	69-79	51-86
	Toluene	3.56	0.0653	0.6478	2.0761	68-78	51-80
Neoprene rubber	Acetone	3.56	0.0478	0.6367	0.1912	70-79	52-87
	Cyclohexane	3.56	0.0480	0.6405	0.4176	69-78	52-73
	Isopropanol	3.56	0.0483	0.6458	0.0274	69-79	52-86
	Toluene	3.56	0.0485	0.6418	1.5090	68-78	52-73
Nitrile rubber	Acetone	3.56	0.0541	0.5635	0.9707	69-78	53-74
	Cyclohexane[a]	3.56	0.0566	0.5981	0.0548	70-79	51-86
	Isopropanol[a]	3.53	0.0554	0.5890	0.1285	70-79	51-86
	Toluene	3.56	0.0559	0.5932	0.7904	69-78	53-72
Poly(vinyl chloride)	Acetone	3.61	0.0160	0.1930	-0.0529	70-72	51-80
	Cyclohexane	3.56	0.0145	0.1718	-0.0510	70-72	51-80
	Isopropanol	3.56	0.0218	0.2187	-0.0635	70-72	51-80
	Toluene	3.56	0.0147	0.1791	-0.0273	70-72	51-80

[a]Some of the nitrile-rubber samples immersed in these solvents continued to gain weight even after 530 hr.

74

TABLE 16. AVERAGE SOLUBILITIES AND DIFFUSION COEFFICIENTS CALCULATED FROM
LIQUID-IMMERSION ABSORPTION AND DESORPTION TEST DATA

Glove	Solvent	Solubility, g/cm^3	Diffusion coefficient,[a,b,c] cm^2/sec			
			$10^6 \times D_a$	$10^6 \times D_d$	$10^6 \times D'_a$	$10^6 \times D'_d$
Butyl rubber	Acetone	0.0457	0.0056	--	0.0050	--
	Cyclohexane	2.7261	-0.15	0.33	0.18	0.28
	Isopropanol	0.0041	0.0071	--	0.00043	--
	Toluene	1.7691	0.38	0.28	0.32	0.21
Natural rubber	Acetone	0.1527	0.40	0.38	0.69	0.45
	Cyclohexane	2.6877	0.25	0.49	0.26	0.48
	Isopropanol	0.0489	0.042	--	0.044	--
	Toluene	3.2067	0.53	0.26	0.58	0.29
Neoprene rubber	Acetone	0.4044	0.25	0.26	0.52	0.31
	Cyclohexane	0.8781	0.037	0.054	0.040	0.043
	Isopropanol	0.0574	0.0013	--	0.00014	--
	Toluene	3.1388	0.35	0.20	0.41	0.21
Nitrile rubber	Acetone	1.8204	0.42	0.45	0.44	0.48
	Cyclohexane[d]	0.0982	0.00025	--	0.00030	--
	Isopropanol[d]	0.2340	0.00035	--	0.00071	--
	Toluene	1.4377	0.059	0.20	0.098	0.15

[a] The term D_a is the diffusion coefficient estimated from the initial slope of the reduced absorption curve. D_d is the diffusion coefficient estimated from the initial slope of the reduced desorption curve. All data points [including (0,0)] for which M_t/M_∞ <0.6 were used in these calculations; if no data points meeting this criterion except (0,0) existed, then the calculation was based on (0,0) and the first data point above M_t/M_∞ = 0.6.

[b] The term D'_a is the diffusion coefficient calculated from a curve-fit of data obtained in an absorption test. D'_d is the diffusion coefficient calculated from a curve-fit of data obtained in a desorption test.

[c] The symbol "--" means that the experiment indicated was not conducted.

[d] Some of the nitrile-rubber samples immersed in these solvents continued to gain weight even after 530 hr.

Solvent	Paul et al.	Southern Research
Acetone	0.00169	0.00263
Cyclohexane	0.0338	0.0319
Isopropanol	0.000528	0.000814
Toluene	0.0387	0.0348

It may be seen that the solubilities determined in this work agree well with Paul's for toluene and cyclohexane, for which high solubilities were obtained. There is less agreement in the two data sets for acetone and isopropanol; however, these solvents are not very soluble in natural rubber.

It should be emphasized that it is important to obtain time-dependent weight-gain data in immersion tests that are conducted to determine the solubilities of organic liquids in polymeric glove materials. Time-dependent data are necessary to establish the attainment of equilibrium weight gain. Although in many cases a true solubility may be obtained by simply immersing a glove sample in an organic liquid for a fixed period of time (24 hr, for example) and then weighing the sample, this single-data-point technique may often give incorrect results if equilibrium weight gain has not been attained. In the immersion tests conducted in this study, for example, the weights of some of the nitrile samples immersed in cyclohexane and some of the nitrile samples immersed in isopropanol were still increasing at the time the final weights were measured (530 hr). Thus, an equilibrium weight gain was not established, and a true solubility could not be determined.

The major problem in determining the solubility of an organic liquid in an unsupported, polymeric glove material (and the major potential problem in the entire immersion test method) is the possible extraction of components of the glove formulation by the immersion solvent. The extraction of components can often be deduced from the liquid-immersion absorption data; for example, the PVC samples in this work that were immersed in solvents lost weight. However, it is conceivable that simultaneous solvent absorption and component extraction could occur during immersion and, thus, that the net weight gain of the glove sample may not be entirely due to the absorption of solvent by the glove. Hence, some caution must be used in interpreting immersion test results. (It should be noted, however, that if the solvent extracts a component of the glove formulation and a weight loss is observed, the glove will probably not provide the required chemical resistance.)

Diffusion Coefficients—

Solvent diffusion coefficients estimated from the immersion data by the two methods described above [that is, from the initial slope of the reduced sorption curve (Equation 16, Section 7) or by a fit of the reduced sorption curve to Equation 12, Section 7] are listed in Table 16 for each glove/solvent combination. There is little data in the literature that contains experimental values for diffusion coefficients of organic liquids in polymeric glove materials with which to compare the diffusion coefficients determined in the immersion tests. For the two glove/solvent combinations for which we found literature values of the diffusion coefficient (natural-rubber/cyclohexane and natural-rubber/toluene), the diffusion coefficients estimated from the immersion absorption and desorption test data are approximately an order of magnitude smaller than the values reported in the literature. However, the diffu-

sion coefficients calculated for each glove/solvent combination with each method of estimation are, in general, self-consistent and in close agreement with apparent diffusion coefficients calculated from the direct permeation tests discussed in this section.

It should be emphasized that the values of the diffusion coefficients determined from the immersion absorption and desorption data are based on approximations that contain several simplifying assumptions. In the curve-fit method, in particular, a concentration-independent diffusion coefficient is assumed. From the frequent lack of coincidence of the absorption and desorption curves shown in the representative figures in Appendix D, however, the diffusion coefficients of the solvents in most of the gloves tested appear to be concentration dependent. Although more sophisticated treatments of the absorption and desorption data are possible, it was decided to first explore the potential of simple data-reduction methods that would yield parameters useful for predictive purposes.

VAPOR ABSORPTION TESTS

Liquid-immersion absorption tests cannot be readily automated; thus, they are labor intensive although they are very simple to conduct. In an attempt to avoid this problem, a brief investigation of a vapor absorption/desorption procedure, which could easily be automated, was conducted. Theoretically, at atmospheric pressure, the process of solvent diffusion into a polymer in contact with a liquid is the same as for a polymer in contact with a saturated vapor. Therefore, the saturated-vapor test and the immersion test should provide the same data; however, differences in test results may be observed for some liquid/polymer systems. For example, a liquid may leach additives from a polymer to a greater extent than does vapor.

Description of the Test

In the vapor absorption test described below, a thin polymeric glove sample was suspended from a sensitive quartz spring, which was calibrated for extension versus load. The sample and spring were enclosed in a chamber containing an organic vapor maintained at the vapor pressure of the liquid at "ambient" temperature. A cathetometer was used to observe the spring extension as a function of time until a constant extension was observed. The data obtained were then converted to weight gain versus time or, in other words, cumulative absorption versus time. Time-dependent vapor absorption and desorption data are treated and analyzed in the same manner as for the immersion tests described above.

Test Apparatus and Procedure

The same glove materials and solvents that were used in the immersion tests were scheduled for use in saturated-vapor absorption and desorption tests. As discussed below, however, because of the long time required to conduct the vapor absorption test, only a single absorption test was conducted with a single glove/solvent combination (nitrile rubber/acetone) during the test program. (No desorption tests were conducted.)

The test apparatus used in the vapor absorption test is shown in Figure 7. The apparatus consisted of a calibrated fused-quartz spring (Ruska Instrument Corporation, Houston, TX) suspended from a hook on the inside upper end of a custom-fabricated jacketed condenser (M.B. Watson Scientific Glassblowing, Tuscaloosa, AL), a round-bottom flask that contained approximately 25 mL of acetone, a water bath to prevent rapid changes in the temperature of the solvent, and a cathetometer to monitor the extension or compression of the quartz spring.

The quartz spring used in the vapor absorption test was precalibrated by the manufacturer to give a spring extension of 1 mm for a 1 mg load. The maximum extension of the spring was 500 mm. Prior to the vapor absorption test, the spring was calibrated over a range of 10 to 500 mm with a set of precision milligram weights (Bitronics, Inc., Bethlehem, PA). The extension of the spring was measured with a sensitive cathetometer graduated in divisions of 0.1 mm. The cathetometer was focused on a "crosshair" reference mark near the end of the spring.

For the test conducted, a 1-cm by 1-cm square sample was cut from a nitrile-rubber glove, and a small hole was punched through the sample near the center of one of the edges. The test sample was mounted on a hook at the bottom of the quartz spring through the hole in the sample. The vertical position of the reference mark on the quartz spring was measured through the cathetometer. About 25 mL of acetone was poured into the 100-mL round bottom flask, and it was connected to the bottom of the condenser. The flask was immersed into the water bath as shown in Figure 7. The extension of the quartz spring as the glove sample absorbed acetone vapor was then monitored with the cathetometer as a function of time over a ten-day period.

Vapor Absorption Test Results

By the time the test method was selected and the required appparatus was designed, fabricated, assembled, and calibrated, little time remained under the contract for testing. As stated previously, because of the long duration required (approximately two weeks) for a single vapor absorption test, only one such test with a single glove/solvent combination--nitrile rubber with acetone--was completed. The data obtained in this test are given in Table 17.

As the data in the table indicate, the measured absorption of acetone by the nitrile-rubber sample fluctuated as a function of time. Consequently, no useful time-dependent absorption data were obtained in the test.

We attribute the fluctuations obtained in the vapor absorption test primarily to the lack of temperature control of the test apparatus. With the addition to the apparatus of a constant-temperature bath to control the temperature of the reservoir of liquid solvent and the circulation of the water from the bath through the outer jacket of the condenser, reliable time-dependent absorption data should be obtained.

The vapor sorption method is experimentally more complex and time-consuming than the liquid-immersion absorption/desorption test method described above, and the vapor sorption method is applicable only to volatile solvents.
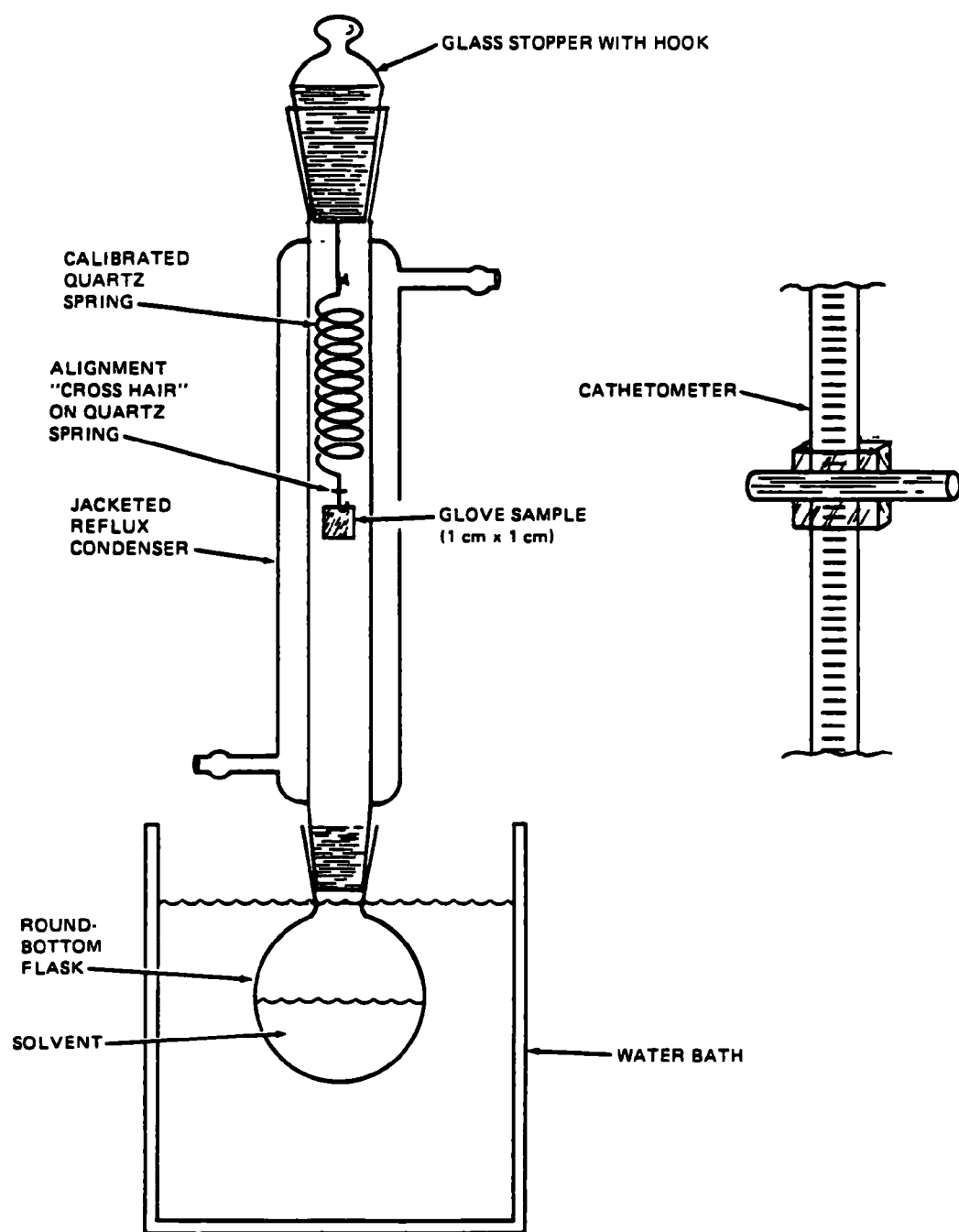
Figure 7. Diagram of vapor sorption apparatus (not drawn to scale).

GLASS STOPPER WITH HOOK

CALIBRATED
QUARTZ
SPRING

ALIGNMENT
"CROSS HAIR"
ON QUARTZ
SPRING

JACKETED
REFLUX
CONDENSER

GLOVE SAMPLE
(1 cm x 1 cm)

CATHETOMETER

ROUND-
BOTTOM
FLASK

SOLVENT

WATER BATH

5749-15

79

TABLE 17. VAPOR ABSORPTION DATA OBTAINED
FOR NITRILE RUBBER AND ACETONE[a]

Time, min	Weight, mg	Weight gain, mg
0	56.55	0
77	55.90	-0.65
147	55.90	-0.65
197	56.41	-0.14
327	58.45	1.90
1,234	83.13	26.58
1,457	82.79	26.24
1,711	83.57	27.02
2,681	97.47	40.92
2,897	93.39	36.84
3,227	89.50	32.95
4,484	94.89	38.34
5,777	100.43	43.88
9,887	105.38	48.83
10,397	95.18	38.63
11,354	103.98	47.43
11,848	101.40	44.85
12,763	107.91	51.36
13,287	100.82	44.27
14,253	107.52	50.97

[a]The initial dimensions of the test sample were
1 cm x 1 cm x 0.0508 cm. The temperature was in
the range of 21 to 28 °C during the test.

Thus, it does not appear to be a widely applicable alternative to permeation testing.

PERMEATION TEST DATA

Direct permeation tests were conducted with each of the glove materials (except PVC) and each of the organic solvents (except isopropanol) to generate permeation-rate-versus-time data to compare with predictions made from the results of the immersion and vapor sorption tests. Direct permeation tests were conducted because sufficient quality time-dependent permeation data to compare with the gravimetric methods proposed do not exist in the literature.

The direct permeation tests were conducted according to the standard ASTM Method F739. The tests were conducted in a 1-in. "ASTM permeation test cell" from Pesce Lab Sales (Kennett Square, PA). All tests were conducted at room temperature using dry nitrogen gas as the collection fluid. Each permeation test was conducted in an "open-loop" mode; that is, fresh nitrogen was continually swept at a flow rate of 100 mL/min across the unchallenged surface of the test sample. At timed intervals, an aliquot of the gas stream from the test cell was sampled with a gas-tight syringe. The sampled portion of the gas stream in the syringe was then injected directly into a Hewlett-Packard Model 5790 gas chromatograph for the detection and quantitation of the solvent in the gas stream.

In each permeation test, the test cell was immersed in a water bath containing tap water at room temperature. The temperature of the water bath was not controlled, but its temperature remained constant at approximately 20 ± 1 °C during each test. The temperature of the nitrogen gas stream that was swept through the collection side of the test cell was preequilibrated to the temperature of the water bath by flowing it through a 50-ft coil of 1/4-in.-OD copper tubing immersed in the water bath.

Prior to each permeation test, the gas chromatograph was calibrated for the organic challenge liquid to be used in the permeation test by injecting dilute solutions of the organic liquid in a suitable solvent into the gas chromatograph. A standard calibration curve that covered the entire working range of the method was determined with five concentrations of standard solutions.

The test data generated in each open-loop permeation test were instantaneous permeation rate as a function of time. Average breakthrough times and steady-state permeation rates obtained in these direct permeation tests are given in Table 18. This table also includes diffusion coefficients and solubilities obtained from curve fits of the permeation-rate data to Equation 3 (Section 3).

TABLE 18. SUMMARY OF AVERAGE PERMEATION-TEST DATA

Glove	Solvent	Thickness, cm	Breakthrough time,[a] min	Steady-state permeation rate, $\mu g/(cm^2 \cdot min)$	Calculated diffusion coefficient,[b] cm^2/sec, $10^6 \times D$	Calculated solubility,[b] g/cm^3
Butyl rubber	Acetone	0.0615	>1115	<0.47	--	--
	Cyclohexane	0.0600	55	437	0.085	7.6
	Toluene	0.0589	24	396	0.19	2.9
Natural rubber	Acetone	0.0616	17	34	0.17	0.33
	Cyclohexane	0.0619	19	572	0.22	3.2
	Isopropanol	0.0617	>150, <1400	1	0.0012	2.6
	Toluene	0.0617	10	782	0.58	1.5
Neoprene rubber	Acetone	0.0480	22	151	0.15	1.1
	Cyclohexane	0.0480	170	26	0.014	7.0
	Toluene	0.0478	12	642	0.26	2.1
Nitrile rubber	Acetone	0.0589	10	962	0.39	3.0
	Cyclohexane	0.0582	>1350	<0.12	--	--
	Toluene	0.0574	52	210	0.066	4.3

[a]The minimum permeation rates that could be detected were: 0.47 $\mu g/(cm^2 \cdot min)$ for acetone, 0.11 $\mu g/(cm^2 \cdot min)$ for toluene, and 0.12 $\mu g/(cm^2 \cdot min)$ for cyclohexane.

[b]The symbol "--" means that no diffusion coefficient or solubility could be calculated.

SECTION 8

PREDICTIVE ALGORITHMS

The purpose of the contract was to develop models and test methods that would allow the prediction of the protection from permeation afforded by polymeric gloves in contact with liquid organic chemicals. The previous sections of this report have included a summary of the results of a literature survey of topics relevant to this purpose and descriptions of the theory and test methods developed to make the required predictions.

In this section of the report, the key results presented previously are used to construct or suggest algorithms or approaches to the evaluation of polymeric gloves proposed as protective clothing for use with specific chemicals.

SPECIFIC ALGORITHM REQUIREMENTS

Among the objectives of this work were that the model or predictive algorithms developed must be relatively simple; must not require data other than that provided in the PMN submittal, in handbooks or in data bases, or obtained in simple, reproducible tests; and must be applicable to a wide variety of chemical substances and polymeric gloves. In addition, the algorithms must be capable of predicting such quantities as maximum (or steady-state) permeation rates; breakthrough times; 1-hr and 8-hr cumulative exposures; and permeation rates versus time. It must also be able to place the protective glove into one of a series of qualitative groupings such as the following:

- The glove will protect against dermal contact with the chemical in question for a limited period (1 hr) or an extended period (full work shift).

- The glove will not protect against dermal contact even for a limited period.

- Experimental data are needed before a prediction can be made.

APPROACH TO THE ALGORITHM

As stated previously in this report, the approach used in the development of the predictive ability outlined above was to base predictions as much as possible on the theory of diffusion in polymers. Thus, this work emphasized the development of models and simple test methods that allow the prediction or determination of diffusion coefficients and solubilities. Given these fundamental parameters, any of the required predictive calculations can be completed using, for example, diffusion equations such as those presented in Section 3.

It should be noted that the predictive algorithms given in this section of the report are based only on simple diffusion theory, and this will limit their usefulness. However, because the development of any predictive algorithm is a stepwise process, it is logical to begin with the simplest approach. The predictive algorithms developed can easily be improved in sophistication under subsequent research efforts conducted in conjunction with confirming the applicability of the algorithms. That is, predictions should be made and compared with available experimental data, and the results should be studied to determine needed improvements to the model. The model (that is, the algorithms) would then be modified, and new predictions would be made and compared to the experimental data, and so forth.

Another point to be made is that the algorithms described here are not "user friendly." That is, for example, the suggested input may not be in a form that would be easily handled by someone processing the PMN submittal. Also, the only "software" that currently exists (except for very simple programs) is described in the various sections of this report. The development of software that would be easy for an "untrained" person to use would not be particularly difficult, but it would be time-consuming.

INPUT TO THE ALGORITHM

The input to the predictive algorithm includes data provided in the PMN submittal as well as data that may be readily available from handbooks or data bases. In addition, the parameters (and associated quantitative values) used to evaluate the degree of protection must be specified. Examples of input data required by the UNIFAP program (which is a part of the predictive algorithm) to calculate solubilities are:

- The temperature of interest.

- The structure, molecular weight, and density of the liquid organic chemical.

- The structure, molecular weight, density, and degree of polymerization of the polymeric glove material.

Other input data* may include those required to calculate diffusion coefficients using the modified Paul model (which is also incorporated in the predictive algorithm):

- Viscosity of the solvent as a function of temperature.

- Density (or specific volume) of the solvent as a function of temperature.

---

*The list of input data given in Section 6 for the Paul model included other parameters that may be determined within software and, thus, be transparent to the user.

84

- Density (or specific volume) of the solvent and the polymer at the temperature of interest.

- The molecular weights of the solvent and the polymer.

Still additional input data may be those obtained in simple immersion tests such as those described in Section 7:

- Initial dimensions of the polymeric glove samples (thickness and area) for each test.

- Temperatures at which experiments were conducted.

- Weight-change-versus-time data for each immersion test.

For the sake of completeness, other data may be input to the predictive algorithm. These may include, for example, the manufacturer or vendor catalog number and other miscellaneous information describing the polymeric glove.

Even with all of the input data listed above, it will not be possible for the predictive algorithm to assess the protection afforded by a given polymeric glove unless some quantitative criteria are specified. These criteria may include one or more of the following:

- The maximum permeation rate per unit area allowed within a specified period (1 hr, 8 hr, and so forth).

- The maximum cumulative exposure per unit area allowed within a specified period (1 hr, 8 hr, and so forth).

- The minimum breakthrough time allowed (based on a specified analytical sensitivity to simulate open-loop or closed-loop permeation tests of a known area of sample).

- Maximum permeation-rate ranges to simulate manufacturers' qualitative recommendations (for example, 0.15 to 1.5 mg/(m^2·sec) to be equivalent to Edmont's permeation rating of "excellent").

- Maximum percentage weight gain within a fixed period (for example, 2 hr) to simulate a degradation test.

The protection criteria specified by the user of the predictive algorithm should be based, if possible, on well-established safety criteria, such as those published by NIOSH, the American Conference of Government Industrial Hygienists, or EPA.

CALCULATIONS OF FUNDAMENTAL PARAMETERS

After data of the type listed above are input to the predictive algorithm, it will calculate the fundamental parameters needed to make the desired predictions--parameters such as solubility (using UNIFAP), solubility (using the 24-hr immersion-test data), the solvent diffusion coefficient versus solvent volume fraction (using the modified Paul model), or the apparent solvent diffusion coefficient (using immersion-test data). The approach used by the predictive algorithm will depend on the data input to it. For example, if only immersion-test data are provided in the PMN submittal (and the glove material is not identified), then the solubility and the diffusion coefficient cannot be calculated using the UNIFAP or Paul models, respectively. Also, only an apparent diffusion coefficient can be determined from the immersion-test data using the technique recommended in this report; that is, concentration-dependent diffusion cannot be modeled. It should be noted, however, that the apparent diffusion coefficient calculated from immersion-test data for systems exhibiting concentration-dependent diffusion coefficients may often be satisfactory for predictive purposes.

Results of the calculation of diffusion coefficients and solubilities using the predictive models and test methods developed in this work were presented in previous tables (11 and 16) and figures (4, 5, and 6) in this report. As stated above, the specific calculations performed by the predictive algorithms will depend on the data input. If insufficient information is input to perform the required calculations, then the predictive algorithm will inform the PMN submittal reviewer that additional information is required; the algorithm could be designed to specify the type of missing data that must be supplied.

CALCULATION OF CUMULATIVE PERMEATION OR PERMEATION RATE

After the algorithm has yielded the solvent solubility and its apparent diffusion coefficient, these data may then be used to calculate the permeation rate versus time (using, for example, Equation 3) and the cumulative permeation versus time (using, for example, Equation 4). If there is sufficient data for the predictive algorithm to yield the solvent diffusion coefficient as a function of solvent volume fraction (as well as to yield the solubility), then numerical methods similar to the example given in Appendix C must be used to determine permeation rate and cumulative permeation as a function of time from Fick's laws, given the initial and boundary conditions (see Section 3). An example of the calculation of permeation rate versus time using a numerical method as well as a computer program for the calculation is also given in Appendix C. (This simple program will not handle concentration-dependent diffusion coefficients.)

If all of the input data listed above were available, then the calculation of J versus t and Q versus t could be performed using several combinations of fundamental parameters and methods. The most likely combinations are:

- UNIFAP solubility, Paul diffusion coefficients, numerical analysis.

- Immersion solubility, Paul diffusion coefficients, numerical analysis.

- UNIFAP solubility, immersion diffusion coefficient, analytical solutions.

- Immersion solubility, immersion diffusion coefficient, analytical solutions.

It would be preferable to perform calculations for all of the combinations listed above or for as many combinations as possible. Any estimate of the protection afforded by a recommended polymeric glove could then be "safe-sided." That is, a predicted failure to meet the specified protection criteria for any combination of input data would result in the rejection of the polymeric gloves recommended in the PMN submittal. It may obviously be desirable to weight evaluations in favor of experimental data, such as immersion-test data.

EVALUATION OF PROTECTION CRITERIA

After the calculation of permeation rate (J) and cumulative permeation (Q) as a function of time, these data may be used to determine whether the protection criteria input to the algorithm have been met (that is, whether the polymeric glove will provide the desired protection). For example, if the criteria specified that the permeation rate per unit area shall not exceed $1\,mg/(m^2 \cdot sec)$ during a 1-hr period, then the permeation rate data (J versus t) calculated need only be checked to ensure that J is less than $1\,mg/(m^2 \cdot sec)$ for times up to 1 hr. Again, more than one J-versus-t curve may have been determined, depending on the data input to the predictive algorithm. Each curve could be compared to the protection criteria specified.

It may be possible to make some definitive statement about the adequacy of a given protective glove even if an estimate of the solvent diffusion coefficient cannot be made because of insufficient data--particularly, if the glove chosen is grossly unsatisfactory. For example, in Table 19, solubilities for various polymer/solvent combinations that were calculated using UNIFAP are compared to manufacturers' degradation and permeation ratings. If the predictive algorithm were written to reject a specified protective glove when UNIFAP predicts complete miscibility of the polymer and the solvent, there would generally be good agreement between UNIFAP and the manufacturers' recommendations. It should be noted, however, that there are many disagreements between the ratings reported by Edmont and those compiled by ADL (4). And such correlations are generally qualitative at best.

TABLE 19. COMPARISON OF SOLUBILITIES CALCULATED USING THE UNIFAP
MODEL OR OBTAINED EXPERIMENTALLY WITH MANUFACTURERS'
CHEMICAL-RESISTANCE GUIDELINES[a,b]

Polymer	Solvent	$10^5 \times C_{uni}$	$10^5 \times C_{exp}$	Degradation rating[c]	Permeation rating[d]
Natural	Methanol	26.5	4.92	E	E, NN
rubber	Ethanol	42.4	8.59	E	VG, NN
	Isopropanol	81.6	52.8 (81.4)	E	E, NN
	n-Butanol	93.3	125	E	G
	n-Pentanol	103	130	NA	NA
	Benzyl alcohol	27.5	142	NA	NA
	n-Propanol	100	146	E	VG
	Acetone	185	169 (263)	E	F, NN
	2-Ethyl-1-butanol	114	259	NA	NA
	t-Butanol	81.5	414	NA	NA
	t-Pentanol	96.9	437	NA	NA
	Diethyl carbonate	202	636	NA	NA
	Methyl ethyl ketone	271	713	G	P, NN
	Ethyl acetate	411	766	G	G, NN
	n-Propyl acetate	581	1270	F	F, NN
	n-Hexane	*[e]	1540	NR	NA
	n-Heptane	*	1580	NA	NN
	Tetralin	*	3330	NA	NA
	Cyclohexane	*	3380 (3190)	NA	NN
	Cyclohexanone	*	3410	NA	NA
	Toluene	*	3870 (3480)	NR	NN
	Tetrachloroethylene	*	4240	NA	NN
	Carbon tetrachloride	*	5370	NR	NN
	Trichloroethylene	*	5690	NA	NN
Butyl	Acetone	322	(78.7)	NA	NA
rubber	Cyclohexane	*	(3240)	NA	RR
	Isopropanol	29.7	(6.8)	NA	NA
	Toluene	*	(1920)	NA	NA
Neoprene	Acetone	*	(696)	G	F, NN
rubber	Cyclohexane	*	(1040)	NA	NN
	Isopropanol	69.8	(95.5)	E	E
	Toluene	--[f]	(3410)	NR	NN

(continued)

TABLE 19 (continued)

Polymer	Solvent	$10^5 \times C_{uni}$	$10^5 \times C_{exp}$	Degradation rating[c]	Permeation rating[d]
Nitrile	Acetone	--	(3130)	NR	NN
rubber	Cyclohexane	--	(117)	NA	RR
	Isopropanol	--	(389)	E	E, RR
	Toluene	--	(1560)	F	F, NN
Poly(vinyl	Acetone	*[g]	(--)[h]	NR	NN
chloride)	Cyclohexane	*	(--)	NA	NN
	Isopropanol	49.5	(--)	G	E
	Toluene	*	(--)	NR	NN

[a] The units of the calculated equilibrium solubilities, C_{uni}, and the experimental solubilities, C_{exp}, are moles/cm^3.

[b] The values in parentheses under the column labeled "$10^5 \times C_{exp}$" were determined during immersion tests conducted under the current effort; the other data under this heading were calculated from data reported in Reference 48.

[c] These are Edmont degradation ratings; E means excellent; G means good; F means fair; NR means not recommended; NA means not available.

[d] For the Edmont ratings, E means excellent (permeation rate <0.15 mg/m^2/sec); VG means very good (permeation rate <1.5 mg/m^2/sec); G means good (permeation rate <15 mg/m^2/sec); F means fair (permeation rate <150 mg/m^2/sec); P means poor (permeation rate <1500 mg/m^2/sec); ND means none detected. The double letters refer to ratings used by ADL (4); RR (recommended) means that a large amount of test data indicates excellent chemical resistance; NN (not recommended) means that a large amount of test data indicates poor chemical resistance; NA means rating not available (or conflicting ratings are reported by ADL).

[e] The symbol "*" in this column means that an activity of one was achieved only for a solvent volume fraction equal to one. (That is, the solvent and the polymer are predicted to be miscible in all proportions.)

[f] The symbol "--" in this column means that no interaction parameters were available for the polymer/solvent pair indicated.

[g] The UNIFAP solubilities for solvents in poly(vinyl chloride) were based on the polymer structure alone; the presence of plasticizer was not considered.

[h] The symbol "--" in this column means that weight loss was observed in the immersion tests with poly(vinyl chloride).

If only "steady-state" or 24-hr solubilities were available from immersion tests, similar correlations between large solubilities and manufacturers' recommendations would be expected. Experimental (or immersion-test solubilities) are also shown in Table 19. Again, there is generally a good correlation between manufacturers' recommendations and experimental solubilities.

OUTPUT OR EVALUATION REPORT

The output of the predictive algorithm could include:

- A reiteration of all of the data input to the algorithm.

- A list of the methods used to calculate solubility and diffusivity data.

- A pass/fail report for all protection criteria.

- Recommendations such as the suitability of the glove for a 1-hr period or for extended periods.

- Recommendations for the submittal of more data on which to base an evaluation.

Other output could include calculated J-versus-t or Q-versus-t curves, D-versus-C curves, and tables of such data. A regulatory style report could also be issued by the computer.

CONFIRMATION

As stated above, the development of a predictive algorithm is an iterative process. That is, the algorithm must be tested or confirmed at various states in its development. An anticipated task to confirm the models and predictive test methods developed under this contract was not completed due to the unavailability of funds.

Some confirmation work has been described previously in this report. This work included the comparison of calculated diffusion coefficients to values published in the scientific literature, the comparison of solubilities calculated using UNIFAP and from immersion-test data to solubilities previously reported, and the comparison of calculated solubilities to manufacturers' degradation and permeation ratings.

Presented below are results obtained in additional efforts to demonstrate the feasibility of the suggested predictive models and test methods described in this report. These efforts included:

- The prediction of a permeation-rate-versus-time curve for benzene in natural rubber using a solubility calculated with the UNIFAP program, concentration-dependent diffusion-coefficient

90

data calculated with the modified Paul model, and a numerical analysis method.

- The prediction of permeation-rate-versus-time curves for several solvents in a series of glove materials using apparent diffusion coefficients and solubilities obtained in liquid-immersion tests and using Equation 3.

- The use of these calculated permeation-rate-versus-time curves to predict breakthrough times and steady-state permeation rates for the glove/solvent combinations used in the liquid-immersion tests and the comparison of these predictions with values obtained in permeation tests.

- The comparison of two predicted permeation-rate-versus-time curves with data obtained in permeation experiments.

It should be noted that much more confirmation work than presented here could be completed using the experimental data obtained under the current contract. Again, the current effort was devoted primarily to the identification of potential predictive models and test methods and the limited demonstration of their feasibility. More extensive confirmation work and additional refinements to the models and test methods proposed here should be the subject of a future contract.

Prediction of a Permeation-Rate Curve Using Theoretical Models

The concentration dependence of the diffusion coefficient for benzene in natural rubber calculated using the modified Paul model was given in Figure 5. The solubility of benzene in natural rubber (0.685 g/cm^3 of swollen polymer) was calculated using the UNIFAP software. These theoretical data were then used to predict a benzene permeation-rate-versus-time curve for an unsupported, 0.046-cm-thick natural-rubber glove (see Figure 8). The calculations needed were performed using a numerical analysis method similar to that described in Appendix C; however, the method was modified to account for a concentration-dependent diffusion coefficient.

Figure 8 includes a permeation-rate curve calculated from experimental cumulative-permeation data reported by Weeks and McLeod (20) for benzene through an unsupported natural-rubber glove of the same thickness as used in the theoretical calculations. Although there is considerable scatter in the experimental data, the relative agreement between the experimental and predicted curves is obvious.

Prediction of Permeation-Rate Curves Using Test Methods

Table 16 includes apparent diffusion coefficients and solubilities calculated from data generated in liquid-immersion tests using 16 glove/solvent combinations. Average apparent diffusion coefficients defined by $[(D_a+D_d)/2]$ and solubilities and Equation 3 were used to predict permeation-rate-versus-
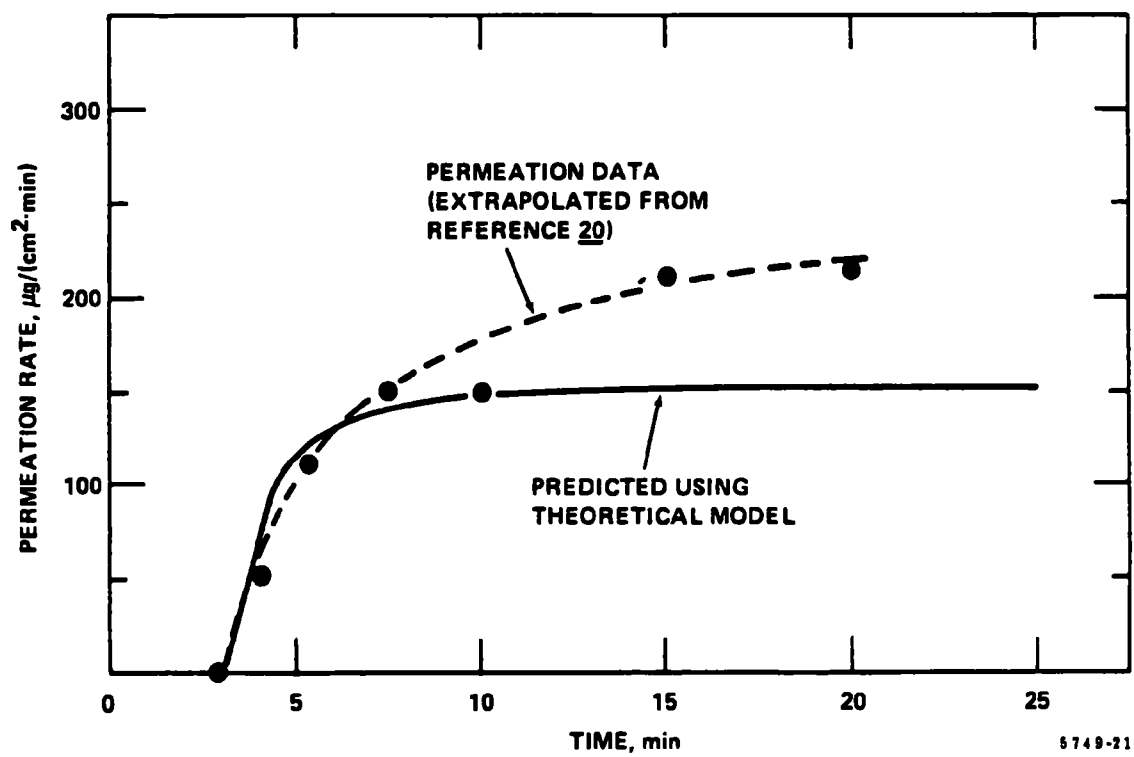
Figure 8. Comparison of predicted and experimental permeation-rate curves for benzene through natural rubber.

time data for acetone in natural rubber and in nitrile rubber. (Permeation tests were also conducted for these glove/solvent combinations.) The predicted permeation-rate data for acetone through a 0.061-cm-thick nitrile-rubber-glove sample are shown in Figure 9. Also shown in the same figure are permeation-rate data obtained in an actual permeation experiment using the same glove/solvent combination (see Test No. D031-45 in Table 27 in Appendix D). The general agreement between the major features of the predicted curve and the actual permeation-rate curve is obvious. The predicted permeation-rate curve for acetone through a 0.061-cm-thick natural-rubber glove is compared to the measured permeation-rate curve (see Test No. D0301-28 in Table 26) in Figure 10.

Due to the lack of time, plots of all of the predicted permeation-rate curves or the actual permeation data could not be prepared. However, the use of the constants (D and S) in Table 16 and Equation 3 to calculate these curves is relatively simple, and the permeation-rate data obtained in permeation experiments are given in a separate data volume. Thus, more comparisons such as those shown in Figures 9 and 10 could easily be made.

Permeation-rate data, predicted as just described, were examined to yield breakthrough times (based on the permeation-rate sensitivities reported in Table 18) and steady-state permeation rates. These predictions and the average observed breakthrough times and steady-state permeation rates measured in permeation experiments are given in Table 20.
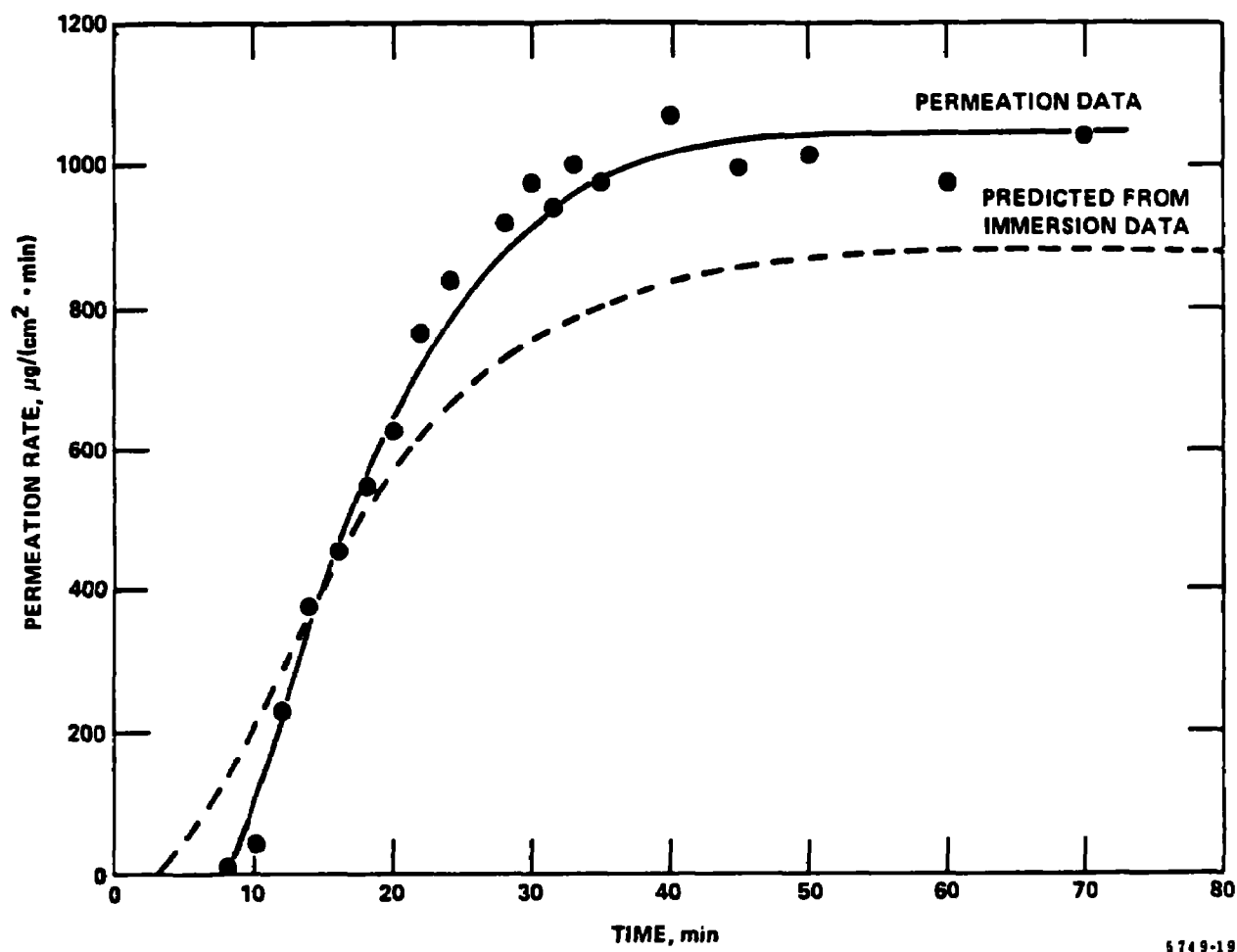
Figure 9. Comparison of predicted and experimental permeation-rate curves for acetone through nitrile rubber.

94
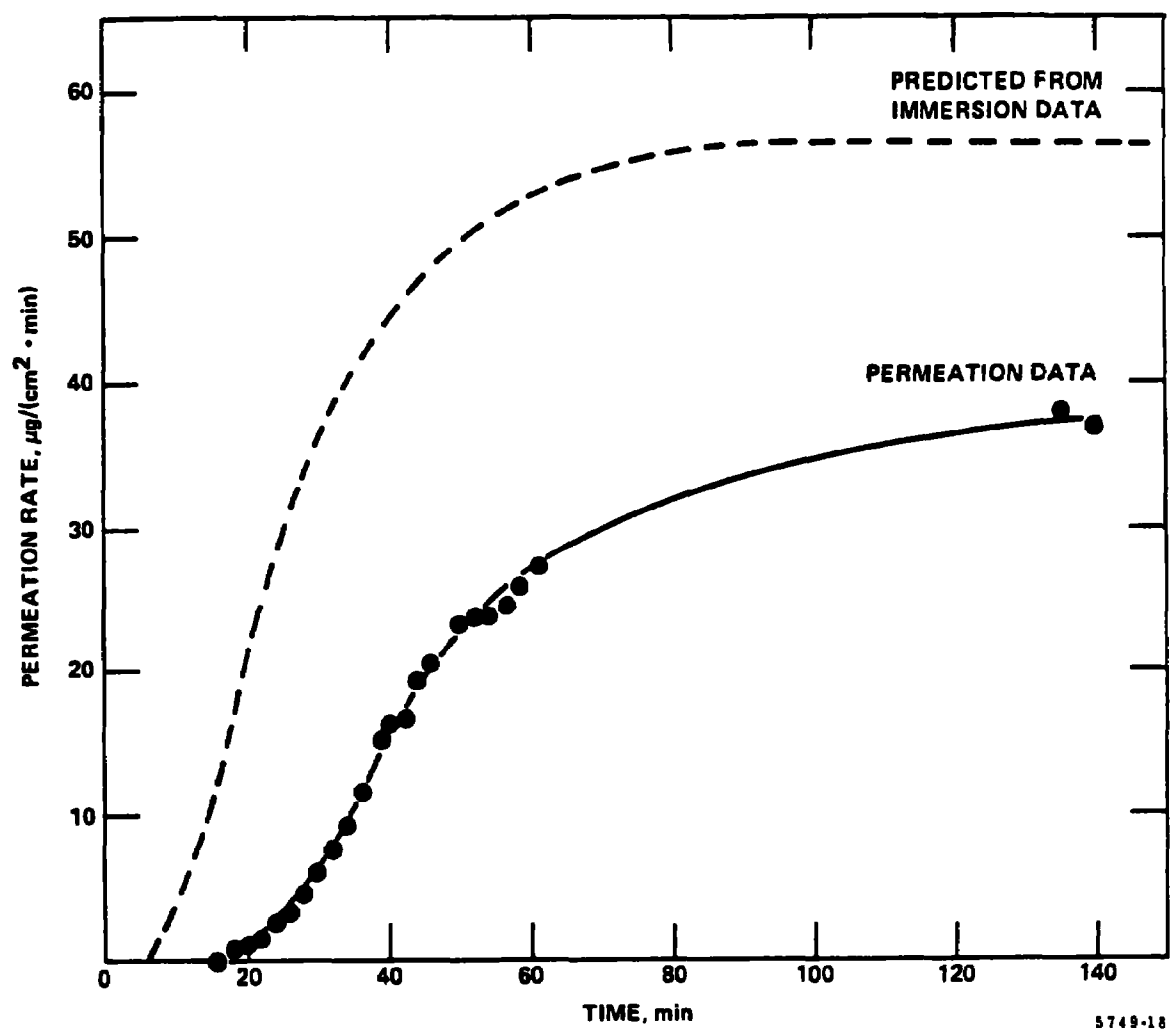
Figure 10. Comprison of predicted and experimental permeation-rate curves for acetone through natural rubber.

95

Glove	Solvent	Breakthrough time,[b] min		Steady-state permeation rate, $\mu g/(cm^2 \cdot min)$	
		Measured	Predicted	Measured	Predicted
Butyl rubber	Acetone	>1115	>10^4	<0.47	0.26
	Cyclohexane	55	6	437	670
	Isopropanol	--	>10^6	--	0.030
	Toluene	24	5	396	59
Natural rubber	Acetone	17	7	34	57
	Cyclohexane	19	5	572	910
	Isopropanol	>150, <1400	130	1	1.9
	Toluene	10	4	782	1200
Neoprene rubber	Acetone	22	6	151	130
	Cyclohexane	>170	28	26	49
	Isopropanol	--	10^6	--	0.095
	Toluene	12	4	642	1100
Nitrile rubber	Acetone	10	3	962	880
	Cyclohexane	>1350	>10^6	<0.12	0.025
	Isopropanol	--	>10^6	--	0.088
	Toluene	52	11	210	200

[a]The symbol "--" means that no permeation test was conducted with this glove/solvent combination.

[b]The predicted breakthrough times are based on the minimum permeation rates that could be detected in permeation tests: 0.47 $\mu g/(cm^2 \cdot min)$ for acetone, 0.12 $\mu g/(cm^2 \cdot min)$ for cyclohexane, and 0.11 $\mu g/(cm^2 \cdot min)$ for toluene, and 0.31 $\mu g/(cm^2 \cdot min)$ for isopropanol.

REFERENCES

1. Waterman, R.R. (Ed.). R.T. Vanderbilt News. 34(2); 1972.

2. Blackley, D.C. High Polymer Latexes, Their Science and Technology, Vol. 2, Testing and Applications. Applied Science Publishers Ltd., London; 1966.

3. Williams, J.R. Permeation of Glove Materials by Physiologically Harmful Chemicals. Am. Ind. Hyg. Assoc. J. 40(10): 877-882; 1979.

4. Schwope, A.D.; Costas, P.P.; Jackson, J.O.; Weitzman, D.J. Guidelines for the Selection of Chemical Protective Clothing, 2nd ed. Volume I: Field Guide. Vol. II: Technical and Reference Manual. Prepared by Arthur D. Little, Inc., for the U.S. Environmental Protection Agency (under subcontract), 1985 March.

5. Schwope, A.D.; Costas, P.P.; Jackson, J.O.; Weitzman, D.J. Guidelines for the Selection of Chemical Protective Clothing. Volume I: Field Guide. Vol. II: Technical and Reference Manual. Prepared by Arthur D. Little, Inc., for the U.S. Environmental Protection Agency (under subcontract), 1983.

6. Bomberger, D.C.; Brauman, S.K.; Podoll, R.T. Studies to Support PMN Review: Effectiveness of Protective Gloves; Final Report. Prepared by SRI International under Contract 68-01-6016 with the US Environmental Protection Agency, Washington, DC, 1984 September.

7. Roder, M.M. Chemical Protective Clothing Monograph. Prepared by the National Institute for Occupational Safety and Health (NIOSH). Draft copy; 1985 January 31.

8. Stampfer, J.F.; McLeod, M.J.; Betts, M.R.; Martinez, A.M.; Berardinelli, S.P. Permeation of Eleven Protective Garment Materials by Four Organic Solvents. Am. Ind. Hyg. Assoc. J. 45(9): 642-654; 1984.

9. Bennett, R.D.; Feigley, C.E.; Oswald, E.O.; Hill, R.H. The Permeation by Liquid Coal of Gloves Used in Coal Liquefaction Pilot Plants. Am. Ind. Hyg. Assoc. J. 44(6): 447-452; 1983.

10. Stampfer, J.F.; McLeod, M.J.; Betts, M.R.; Martinez, A.M.; Berardinelli, S.P. Permeation of Polychlorinated Biphenyls and Solutions of These Substances Through Selected Protective Clothing Materials. Am. Ind. Hyg. Assoc. J. 45(9): 634-641; 1984.

11. Silkowski, J.B.; Horstman, S.W.; Morgan, M.S. Permeation Through Five Commercially Available Glove Materials by Two Pentachlorophenol Formulations. Am. Ind. Hyg. Assoc. J. 45(8): 501-504; 1984.

12. Schwope, A.D.; Randel, M.A.; Broome, M.G. Dimethyl Sulfoxide Permeation Through Glove Materials. Am. Ind. Hyg. Assoc. J. 42(10): 722-725; 1981.

13. Williams, J.R. Evaluation of Intact Gloves and Boots for Chemical Protection. Am. Ind. Hyg. Assoc. J. 42(6): 468-471; 1981.

14. Weeks, Jr., R.W.; Dean, B.J. Permeation of Methanolic Aromatic Amine Solutions Through Commercially Available Glove Materials. Am. Ind. Hyg. Assoc. J. 38(12): 721-725; 1977.

15. Sansone, E.B.; Tewari, Y.B. The Permeability of Laboratory Gloves to Selected Solvents. Am. Ind. Hyg. Assoc. J. 39(2): 169-174; 1978.

16. Walker, E.A.; Castegnaro, M.; Garren, L.; Pignatelli, B. Limitations to the Protective Effect of Rubber Gloves for Handling Nitrosamines. In: Proceedings of a Conference on Environmental Aspects of N-Nitroso Compounds; 1977 August 22-24; Durham, NH. pp. 535-543.

17. Gough, T.A.; Webb, K.S.; McPhail, M.F. Diffusion of Nitrosamines Through Protective Gloves. In: Proceedings of a Conference on Environmental Aspects of N-Nitroso Compounds; 1977 August 22-24; Durham, NH. pp. 531-534.

18. Sansone, E.B.; Tewari, Y.B. The Permeability of Laboratory Gloves to Selected Nitrosamines. In: Proceedings of a Conference on Environmental Aspects of N-Nitroso Compounds; 1977 August 22-24; Durham, NH. pp. 517-529.

19. Henry III, N.W.; Schlatter, C.N. The Development of a Standard Method for Evaluating Chemical Protective Clothing to Permeation by Hazardous Chemicals. Am. Ind. Hyg. Assoc. J. 42(3): 202-207; 1981.

20. Weeks, Jr., R.W.; McLeod, M.J. Permeation of Protective Garment Material by Liquid Benzene and by Tritiated Water. Am. Ind. Hyg. Assoc. J. 43(3): 201-211; 1982.

21. Mikatavage, M.; Que Hee, S.S.; Ayer, H.E. Permeation of Chlorinated Aromatic Compounds Through Viton and Nitrile Glove Materials. Am. Ind. Hyg. Assoc. J. 45(9): 617-621; 1984.

22. Nelson, G.O.; Lum, B.Y.; Carlson, G.J.; Wong, C.M.; Johnson, J.S. Glove Permeation by Organic Solvents. Am. Ind. Hyg. Assoc. J. 42(3): 217-225; 1981.

23. Abernathy, R.N.; Cohen, R.B.; Shirtz, J.J. Measurements of Hypergolic Fuels and Oxidants' Permeation Through Commercial Protective Materials--Part I: Inhibited Red Fuming Nitric Acid and Unsymmetrical Dimethylhydrazine. Am. Ind. Hyg. Assoc. J. 44(7): 505-513; 1983.

24. Johnson, T.C.; Merciez, W.D. Permeation of Halogenated Solvents Through Drybox Gloves. Report RFP-1608. Prepared by the Dow Chemical Company on Contract AT(2901)-1106 for the Atomic Energy Commission; 1971 April 16.

25. Sansone, E.B.; Tewari, Y.B. Penetration of Protective Clothing Materials by 1,2-Dibromo-3-Chloropropane, Ethylene Dibromide, and Acrylonitrile. Am. Ind. Hyg. Assoc. J. 39(11): 921-922; 1978.

26. Calingaert, G.; Shapiro, H. Permeability of Protective Glove Materials to Tetraethyllead and Ethylene Bromide. Ind. and Eng. Chem. 40(2): 322-335; 1948.

27. Sansone, E.G.; Tewari, Y.B. Differences in the Extent of Solvent Penetration Through Natural Rubber and Nitrile Gloves from Various Manufacturers. Am. Ind. Hyg. Assoc. J. 41(7): 527-528; 1980.

28. McFee, D.R. How Well Do Gloves Protect Hands Against Solvents? A.S.S.E. J. IX(5): 1-16; 1964.

29. Sansone, E.B.; Jonas, L.J. Resistance of Protective Clothing Materials to Permeation by Solvent "Splash". Environ. Res. 26: 340-346; 1981.

30. Sansone, E.B.; Tewari, Y.B. The Permeability of Protective Clothing Materials to Benzene Vapor. Am. Ind. Hyg. Assoc. J. 41(3): 170-174; 1980.

31. Hogstedt, C.; Stahl, R. Skin Absorption and Protective Gloves in Dynamite Work. Am. Ind. Hyg. Assoc. J. 41(5): 367-372; 1980.

32. Williams, J.L.; Hopfenberg, H.B.; Stannett, V. Water Transport and Clustering in Poly(Vinyl Chloride), Poly(Oxymethylene), and Other Polymers. J. Macromol. Sci. B3(4): 711-725; 1969.

33. Sweeney, R.F.; Rose, A. Factors Determining Rates and Separation in Barrier Membrane Permeation. I & EC Prod. R. & D. 4(4): 248-251; 1965.

34. Simril, V.L.; Hershberger, A. Permeability of Polymeric Films to Organic Vapors. Mod. Plas.: 97-102, 150-158; 1950 June.

35. Aboul-Nasr, O.T.; Huang, R.Y.M. Diffusivity and Solubility of Organic Vapors in Modified Polyethylene Films; II. Diffusivity Studies. J. Appl. Polym. Sci. 23: 1833-1849; 1979.

36. Aboul-Nasr, O.T.; Huang, R.Y.M. Diffusivity and Solubility of Organic Vapors in Modified Polyethylene Films: III. Solubility Studies. J. Appl. Polym. Sci. 23: 1851-1862; 1979.

37. Sefcik, M.D.; Schaefer, J.; May, F.L.; Raucher, D.; Dub, S.M. Diffusivity of Gases and Main-Chain Cooperative Motions in Plasticized Poly(Vinyl Chloride). J. Polym. Sci. Polym. Phys. Ed. 21: 1041-1054; 1983.

38. Barrer, R.M.; Skirrow, G. Transport and Equilibrium Phenomena in Gas-Elastomer Systems: I. Kinetic Phenomena. J. Polym. Sci. 3(4): 549-563; 1948.

39. Podkówka, J.; Puchalik, A. Comparative Evaluation of Diffusion Coefficients for Gases and Vapors of Organic Substances Through Polyethylene Membranes Determined by Adsorption and Desorption Upstream Time Lag Method. J. App. Polym. Sci. 27: 1471-1478; 1982.

40. Mueller, W.J. Permeability of Rubber to Organic Liquids. Rubber Age. . 81: 982-987; 1957.

41. Kulkarni, S.S.; Stern, S.A. The Diffusion of CO_2, CH_4, C_2H_4, and C_3H_8 in Polyethylene at Elevated Pressures. J. Polym. Sci. Polym. Phys. Ed. 21: 441-465; 1983.

42. Lebovits, A. Permeability of Polymers to Gases, Vapors, and Liquids. Mod. Plas.: 139-150, 194-213: 1966 March.

43. Schott, H. Solubility Parameter, Specific Molar Cohesion, and the Solubility of Ethylene Oxide in Polymers. Biomaterials. 3: 195-198; 1982.

44. Curry, J.E.; McKinley, M.D. Transient Permeation of Organic Vapors Through Elastomeric Membranes. J. Polym. Sci. Polym. Phys. Ed. 11: 2209-2225; 1973.

45. Paul, D.R.; Ebra-Lima, O.M. Pressure-Induced Diffusion of Organic Liquids Through Highly Swollen Polymer Membranes. J. Appl. Polym. Sci. 14: 2201-2224; 1970.

46. Paul, D.R.; Ebra-Lima, O.M. The Mechanism of Liquid Transport Through Swollen Polymer Membranes. J. Appl. Polym. Sci. 15: 2199-2210; 1971.

47. Paul, D.R.; Paciotti, J.D.; Ebra-Lima, O.M. Hydraulic Permeation of Liquids Through Swollen Polymeric Networks. II. Liquid Mixtures. J. Appl. Polym. Sci. 19: 1837-1845; 1975.

48. Paul, D.R.; Garcin, M.; Garmon, W.E. Solute Diffusion Through Swollen Polymer Membranes. J. Appl. Polym. Sci. 20: 609-625; 1976.

49. Coletta, G.C.; Schwope, A.D.; Arons, I.J.; King, J.W.; Sivak, A. Development of Performance Criteria for Protective Clothing Used Against Carcinogenic Liquids; Final Report. Prepared by Arthur D. Little, Inc., for the National Institute for Occupational Safety and Health under Contract 210-76-0130, 1978 October.

50. Fujita, H. Diffusion. In: Encyclopedia of Polymer Science and Technology, Vol. 5. John Wiley & Sons, Inc., New York; 1966. pp. 65-81.

51. Hayes, M.J.; Park, G.S. The Diffusion of Benzene in Rubber. Part 2--High Concentrations of Benzene. Trans. Faraday Soc. 52: 949-955; 1956. Hayes, M.J.; Park, G.S. The Diffusion of Benzene in Rubber. Part 1--Low Concentrations of Benzene. Trans. Faraday Soc. 51: 1134-1142; 1951.

52. Crank, J. The Mathematics of Diffusion. Oxford University Press, New York; 1956.

53. Jost, W. Diffusion in Solids, Liquids, and Gases. Academic Press, New York; 1952.

54. Crank, J.; Park, G.S. (Ed.). Diffusion in Polymers. Academic Press, London; 1968.

55. Holstein, T. Westinghouse Research Report 411-9-D.

56. Barton, A.F.M. CRC Handbook of Solubility Parameters and Other Cohesion Parameters. CRC Press, Inc., Boca Raton, Florida; 1983.

57. Haxo, H.E., Jr.; Nelson, N.A.; Miedema, J.A. Solubility Parameters for Predicting Membrane-Waste Liquid Compatibility. In: Proceedings of the Eleventh Annual Research Symposium on Land Disposal of Hazardous Waste; 1985 April 29-May 1; Cincinnati, OH.

58. Waters, M.J. Laboratory Methods for Evaluating Protective Clothing Systems Against Chemical Agents. Report CRDC-SP-84010. Prepared by the Chemical Research and Development Center, 1984 June.

59. Hildebrand, J.H. Solubility. XII. Regular Solutions. J. Am. Chem. Soc. 51: 66; 1929.

60. Flory, P.J. Thermodynamics of High Polymer Solutions. J. Chem. Phys. 9: 660; 1941. Flory, P.J. Thermodynamics of High Polymer Solutions. J. Chem. Phys. 10: 51; 1942.

61. Huggins, M.L. Solutions of Long Chain Compounds. J. Chem. Phys. 9: 440; 1941.

62. Huggins, M.L. Some Properties of Solutions of Long-Chain Compounds. J. Phys. Chem. 46: 151; 1942

63. Huggins, M.L. Theory of Solutions of High Polymers. J. Am. Chem. Soc. 64: 1712; 1942.

64. Henriksen, H. Selection of Materials for Safety Gloves, Polymer Membranes to Protect Against Contact with Epoxy Products. Directorate of Labor Inspection, Copenhagen; 1982. (Translation from National Institute for Occupational Safety and Health, Morgantown, WV).

65. Hansen, C.; Beerbower, A. Solubility Parameters. In: Kirk-Othmer: Encyclopedia of Chemical Technology, Supplement Vol., 2nd ed. Wiley & Sons, New York; 1971. pp. 889-910.

66. Prausnitz, J.M. Molecular Thermodynamics of Fluid Phase Equilibria. Prentice-Hall, Inc., Englewood Cliffs, New Jersey; 1969.

67. Heil, J.F.; Prausnitz, J.M. Phase Equilibria in Polymer Solutions. AIChE J. 12(4): 678-685; 1966.

68. Abrams, D.S.; Prausnitz, J.M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of a Partly or Completely Miscible Systems. AIChE J. 21(1): 116-128; 1975.

69. Fredenslund, A.; Jones, R.L.; Prausnitz, J.M. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. AIChE J. 21(6): 1086-1099; 1975.

70. Fredenslund, A.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria Using UNIFAC: A Group-Contribution Method. Elsevier Scientific Publishing Company, New York; 1977.

71. Skjold-Jorgensen, S.; Kolbe, B.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. Ind. Eng. Chem. Process Des. Dev. 18(4): 714-722; 1979.

72. Gmehling, J.; Rasmussen, P.; Fredenslund, A. Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2. Ind. Eng. Chem. Process Des. Dev. 21: 118-127; 1982.

73. Macedo, E.A.; Weidlich, U.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 3. Ind. Eng. Chem Process Des. Dev. 22(4): 676-678; 1983.

74. Wilcox, R.F. Expanding the Boundaries of UNIFAC. Chemical Engineering, October 17, 1983; 66-68.

75. Oishi, T.; Prausnitz, J.M. Estimation of Solvent Activities in Polymer Solutions Using a Group-Contribution Method. Ind. Eng. Chem. Process Des. Dev. 17: 333-339; 1978.

76. Tseng, H.S.; Lloyd, D.R. Influence of Polymer Molecular Weight on Selected Thermodynamic Properties of Polymer/Solvent Systems and the Application of the UNIFAC theory. Polymer. 25: 670-680; 1984.

77. Georgeton, G.K.; Sommerfeld, J.T. Estimating vapor-liquid equilibria with UNIFAC. Chemical Engineering, October 17, 1983; 61-65.

78. Magnussen, T.; Rasmussen, P.; Fredenslund, A. UNIFAC Parameter Tables for Prediction of Liquid-Liquid Equilibria. Ind. Eng. Chem. Process Des. Dev. 20: 331-339; 1981.

79. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. The Properties of Gases and Liquids, 3rd ed. McGraw-Hill, New York; 1977.

80. Vrentas, J.S.; Duda, J.L. Diffusion in Polymer-Solvent Systems. I. Reexamination of the Free-Volume Theory. J. Poly. Sci. Polym. Phys. Ed. 15: 403-416; 1977.

81. Vrentas, J.S.; Duda, J.L. Diffusion in Polymer-Solvent Systems. II. A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration and Molecular Weight. J. Polym. Sci. Polym. Phys. Ed. 15: 417-439; 1977.

82. Vrentas, J.S.; Duda, J.L. Diffusion in Polymer-Solvent Systems. III. Construction of Deborah Number Diagrams. J. Polym. Sci. Polym. Phys. Ed. 15: 441-453; 1977.

83. Paul, C.W. A Model for Predicting Solvent Self-Diffusion Coefficients in Nonglassy Polymer/Solvent Solutions. J. Polym. Sci. Polym. Phys. Ed. 21: 425-439; 1983.

84. Chalykh, A.E.; Vasenin, R.M. Diffusion in Polymer-Solvent Systems. Polym. Sci. USSR. 8: 1908-1916; 1966.

85. Rehage, G.; Ernst, O.; Fuhrmann, J. Fickian and Non-Fickian Diffusion in High Polymer Systems. Discuss. Faraday Soc. 49: 208-221; 1970.

86. Berry, G.C.; Fox, T.G. The Viscosity of Polymers and Their Concentrated Solutions. Adv. Polym. Sci. 5: 261; 1968.

87. Loflin, T.; McLaughlin, E. Diffusion in Binary Liquid Mixtures. J. Phys. Chem. 73: 186-190; 1969.

88. Cohen, M.H.; Turnbull, D. Molecular Transport in Liquids and Glasses. J. Chem. Phys. 31: 1164-1169; 1959.

89. Dullien, F.A.L. Predictive Equations for Self-Diffusion in Liquids; A Different Approach. AIChE J. 18: 62-70; 1972.

90. Haward, R.N. Occupied Volume of Liquids and Polymers. Macromol. Sci. Revs. Macromol. Chem. C4: 191-202; 1970.

91. Flory, P.J. Thermodynamics of Polymer Solutions. Discuss. Faraday Soc. 49: 7-29; 1970.

92. Likey, P.E.; Gambill, W.R. Physical and Chemical Data. In: Chemical Engineers' Handbook. McGraw-Hill, New York; 1973. p. 3-212.

93. Lange's Handbook of Chemistry, Physical Properties. McGraw-Hill, New York; 1979. pp. 10-127 and 10-128.

94. Rodriguez, F. Principles of Polymer Systems. McGraw-Hill, New York; 1982.

95. Smith, J.M.; Van Ness, H.C. Introduction to Chemical Engineering Thermodynamics, 3rd ed. McGraw-Hill, New York; 1975. pp. 569-570.

96. Viscosity: Pure Liquids. In: International Critical Tables, Vol. VII. McGraw-Hill, New York; 1930. p. 219.

97. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds. American Petroleum Institute Project 44, Carnegie Press, Pittsburgh, PA; 1953.

98. Gerald, C.F. Applied Numerical Analysis, 2nd ed. Addison-Wesley Publishing Company, Reading, MA; 1980. pp. 390-432.

APPENDIX A

SUMMARY OF TEST METHODS FOR EVALUATING PROTECTIVE MATERIALS

SUMMARY OF MECHANICAL-PROPERTIES TESTS

ASTM Method D751-79 -- Standard Methods of Testing Coated Fabrics

The purpose of this method, first published in 1943, is to test coated fabrics for a wide variety of mechanical properties. The method describes standard procedures for determining length, width, thickness, and mass of coated fabric samples, breaking strength, elongation, bursting strength, tearing strength (by both a pendulum method and a tongue tear method), hydrostatic resistance, adhesion of coating to fabric, tack-tear resistance, low-temperature bend strength, low-temperature impact strength, and seam strength. In terms of glove evaluation, Method D751-79 is directly applicable to the evaluation of fabric-supported rubber gloves.

ASTM Method D412-83 -- Standard Test Methods for Rubber Properties in Tension

This method, first published in 1935, is used to determine the tensile properties of rubber at various temperatures. The method describes the specifications of the testing machine (such as an Instron tester) and the test chamber, the preparation of the test specimens, and the procedures for determining tensile strength, tensile stress, ultimate elongation, and tensile set. The method is directly applicable to the evaluation of unsupported rubber glove material or elastomeric sheets or films.

ASTM Method D1682-64 -- Standard Test Methods for Breaking Load and Elongation of Textile Fabrics

This test method, first issued in 1959, is used to determine the breaking load and elongation of textile fabrics with a tensile test machine using the grab, raveled-strip, and cut-strip methods. The grab test is a tension test in which only a part of the width of the fabric specimen is gripped in the clamps of a tensile testing machine. The raveled-strip test is a tension test in which the full width of the specimen is gripped in the clamps and the specified specimen width is secured by raveling away yarns. The cut-strip method is a tension test in which the full width of the specimen is gripped in the clamps and the specimen width is secured by cutting the fabric. This method is not directly applicable to the evaluation of glove samples but may have some utility in evaluating the fabric portion of fabric-supported gloves.

ASTM Method D2261-83 -- Standard Test Method for Tearing Strength of Woven Fabrics by the Tongue (Single Rip) Method (Constant-Rate-of-Extension Tensile Testing Machine)

Originally issued in 1964, this method describes procedures for the determination of the tearing strength of woven fabrics by the tongue (single rip)

method using a recording constant-rate-of-extension (CRE) tensile testing machine. In the method, tearing strength is defined as the force required to continue or propagate a lengthwise tear started previously in the specimen. The method may be applicable to the evaluation of the fabric portion of fabric-supported gloves.

ASTM Draft Test Method Fxxx -- Test Method for Resistance to Cut

This draft ASTM test method describes procedures for determining the resistance of a rectangular test specimen (either a single layer or a composite material) to static cut by measuring the force required to cause a sharp-edged blade to cut the surface of the test specimen. The test method defines the test procedure, test apparatus, blade dimensions, the size and conditioning of the test specimen, and the positioning of the test specimen on the test apparatus.

ASTM Draft Test Method Fxxx -- A Test Method for Resistance to Puncture

This draft ASTM test method describes procedures for determining the resistance of a rectangular test specimen (either a single layer or a composite material) to puncture by measuring the force required to cause a pointed penetrometer to puncture the material specimen. The test method defines the test procedure, the test apparatus, the dimensions of the penetrometer, and the test specimen size, condition, and position in the test apparatus.

ASTM Method D4157-82 -- Standard Test Method for Abrasion Resistance of Textile Fabrics (Oscillatory Cylinder Method)

This method defines a standard procedure for measuring the abrasion resistance of textile fabrics by subjecting the test specimen to unidirectional rubbing action under known conditions of pressure, tension, and abrasive action. The test is conducted in a special apparatus, described in the method, that contains an oscillating cylinder section. The method may be useful in evaluating the fabric portion of fabric-supported protective gloves.

ASTM Method D1388-64 -- Standard Test Methods for Stiffness of Fabrics

Originally issued in 1956, ASTM Method D1388-64 describes two test methods for determining the stiffness of fabrics, particularly woven fabrics: the cantilever test and the heart loop test. Both methods are based on the bending of a fabric in one plane under the force of gravity. The method may be useful in evaluating the fabric portion of fabric-supported protective gloves.

ASTM Method D3041-79 -- Standard Method for Testing Coated Fabrics -- Ozone Cracking in a Chamber

This method defines a standard procedure for determining the resistance of elastomer-coated fabrics to cracking when exposed to an atmosphere containing ozone. Each test specimen is kept under a controlled surface strain, and the ozone concentration in the test chamber is maintained at a fixed value. The

method is directly applicable to the evaluation of fabric-supported rubber gloves.

ASTM Method D1149-81 -- Standard Method for Rubber Deterioration -- Surface Ozone Cracking in a Chamber (Flat Specimen)

Originally issued in 1951, this method defines a standard procedure for determining the resistance of vulcanized rubber to cracking when exposed to an atmosphere containing ozone. Each rubber specimen is kept under a surface tensile strain, and the ozone concentration in the test chamber is maintained at a fixed value. The method is directly applicable to the evaluation of unsupported rubber gloves.

ASTM Method G26-83 -- Standard Practice for Operating Light-Exposure Apparatus (Xenon-Arc Type) With and Without Water for Exposure of Nonmetallic Materials

This method is a combination of two previous ASTM Methods--G26 and G27. The method describes the basic principles and operating procedure for exposing samples of nonmetallic materials to ultraviolet radiation with a xenon-arc light source. The method is concerned only with the exposure method and does not cover sample preparation, test conditions, or evaluation of results. The method is applicable to the evaluation of both supported and unsupported rubber gloves.

SUMMARY OF CHEMICAL-RESISTANCE TESTS

ASTM Method F739-81 -- Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals

This relatively recent method defines standard test procedures for determining the resistance of protective-clothing materials to permeation by hazardous liquid chemicals in direct, continuous contact with the normal outer surface of the material specimen. The permeation resistance of the test specimen is determined by measuring the breakthrough time of the challenge chemical through the test sample and then monitoring the subsequent permeation rate of the chemical through the sample.

The method specifies the use of a specially constructed glass permeation-test cell. When mounted in the test cell, the material specimen acts as a barrier separating the liquid challenge chemical from a collecting medium. The collecting fluid, either a liquid or a gas, is sampled and quantitatively analyzed for hazardous permeant as a function of time after initial liquid contact. Both the initial breakthrough time and the permeation rate of the hazardous chemical are determined from the time-dependent chemical analysis of the collecting fluid by means of direct calculations or graphical analysis.

ASTM Draft Method F739-8X (Revision 4) -- Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases

This draft test method is an extension of Method F739-81 that incorporates a standard test procedure for determining the resistance of protective clothing materials to permeation by potentially hazardous gaseous chemicals in continuous contact with the normal outer surface of the material. Otherwise the method is essentially identical to Method F739-81. An earlier revision of the draft test method included as an appendix a statistical procedure for determining the equivalency of permeation-test cells of different designs. Under the current revision of test method F739-81, the equivalency appendix has been deleted from the method and is slated to be developed into a separate test method.

ASTM Draft Method F739-8X (Draft 3) -- Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquid, Liquid Splashes, and Gases

This is the latest draft revision of Method F739-81. The method includes a standard procedure for determining the resistance of protective-clothing materials to permeation by liquid chemicals in intermittent contact with the normal outer surface of the material. The remainder of the method is essentially identical to Draft Method F739-8X (Revision 4) discussed above.

Permeation Test Methods Contained in CRDC-SP-84010 -- Laboratory Methods for Evaluating Protective Clothing Systems Against Chemical Agents

CRDC-SP-84010 is a special publication (58) issued by the US Army Chemical Research and Development Center. The publication specifies standard test procedures for evaluating the resistance of protective clothing materials to permeation by chemical-warfare agents. The methods specify test cells design, test procedures, analytical methods, and criteria for interpreting the test results.

ASTM Draft Method F903 (Revision 7) -- New Standard Test Method for Resistance of Protective Clothing Materials to Penetration by Liquids

This proposed test method defines standard procedures for determining the resistance of protective clothing materials to visible penetration by liquids in direct, continuous contact with the normal outer surface of the material. The method determines resistance to penetration only and not the resistance to permeation or chemical degradation. The method involves mounting a sample of a protective material in a specially designed test cell so that the sample divides the cell into two chambers. The normal outer surface of the sample is then exposed to a liquid chemical under pressure (2 psig), and the normal inner surface of the sample is observed (through the transparent cover plate of the test cell) for visible penetration of the liquid.

ASTM Draft Method Fxxx -- Test Method for Evaluating Protective Clothing Materials for Resistance to Degradation by Liquid Chemicals

This proposed test method is a semiquantitative method for determining the resistance of protective-clothing materials to degradation by liquid chemicals in direct, continuous contact with the normal outer surface of the material. The method consists of measuring the thickness, weight, and elongation of a material specimen, exposing separate identical specimens of the same material to a liquid chemical, and measuring the thickness, weight, and elongation of the additional specimens to identify changes resulting from contact with the liquid chemical.

ASTM Method D471-79 -- Standard Test Method for Rubber Property -- Effect of Liquids

Originally published in 1937, this well-established method measures the comparative ability of rubber and elastomeric materials to withstand the effect of liquids. The method involves immersing a sample of a material in a liquid chemical at a constant temperature and measuring selected physical properties of the sample as a function of immersion time. Any deterioration of the material sample is determined by noting the changes in physical properties before and after immersion in the test liquid over various time intervals. The physical properties that are measured during the test are weight, volume, thickness, soluble extracted matter, tensile strength, elongation, hardness, breaking strength, burst strength, tear strength, and adhesion (for coated fabrics).

APPENDIX B

THE DERIVATION OF THE MODIFIED PAUL MODEL AND A COMPUTER PROGRAM

DERIVATION OF THE MODIFIED PAUL MODEL

The Paul model for predicting the solvent self-diffusion coefficient is based on free-volume theory. A *self-diffusion coefficient* may be defined as the diffusion coefficient of a component within itself. No concentration gradient exists. A *mutual-diffusion coefficient* may be defined as the diffusion coefficient of a component within another, for example, a solvent within a polymer. It can be shown that (87):

$$D = [f(D_1,x_1,D_2,x_2)/RT] \; (\partial\mu_1/\partial\ln x_1)_{T,P} \qquad (32)$$

where D is the mutual diffusion coefficient; D_1 and D_2 are the solvent and polymer self-diffusion coefficients, respectively; x_1 and x_2 are solvent and polymer mole fractions, respectively; R is the universal gas constant; T is the absolute temperature; μ_1 is the solvent chemical potential; and P is the pressure. The quantity $f(D_1,x_1,D_2,x_2)$ represents a function yet to be determined.

Vrentas and Duda (80-82) proposed that because D_2 is much smaller than D_1 for most systems, D_2 may be neglected in $f(D_1,x_1,D_2,x_2)$ over a large concentration interval from almost pure polymer to about 85% solvent in some systems. In this range, they suggest the use of:

$$D = (x_2D_1/RT)(\partial\mu_1/\partial\ln x_1)_{T,P} \qquad (33)$$

Paul's model, an extension of the Cohen-Turnbull model (88), is based on the following expression:

$$D_1 = J \; D_{01} \; T^{1/2} \exp \; (-\gamma\bar{v}_1^*/\bar{v}_f) \qquad (34)$$

where J is the jump-back factor described below, D_{01} is a constant evaluated from experimental data, and γ is a numerical factor between 1/2 and 1, which accounts for the fact that a given free-volume element is available to more than one molecule. The term $\bar{v}_1^*$ is the specific critical volume for diffusion, which is the minimum free-volume element necessary for diffusion, and $\bar{v}_f$ is the specific free volume of the mixture. The parameters J, D_{01}, γ, $\bar{v}_1^*$, and $\bar{v}_f$ must be evaluated.

The jump-back factor, J, represents the ratio of the probability in the mixture that a solvent diffusive jump is successful to the probability in a pure solvent that a diffusive jump is successful. A successful jump by a solvent molecule is defined as one which is not immediately followed by a

return jump to its original position. Analytically,

$$J = [(z+1)/z] \sum_{n=1}^{z} [n/(n+1)] \; P(s=n) \qquad (35)$$

where z is the number of sites available to a diffusing solvent molecule (usually $4<z<10$), s is the number of solvent molecules at z sites, and P is a probability, which may be easily evaluated using Pascal's triangle. P can be related to s, z, the solvent volume fraction ϕ_1, and the polymer volume fraction ϕ_2 by:

$$P(s) = \binom{z}{s} \phi_1^{s} \phi_2^{z-s} = [z!/(s!(z-s)!)] \phi_1^{s} \phi_2^{z-s} \qquad (36)$$

Figures which graphically represent Equation 36 can be found in the literature (83). It should be noted that $J(z=10)/J(z=4)$ is less than 2 for $\phi_1 > 0.05$. This implies a weak dependence of J on z except at very low solvent concentrations.

The parameters D_{01}, $\bar{v}_f$, and the product $\gamma\bar{v}_1^{*}$ may be evaluated using viscosity and specific-volume data for the pure solvent. Only a limited amount of binary data are also needed, but these may be approximated from equations of state. Paul (83) used a correlation presented by Dullien (89):

$$\eta_1 D_1^{0} = (RT/v_1)(0.124 \times 10^{-16} \; mol^{2/3}) \; v_{c_1}^{2/3} \qquad (37)$$

where η_1 is the solvent viscosity at temperature T, D_1^{0} is the self-diffusion coefficient of pure solvent, v_1 is the solvent molar volume at temperature T, and v_c is the solvent critical molar volume. For pure solvent ($\mathcal{J}=1$), Equation 34 reduces to:

$$D_1^{0} = D_{01} T^{1/2} exp\{\gamma\bar{v}_1^{*}/[\bar{v}_1 - \bar{v}_1(0\;K)]\} \qquad (38)$$

Note that

$$\bar{v}_f = \bar{v}_1 - \bar{v}_1(0\;K) \qquad (39)$$

has been used. Equation 39 implies that the free volume is identically zero at 0 K (absolute zero). The value of $\bar{v}_1(0\;K)$ may be estimated by a variety of methods (90). Substituting Equation 38 into Equation 37 and taking the ratio of the resulting equation evaluated at T to the same equation evaluated at T_{ref}, some reference temperature, yields:

$$\ln[(\eta_1/\eta_{1ref})(v_1/v_{1ref})(T_{ref}/T)^{1/2}]$$
$$= \gamma\bar{v}_1^{*}\{[\bar{v}_1 - \bar{v}_1(0\;K)]^{-1} - [\bar{v}_{1ref} - \bar{v}_1(0\;K)]^{-1}\} \qquad (40)$$

A plot of the left-hand side of Equation 40 against the expression in parentheses on the right-hand side yields a straight line of slope $\gamma\bar{v}_1^{*}$. Vis-

cosity and specific-volume (or molar-volume) data are present in the literature for most solvents. However, these data would have to be determined if they are unavailable.

Knowing $\gamma \bar{v}_1^*$, we can evaluate D_{01} from Equations 37 and 38. The only remaining parameter is $\bar{V}_f$ which may be expressed as:

$$\bar{V}_f = \bar{V} - \bar{V}(0 \text{ K}) \qquad (41)$$

where $\bar{V}$ is the specific volume for the mixture.

If $\bar{V}$ is not available in the literature, a rough estimate of this quantity may be obtained using the Flory-Prigogne theory (91) of excess volume:

$$\bar{V}^E \equiv \bar{V} - (w_1\bar{V}_1^0 + w_2\bar{V}_2^0) \qquad (42)$$

where $\bar{V}^E$ is the excess specific volume and w_1 and w_2 are the weight fractions of the solvent and the polymer, respectively. The terms $\bar{V}_1^0$ and $\bar{V}_2^0$ are the specific volume of pure solvent and pure polymer, respectively.

Rough estimates are also possible by setting $\bar{V}^E = 0$. This may be done because generally at room temperature, the maximum value of $\bar{V}^E$ is less than 1% of the actual volume whereas $\bar{V}_f$ is about 15%. Increasing the temperature increases $\bar{V}^E$ but $\bar{V}_f$ increases more rapidly (83). For the calculations presented in this report, $\bar{V}^E$ was assumed to be zero.

One drawback to the Paul model is that the value of D_1 calculated is less accurate when the solvent volume fraction, ϕ_1, is less than 0.1. This is because the choice of z affects J more strongly at small solvent volume fractions than at large volume fractions. More significantly however, the polymer segments may contribute substantially to the refilling of voids even if solvent molecules are nearby; thus, an assumption made in Paul's derivation of Equation 34 is invalidated (83). Under such conditions, that is, for $\phi_1 < 0.1$, the Vrentas-Duda model should be used.

After the calculation of D_1, the only remaining quantity to be evaluated in order to obtain D is the derivative shown in Equation 33. This may be calculated by noting that:

$$(\partial \mu_1 / \partial \ln x_1)_{T,P} = RT(\partial \ln a_1 / \partial \ln x_1)_{T,P} \qquad (43)$$

where a_1 is the activity of the solvent in the mixture.

The expression on the right-hand side of Equation 43 may be evaluated from a_1-versus-x_1 data generated by the UNIFAP program. This information can then be used with D_1 and Equation 33 to calculate the mutual-diffusion coefficient, D.

COMPUTER PROGRAM FOR THE CALCULATION OF D

A computer program based on the Paul model was written using FORTRAN 77, and a DEC 2040 computer was used to perform the series of calculations needed to estimate the diffusion coefficient, D. A copy of the program is included at the end of this section. Because time limitations, the software was not made "user friendly"; however, it can be easily followed.

The first parameter to be calculated by the program is the quantity $\gamma \bar{v}_1^*$. Viscosity-versus-temperature and specific-volume-versus-temperature data in Equation 40 are used by a linear-regression subroutine. Next Equations 37 and 38 are used to calculate the constant D_{01}. The jump-back factor is calculated by Equations 35 and 36. UNIFAP data are used to calculate the derivative in Equation 32 by noting the relationship shown in Equation 43. Next, D is calculated using Equation 32. A library graphics package is used to plot D as a function of solvent weight fraction. Tables 21 through 24 show the data used in the calculations presented in Section 6 of this report.

TABLE 21. VISCOSITY AND SPECIFIC VOLUME OF BENZENE
AS A FUNCTION OF TEMPERATURE

Temperature, K	Viscosity,[a] cp	Specific volume,[b] cm^3/g
284[c]	0.75	1.1254
293	0.65	1.1376
303	0.57	1.1516
313	0.50	1.1660
323	0.66	1.1809
333	0.39	1.1963
343	0.35	1.2124
353	0.31	1.2291

[a]From Reference 92.

[b]From Reference 93.

[c]Data used as the reference condition in Equation 40.

TABLE 22. OTHER PARAMETERS USED IN THE CALCULATION OF DIFFUSION
COEFFICIENTS FOR BENZENE IN NATURAL RUBBER

Parameter	Value	Reference
$\bar{v}_1^0$	$1.1109 \text{ cm}^3/\text{g}$	93
$\bar{v}_2^0$	$1.0753 \text{ cm}^3/\text{g}$	94
$\bar{v}_1$ (0 K)	$0.9115 \text{ cm}^3/\text{g}$	90
$\bar{v}_2$ (0 K)	$\approx 0.9 \text{ cm}^3/\text{g}$	90
$\bar{v}_{c_1}$	$258.7 \text{ cm}^3/\text{g}$	95
T_{int}	298 K	--
MW_1	78.11	--
MW_2	68.12[a]	--
z	6	--

[a]Given as the molecular weight of a monomer unit.

115

TABLE.23. VISCOSITY AND SPECIFIC VOLUME OF n-HEPTANE
AS A FUNCTION OF TEMPERATURE

Temperature, K	Viscosity,[a] cp	Specific volume,[b] cm^3/g
289[c]	0.2271	1.4544
300	0.2156	1.4748
311	0.2045	1.4960
322	0.1947	1.5181
333	0.1857	1.5412
344	0.1775	1.5653
355	0.1700	1.5907
366	0.1631	1.6174
378	0.1567	1.6456
389	0.1508	1.6754

[a]From Reference 96.

[b]From Reference 97.

[c]Data used as the reference condition in Equation 40.

TABLE 24. OTHER PARAMETERS USED IN THE CALCULATION OF DIFFUSION COEFFICIENTS FOR $\underline{n}$-HEPTANE IN NATURAL RUBBER

Parameter	Value	Reference
$\bar{v}_1^0$	1.4327 cm^3/g	93
$\bar{v}_2^0$	1.0753 cm^3/g	94
$\bar{v}_1$ (0 K)	1.0941 cm^3/g	90
$\bar{v}_2$ (0 K)	≈ 0.9 cm^3/g	90
$\bar{v}_{c_1}$	432.0 cm^3/g	94
T_{int}	298 K	--
MW_1	100.20	--
MW_2	68.12[a]	--
z	6	--

[a]Given as the molecular weight of a monomer unit.

```
C
C
C====================================================================
C
C     THIS PROGRAM WILL CALCULATE DIFFUSION COEFFICIENTS FOR VARIOUS
C     SOLVENT/POLYMER COMBINATIONS AS A FUNCTION OF SOLVENT
C     CONCENTRATION.
C
C
C     PROGRAM WRITTEN BY ABHOYJIT BHOWN      8/85
C
C====================================================================
C
C
C------ALLOCATE VARIABLES
C
      INTEGER OUT
      REAL TEMP(50),VISC(50),SVOL(50),X(50),Y(50),N,J,MW1,MW2,XP(50),
     +     YP(50)
      INTEGER Z
      R = 8.31441
C
C
C------OPEN DATA FILES
C
      OPEN (UNIT=1,FILE='DIFFDAT.DAT',TYPE='OLD')
      OPEN (UNIT=2,FILE='UNIFDAT.DAT',TYPE='OLD',DEVICE='DSK')
C
C
C------INPUT DATA
C
      READ (1,*) N
      DO 100 I=1,N
  100 READ (1,*) TEMP(I),VISC(I),SVOL(I)
      READ (1,*) V10,V20,V10K,V20K,V1C
      READ (1,*) TREF,VREF,SREF,TINT,MW1,MW2,Z
      READ (1,*) W1B,W1E,W1I
C
C
C------CALCULATE GAMMA-VSTAR
C
      DO 200 I=1,N
            X(I) = 1/(SVOL(I)-V10K) - 1/(SREF-V10K)
  200 Y(I) = LOG (VISC(I)/VREF * SVOL(I)/SREF * SQRT(TREF/TEMP(I)))
      CALL LINREG (N,X,Y,SLOPE,YINT,CORR)
      GAVS = SLOPE
C
C
C------CALCULATE CONSTANT D01
C
      DO 300 I=1,N
            X(I) = SQRT (TEMP(I)) * EXP(-GAVS/(SVOL(I)-V10K))
  300 Y(I) = 0.124E-16 * R * TEMP(I) / SVOL(I) / VISC(I) * V1C**(2./3.)
     +            * 1.0E9 / MW1
      CALL LINREG (N,X,Y,SLOPE,YINT,CORR)
      D01 = SLOPE
C
C
C------START CONCENTRATION-DEPENDANT DIFFUSION COEFFICIENT CALCULATIONS
C
```

118

```
      WRITE (3,1)
      IC = 0
      DO 400 W1=W1B,W1E,W1I
      IC = IC + 1
C
C
C----------READ UNIFAP DATA AND CALCULATE DERIVATIVE OF A VS X
C
  350     READ (2,*) WEI1,ACT1
          IF (NINT(100.*WEI1).NE.NINT(100.*W1)) GOTO 350
          READ (2,*) WEI2,ACT2
          XWEI1 = WEI1/MW1/(WEI1/MW1+(1-WEI1)/MW2)
          XWEI2 = WEI2/MW1/(WEI2/MW1+(1-WEI2)/MW2)
          DERV  = (LOG(ACT1)-LOG(ACT2)) / (LOG(XWEI1)-LOG(XWEI2))
          VF    = W1 * (V10-V10K) + (1-W1)*(V20-V20K)
          VFRA1 = W1*V10/(W1*V10+(1-W1)*V20)
C
C
C----------CALCULATE J
C
          CALL FACT (Z,I1)
          SUM = 0.
          DO 370 I=1,Z
               CALL FACT (I,I2)
               CALL FACT (Z-I,I3)
               P = FLOAT(I1/I2/I3)*VFRA1**I*(1.-VFRA1)**(Z-I)
  370     SUM  = SUM + I/(I+1.)*P
          J    = (Z+1.)/Z*SUM
C
C
C----------CALCULATE D
C
          D1    = J*D01*SQRT(TINT)*EXP(-GAVS/VF)
          X1    = W1/MW1/(W1/MW1+(1.-W1)/MW2)
          D     = (1.-X1)*D1*DERV
          XP(IC) = VFRA1
          YP(IC) = D
  400 WRITE (3,2) W1,VFRA1,D
C
C
C-----FORMAT STATEMENTS
C
    1 FORMAT (1X,'WEIGHT FRACTION',5X,'VOLUME FRACTION',5X,
     +         'MUTUAL-DIFF COEFF (CM**2/S)')
    2 FORMAT (1X,F10.4,10X,F10.4,15X,E14.7)
C
C
C-----CLOSE FILES, CALL PLOTTING ROUTINE, AND END PROGRAM
C
      CLOSE (UNIT=1)
      CLOSE (UNIT=2)
      CALL PLOTS (0,0,6)
      CALL PLOT (0.0,0.0,-3)
      CALL SAMLOG (XP,YP,IC,1,1,1,1,1,II)
      CALL PLOT (12.0,0.0,-999)
      END
C
C
C-----LINEAR REGRESSION SUBROUTINE
C
```

```
      SUBROUTINE LINREG (DN,DX,DY,DSLOPE,DYINT,DCORR)
C
C
C-----ALLOCATE AND RESET VARIABLES
C
      DIMENSION DX(50),DY(50)
      SUMX  = 0.
      SUMY  = 0.
      SUMXY = 0.
      SUMX2 = 0.
      SUMY2 = 0.
C
C
C-----CALCULATE VARIOUS SUMS
C
      DO 100 I=1,DN
            SUMX  = SUMX + DX(I)
            SUMY  = SUMY + DY(I)
            SUMXY = SUMXY + DX(I)*DY(I)
            SUMX2 = SUMX2 + DX(I)**2
  100 SUMY2 = SUMY2 + DY(I)**2
C
C
C-----CALCULATE SLOPE,YINT,CORR
C
      DSLOPE = (SUMXY-SUMX*SUMY/DN)/(SUMX2-SUMX**2/DN)
      DYINT  = (SUMY-DSLOPE*SUMX)/DN
      SDEVX  = SQRT ((SUMX2-SUMX**2/DN)/(DN-1))
      SDEVY  = SQRT ((SUMY2-SUMY**2/DN)/(DN-1))
      DCORR  = DSLOPE*SDEVX/SDEVY
      END
C
C
C-----FACTORIAL SUBROUTINE
C
      SUBROUTINE FACT (J1,J2)
      J2=1
      DO 100 J=2,J1
  100 J2=J2*J
      END
```

APPENDIX C

NUMERICAL METHODS FOR SOLVING DIFFUSION PROBLEMS

Permeation-rate-versus-time data may be calculated using the fundamental parameters D and S and analytical solutions of Fick's first and second laws for given initial and boundary conditions (for example, see Equation 3 in this report). However, frequently the initial and boundary conditions are complex and phenomena such as concentration-dependent diffusion must be considered. For these reasons, an exact analytical solution to a given diffusion problem is often not possible. Thus, during the current effort, numerical methods for solving such problems were explored briefly.

Presented below is a trivial example in which the Crank-Nicolson implicit finite differences method (98) was used to determine the permeation rate versus time for a given D (which was held constant) and a given C_s, the concentration of solvent on one side of a polymeric membrane. The concentration of solvent in the receiving fluid on the other side of the membrane was assumed to be zero. The initial concentration of solvent throughout the membrane was assumed to be zero, although the computer program listed will accept any valid concentration profile.

The parameters needed for the calculation of permeation rate versus time are:

- n, which is the number of nodes at which the concentration will be calculated within the membrane.

- C_s, which is the solvent concentration on one side of the membrane, usually taken as the solubility of the solvent in the polymer.

- ℓ, which is the thickness of the membrane.

- Δt, which is the time increment.

- The maximum time to which calculations should be carried out.

Table 25 shows results from calculations done by two computer systems, an Osborne I microcomputer using BASIC and a DEC 2040 using FORTRAN. A comparison of permeation rates versus time calculated numerically with those calculated using the exact analytical solution is also given in the table. The results obtained with the two computers differ slightly for two reasons. First, the DEC 2040 is based on a higher-bit microprocessor than the Osborne I; this enables the DEC 2040 to carry operations to higher significant figures. Second, the method of actually solving the equations set up by the Crank-Nicolson scheme was different in the two programs. (The program listed after the table was written for the DEC 2040.)

TABLE 25. PERMEATION RATE VERSUS TIME CALCULATED USING THE CRANK-NICOLSON METHOD[a,b,c]

Time, sec	Calculated permeation rate, ng/(cm^2.sec)			Relative difference, %	
	Osborne I	DEC 2040	Analytical[d]	Osborne I	DEC 2040
1800	0.06868	0.06779	0.06713	2.3	1.0
2025	0.1084	0.1070	0.1067	1.6	0.3
2250	0.1555	0.1539	0.1536	1.2	0.2
2475	0.2081	0.2065	0.2061	1.0	0.2
2700	0.2643	0.2628	0.2623	0.8	0.2
2925	0.3227	0.3214	0.3207	0.6	0.2
3150	0.3818	0.3807	0.3799	0.5	0.2
3375	0.4408	0.4399	0.4389	0.4	0.2
3600	0.3988	0.4981	0.4970	0.4	0.2
3825	0.5554	0.5548	0.5536	0.3	0.2
4050	0.6100	0.6095	0.6083	0.3	0.2
5275	0.6625	0.6621	0.6608	0.3	0.2
4500	0.7127	0.7123	0.7110	0.2	0.2

[a]The solubility used was 0.01078 g/cm^3, the diffusion coefficient was 6.59 x 10^{-10} cm^2/sec, and the thickness of the polymer sample, ℓ, was 0.00472 cm. The initial condition was $C(x,0) = 0$; the boundary conditions were $C(0,t) = 0.01078$ g/cm^3 and $C(\ell,t) = 0$.

[b]For the Osborne I calculation, the number of x intervals was 40 and Δt was 6.25 sec. The software was written in BASIC. The execution time was about 5 min.

[c]For the DEC 2040 calculation, the number of x intervals was 40 and Δt was 225 sec. The software was written in FORTRAN. The execution time was 1.96 sec.

[d]Thirty terms of the infinite series analytical solution were used in this calculation.

```
C
C
C*********************************************************************
C
C       THIS PROGRAM WILL CALCUATE CONCENTRATION PROFILES WITHIN A MEMBRANE
C       EXPOSED TO CONSTANT BOUNDRY CONDITIONS USING FINITE DIFFERENCES.
C       IT WILL ALSO CALCULATE THE FLUX AT X=L.
C
C
C
C       PROGRAM WRITTEN BY ABHOYJIT BHOWN        8/85
C
C*********************************************************************
C
C
C------ALLOCATE VARIABLES
C
        DIMENSION UOLD(100),UNEW(100),W(100),G(100),BR(100),D(100)
        REAL LBC,L
C
C
C------READ PARAMETERS
C
        OPEN (UNIT=1,FILF='PARAM.DAT',TYPE='OLD')
        N = 40
        LBC = 0.
        RBC = 1.0
        THICK = 1.
        L = 0.00472
        CS = 0.01078
C
C
C------SET BOUNDARY CONDITIONS
C
        UOLD(1)=LBC
        UOLD(N)=RBC
        UNEW(1)=LBC
        UNEW(N)=RBC
C
C
C------SET INITIAL CONDITIONS
C
        WRITE (3,1),0.
        WRITE (3,*)
        WRITE (3,2),1,UOLD(1)*CS
        DO 100 I=2,N-1
        UOLD(I)=0.
  100   WRITE (3,2),I,UOLD(I)*CS
        WRITE (3,2),N,UOLD(N)*CS
        WRITE (3,*)
        WRITE (3,*)
        WRITE (3,*)
C
C
C------INITIALIZE ITERATION
C
        DIFF = 6.59E-10
        TINIT = 225.*DIFF/L**2
        TMAX = 4500.*DIFF/L**2
        TINC = 225.*DIFF/L**2
        DELX = THICK/(N-1)                    123
```

```fortran
      R = TINC/DELX**2
      A = R/2
      B = -(1+R)
      C = R/2
C
C
C-----START TIME
C
      DO 700 T=TINIT,TMAX,TINC
C
C
C----------INITIALIZE THOMAS ALGORITHM
C
          DO 200 I=2,N-1
  200     D(I)    = -(R/2*UOLD(I-1)-(R-1)*UOLD(I)+R/2*UOLD(I+1))
          D(2)    = D(2)-A*UOLD(1)
          D(N-1)  = D(N-1)-C*UOLD(N)
          W(2)    = 1/B
          G(2)    = W(2)*D(2)
          BB(2)   = W(2)*C
C
C
C-----------START THOMAS ALGORITHM
C
          DO 300 I=3,N-1
              W(I)  = 1/(B-A*BB(I-1))
              BB(I) = W(I)*C
  300     G(I) = W(I)*(D(I)-A*G(I-1))
          UNEW(N-1) = G(N-1)
          DO 400 I=N-2,2,-1
  400     UNEW(I) = G(I)-BB(I)*UNEW(I+1)
C
C
C---------- PRINT VALUES
C
          WRITE (3,1),T*L**2/DIFF
          WRITE (3,*)
          DO 600 I=1,N
              WRITE (3,3),I,I*L,UNEW(I)*CS
  600     UOLD(I) = UNEW(I)
          FLUX = UOLD(2)*DIFF*CS/L/DELX*1.E9
          WRITE (3,*)
          WRITE (3,4) FLUX
          WRITE (3,*)
          WRITE (3,*)
          WRITE (3,*)
  700 CONTINUE
C
C
C-----FORMAT STATMENTS
C
    1 FORMAT (1X,'TIME =',F10.0)
    2 FORMAT (1X,'NODE =',I3,5X,'FEILD =',F10.6)
    3 FORMAT (1X,'NODE =',I3,5X,'X =',F10.6,5X,'FEILD =',F10.6)
    4 FORMAT (1X,'FLUX =',F10.6)
C
C
C-----CLOSE FILES AND END PROGRAM
C
      CLOSE (UNIT=1)
      END                        124
```

APPENDIX D

SUMMARY OF LIQUID-IMMERSION ABSORPTION
DATA AND PERMEATION-TEST RESULTS

TABLE 26. SUMMARY OF LIQUID-IMMERSION ABSORPTION TEST DATA

Glove	Solvent	Test Number	Diameter, in Initial	Diameter, in Final	Thickness, mil Initial	Thickness, mil Final	Temp. range, °F	R.H. range, %	Initial weight, g	Max. weight gain, g	Solubility, g/cm³
Butyl rubber	Acetone	D0220-27-3	1.37	1.41	25.62	25.98	70-76	65-71	0.7155	0.0281	0.0454
		D0220-45-3	1.38	1.42	22.5	22.9	70-76	63-71	0.6343	0.0257	0.0466
		D0220-46-3	1.39	1.42	21.24	21.4	70-76	63-65	0.5971	0.0232	0.0439
		D0265-93-1	1.40	1.42	21.78	22.06	74-79	66-86	0.8100	0.0255	0.0464
		D0265-93-3	1.40	1.42	25.6	26.08	74-79	66-86	0.7132	0 0295	0.0457
		D0265-93-5	1.40	1.42	24.5	24.86	74-79	66-86	0.6921	0.0287	0.0464
	Cyclohexane	D0220-27-1	1.37	2.24	24.3	36.8	73-76	66-71	0.6743	1.6162	2.7533
		D0220-45-1	1.40	2.24	20.4	29.54	70-75	63-71	0.5740	1.4282	2.7753
		D0220-46-1	1.36	2.26	24.52	36.0	71-76	66-71	0 6925	1.6738	2.8676
		D0265-36	1.41	2.18	23.36	35.64	67-68	55-60	0.6622	1.5368	2.5711
		D0265-54	1.40	2.19	22.94	35.12	74-77	62-72	0.6461	1.5185	2.6240
		D0265-74	1.39	2.21	22.12	34.54	76-78	63-75	0.6237	1.5209	2.7650
	Isopropanol	D0220-27-4	1.39	1.41	24.8	25.0	70-76	65-71	0.7012	0.0025	0.0040
		D0220-45-4	1.38	1.41	21.0	20.7	70-76	63-71	0.5919	0 0019	0.0037
		D0220-46-4	1.39	1.39	24.1	23.96	70-76	63-65	0 6767	0 0020	0 0033
		D0265-93-2	1.40	1.40	26.1	26.11	74-79	66-86	0.7315	0.0022	0.0033
		D0265-93-4	1.40	1.40	22.4	22.36	74-79	66-86	0 6252	0.0025	0 0044
		D0265-93-6	1.40	1.40	21.54	21.62	74-79	66-86	0.6064	0.0032.	0.0059
	Toluene	D0220-27-2	1.39	1.98	22.1	29.8	73-76	66-71	0.6168	0.9771	1.7780
		D0220-45-2	1.40	1.95	23.1	30.2	70-75	63-71	0 6507	1 0332	1.7731
		D0220-46-2	1.38	1.99	21.0	27.2	71-76	66-71	0.5914	0.9373	1.8210
		D0265-38	1.41	1.92	22.18	29.64	67-71	55-61	0 6246	0 9677	1.7051
		D0265-56	1.40	1.96	25.48	35.32	74-78	62-72	0.7068	1 3330	1.7646
		D0265-76	1.40	1.96	24.80	35.30	76-78	67-74	0 6999	1.1090	1.7727

(continued)

TABLE 26 (continued)

Glove	Solvent	Test Number	Diameter, in		Thickness, mil		Temp. range, °F	R.H. range, %	Initial weight, g	Max weight gain, g	Solubility, g/cm³
			Initial	Final	Initial	Final					
Natural rubber	Acetone	D0220-116-3	1.40	1.45	25.14	26.0	69-73	52-80	0.6466	0.0919	0.1449
		D0220-130-3	1.39	1.45	23.96	25.06	70-71	51-74	0.6162	0 0831	0.1395
		D0220-131-3	1.40	1.46	23.82	24.84	70-73	51-76	0.6068	0.0832	0.1385
		D0265-92-1	1.40	1.46	24.9	25.9	74-79	66-86	0.6332	0.1012	0.1611
		D0265-92-3	1.40	1.47	23.82	24.80	74-79	66-86	0.6065	0.0955	0.1589
		D0265-92-5	1.40	1.46	26.3	27.44	74-79	66-86	0.6649	0 1099	0.1656
		D0265-102	1.40	--	25.40	--	74-76	80-88	0.6531	0.0979	0.1528
		D0265-104	1.40	1.45	24.28	25.60	76	78-82	0.6177	0 0931	0.1520
		D0265-111	1.40	1.45	25.48	26.48	75-76	73-76	0.6404	0.0932	0.1450
		D0265-120	1.40	1.45	24.66	25.52	78-79	73-74	0.6161	0.1037	0.1667
		D0265-122	1.40	1.46	25.78	26.84	76-77	68-69	0.6544	0.1009	0.1551
	Cyclohexane	D0220-116-1	1.41	2.23	25.86	38.7	69-73	52-80	0.6655	1 8424	2.7844
		D0220-130-1	1.40	2.18	25.46	38.20	70-71	51-74	0.6528	1.6602	2.5850
		D0220-131-1	1.40	2.24	25.9	38.4	70-73	52-76	0.6699	1.7526	2.6825
		D0265-50	1.40	2.21	25.88	40.12	69-70	66-69	0.6514	1 7640	2.7020
		D0265-66	1.40	2.17	26.78	40.9	73-76	59-61	0.6674	1.8177	2.6907
		D0265-86	1.39	2.17	26.14	40.46	77-78	63-71	0.6604	1.7429	2 6813
	Isopropanol	D0220-116-4	1.40	1.43	26.08	26.4	69-73	52-80	0.6536	0.0309	0.0470
		D0220-130-4	1.40	1.43	25.86	26.70	70-71	51-74	0.6502	0 0306	0.0465
		D0220-131-4	1.40	1.42	27.74	27.82	70-73	51-76	0.6816	0.0319	0.0489
		D0265-92-2	1.40	1.42	24.5	25.04	74-79	66-86	0 6267	0 0307	0 0497
		D0265-92-4	1.40	1.41	26.3	26.6	74-79	66-86	0.6652	0.0343	0 0517
		D0265-92-6	1.40	1.40	24.1	24.5	74-79	66-86	0.6141	0 0302	0.0497
	Toluene	D0220-116-2	1.40	2.28	25.30	38.6	69-73	52-80	0.6321	2 0086	3.1472
		D0220-130-2	1.40	2.31	25.34	40.74	70-71	51-74	0.6512	2 0541	3 2212
		D0220-131-2	1.40	2.32	25.7	39.6	70-73	52-76	0.6567	2.0732	3 1979
		D0265-48	1.40	--	26.74	--	68-70	67-71	0 6537	2 0637	3.0594
		D0265-70	1.40	2.34	24.38	40.5	71-76	61-75	0.6207	2.1494	3.4949
		D0265-88	1.40	2.27	26.72	43.52	74-78	63-72	0 6724	2.1026	3.1194

(continued)

127

TABLE 26 (continued)

Glove	Solvent	Test Number	Diameter, in Initial	Final	Thickness, mil Initial	Final	Temp. range, °F	R.H. range, %	Initial weight, g	Max weight gain, g	Solubility, g/cm³
Neoprene rubber	Acetone	DO220-73-3	1.39	1.52	18.58	20.12	70-76	52-73	0 6224	0 1662	0.3597
		DO220-93-3	1.39	1.54	18.32	20.46	71-73	52-73	0 6206	0 1915	0.4204
		DO220-94-3	1.38	1.50	18.40	20.42	70-73	52-72	0 6195	0.1595	0.3537
		DO265-94-1	1.40	1.55	18.59	20.74	74-79	66-86	0 6310	0 1976	0.4214
		DO265-94-3	1.40	1.55	19.12	21.08	74-79	66-86	0.6385	0 2026	0 4200
		DO265-94-5	1.40	1.57	19.4	21.36	74-79	66-86	0 6477	0 2054	0 4197
		DO265-106	1.40	1.54	19.24	21.06	74-75	80-87	0 6365	0 2033	0.4189
		DO265-112	1.40	1.58	19.06	21.64	76	71-74	0 6995	0 1908	0.3968
		DO265-118	1.40	1.55	18.52	20.80	78-79	73-74	0 6156	0 1958	0.4191
		DO265-124	1.40	1.55	19.08	20.98	76-77	68-69	0 6360	0 1993	0 4140
	Cyclohexane	DO220-73-1	1.40	1.76	18.54	23.06	71-76	52-73	0.6219	0.4025	0.8606
		DO220-93-1	1.39	1.78	18.58	23.00	69-73	53-73	0 6351	0 4006	0.8670
		DO220-94-1	1.39	1.78	19.16	24.46	70-73	52-72	0.6463	0 4167	0.8746
		DO265-46	1 40	1.80	19.02	24.04	69-74	66-71	0.6447	0 4220	0 8795
		DO265-62	1.40	1.73	19.04	23.92	73-76	62-67	0.6461	0.4317	0 8988
		DO265-82	1.40	1.77	19.28	24.70	73-78	59-63	0.6491	0 4319	0 8880
	Isopropanol	DO220-73-4	1.39	1.44	18.74	19.1	70-76	52-73	0.6303	0.0279	0.0599
		DO220-93-4	1.39	1.42	18.70	19.16	69-73	52-73	0.6333	0.0224	0.0482
		DO220-94-4	1.40	1.43	19.24	19.54	70-73	52-72	0.6512	0.0232	0.0478
		DO265-94-2	1.40	1.42	19.8	20.32	74-79	66-86	0.6689	0.0313	0.0627
		DO265-94-4	1.40	1.41	19.5	20.06	74-79	66-86	0.6554	0.0287	0.0583
		DO265-94-6	1.40	1.43	18.2	19.2	74-79	66-86	0.6358	0.0310	0.0675
	Toluene	DO220-73-2	1.40	2.28	19.2	29.1	71-76	52-73	0 6490	1.5244	3.1473
		DO220-93-2	1.39	2.29	19.04	29.40	69-73	52-73	0 6441	1.5030	3.1745
		DO220-94-2	1.39	2.33	19.68	30.68	70-73	52-72	0.6666	1.6134	3 2968
		DO265-44	1.40	--	19.26	--	68-70	65-71	0.6365	1.4840	3.0544
		DO265-64	1.40	2.26	18.54	28.92	71-75	62-73	0.6143	1.4280	3 0533
		DO265-84	1.40	2.26	19.16	30.20	73-78	62-64	0.6403	1 5013	3.1062

(continued)

128

TABLE 26 (continued)

Glove	Solvent	Test Number	Diameter, in Initial	Diameter, in Final	Thickness, mil Initial	Thickness, mil Final	Temp. range, °F	R.H. range, %	Initial weight, g	Max. weight gain, g	Solubility, g/cm³
Nitrile rubber	Acetone	D0220-50-3	1.40	1.99	20.7	29.0	70-76	53-72	0.5575	0.9497	1.8187
		D0220-51-4	1.39	1.93	19.5	26.3	71-75	63-66	0.5382	0.9451	1.9490
		D0220-52-3	1.39	1.94	21.9	28.5	70-75	63-66	0.5970	1.0851	1.9925
		D0265-42	1.40	1.84	20.40	28.06	69-71	64-70	0.5318	0.8854	1.7205
		D0265-58	1.40	1.92	21.92	31.02	74-78	63-72	0.5517	0.9438	1.7068
		D0265-78	1.40	1.89	23.20	32.02	77-78	66-74	0.6048	1.0154	1.7350
	Cyclohexane	D0220-50-1	1.40	1.45	21.4	22.1	70-76	53-72	0.5713	0.0629	0.1165
		D0220-51-2	1.40	1.43	22.9	23.6	70-75	51-71	0.6116	0.0556	0.0962
		D0220-52-1	1.37	1.43	22.0	23.1	70-75	51-71	0.5947	0.0404	0.0760
		D0265-91-1	1.40	1.44	23.4	24.68	74-79	66-86	0.6305	0.0544	0.0922
		D0265-91-3	1.40	1.46	21.7	22.98	74-79	66-86	0.5826	0.0690	0.1260
		D0265-91-5	1.40	1.43	22.3	23.0	74-79	66-86	0.5979	0.0463	0.0823
	Isopropanol	D0220-50-4	1.39	1.50	21.2	23.34	70-76	53-72	0.5768	0.1149	0.2180
		D0220-51-1	1.39	1.51	23.0	25.72	70-76	65-71	0.6243	0.1482	0.2591
		D0220-52-4	1.37	1.50	19.4	20.9	70-75	51-71	0.5082	0.0971	0.2072
		D0265-91-2	1.40	1.51	22.7	25.18	74-79	66-86	0.6153	0.1375	0.2401
		D0265-91-4	1.40	1.50	21.5	23.64	74-79	66-86	0.5717	0.1178	0.2172
		D0265-91-6	1.40	1.51	23.5	26.14	74-79	66-86	0.6373	0.1557	0.2626
	Toluene	D0220-50-2	1.40	1.88	20.5	27.48	70-76	53-72	0.5545	0.7491	1.4486
		D0220-51-3	1.38	1.85	20.66	28.1	71-75	63-66	0.5663	0.7607	1.5022
		D0220-52-2	1.39	1.89	21.7	29.7	70-76	63-66	0.5914	0.7966	1.4763
		D0265-40	1.40	1.81	20.70	27.82	69-74	64-70	0.5617	0.7218	1.3823
		D0265-61	1.40	1.86	24.72	32.78	74-77	62-72	0.6575	0.8727	1.3995
		D0265-80	1.40	1.84	23.54	32.04	74-78	59-64	0.6277	0.8416	1.4173

129

(continued)

TABLE 26 (continued)

Glove	Solvent	Test Number	Diameter, in		Thickness, mil		Temp. range, °F	R.H. range, %	Initial weight, g	Max weight gain, g	Solubility, g/cm³
			Initial	Final	Initial	Final					
Poly(vinyl chloride)	Acetone	D0220-150-3	1.41	1.24	6.70	5.24	70-71	51-80	0 2047	-0.0531	--[a]
		D0220-151-3	1.42	1.29	5.88	4.6	69-72	52-71	0.1814	-0.0528	--
	Cyclohexane	D0220-150-1	1.39	1.23	5.14	6.04	70-71	51-80	0.1573	-0 0492	--
		D0220-151-1	1.41	1.29	6.22	6.2	70-72	52-71	0.1864	-0 0528	--
	Isopropanol	D0220-150-4	1.39	1.26	8.42	11.80	70-71	51-80	0.2596	-0 0747	--
		D0220-151-4	1.40	1.29	8.80	5.68	70-72	52-71	0.1778	-0.0460	--
	Toluene	D0220-150-2	1.40	1.24	6.20	5.18	70-71	51-80	0.1923	-0.0310	--
		D0220-151-2	1.40	1.31	5.38	4.74	70-72	52-71	0 1660	-0.0236	--

[a] The symbol "--" in the column labeled "Solubility, g/cm³" means that a weight loss was observed, thus, no solubility could be calculated.

TABLE 27. SUMMARY OF INDIVIDUAL PERMEATION-TEST RESULTS

Glove	Solvent	Test No.	Thickness, cm	Breakthrough time,[a] min	Steady-state permeation rate, µg/(cm^2·min)	Calculated diffusion coefficient,[b] cm^2/sec	Calculated solubility,[b] g/cm^3
Butyl rubber	Acetone	D0301-40	0.0615	>1115	<0.47	--	--
	Cyclohexane	D0301-53	0.0607	50	468	1.2 x 10^{-7}	5.4
		D0301-56	0.0597	50	565	0.93 x 10^{-7}	6.7
		D0301-59	0.0597	57	403	0.72 x 10^{-7}	7.9
		D0301-87	0.0625	63	311	0.60 x 10^{-7}	10
	Toluene	D0301-84	0.0589	24	396	1.9 x 10^{-7}	2.9
Natural rubber	Acetone	D0301-24	0.0610	18	30	1.5 x 10^{-7}	0.46
		D0301-27	0.0630	16	34	1.8 x 10^{-7}	0.28
		D0301-28	0.0607	18	37	1.7 x 10^{-7}	0.26
	Cyclohexane	D0301-73	0.0602	18	572	2.3 x 10^{-7}	2.9
		D0301-74	0.0617	21	528	1.8 x 10^{-7}	4.6
		D0301-76	0.0638	18	476	2.5 x 10^{-7}	2.4
	Toluene	D0301-66	0.0635	10	775	7.1 X 10^{-7}	1.2
		D0301-70	0.0617	8	760	5.9 x 10^{-7}	1.4
		D0301-71	0.0599	11	812	4.3 x 10^{-7}	2.0
	Isopropanol	D0301-95	0.0617	>150	1	1.2 x 10^{-9}	2.6
Neoprene rubber	Acetone	D0301-34	0.0488	20	171	1.6 x 10^{-7}	1.0
		D0301-38	0.0480	24	149	1.3 x 10^{-7}	1.2
		D0301-39	0.0472	22	132	1.4 x 10^{-7}	0.98
	Cyclohexane	D0301-62	0.048	60	55	3.4 x 10^{-8}	0.78
		D0301-85	0.0493	>60	16	3.3 x 10^{-9}	7.6
		D0301-88	0.0485	>160	7	3.4 x 10^{-9}	17
		D0301-93	0.0483	135	61	1.7 x 10^{-8}	3.1
	Toluene	D0301-80	0.0478	12	642	2.6 x 10^{-7}	2.1
Nitrile rubber	Acetone	D0301-44	0.0572	10	984	3.8 x 10^{-7}	2.8
		D0301-45	0.0584	8	933	4.2 x 10^{-7}	2.7
		D0301-48	0.0612	12	969	3.7 x 10^{-7}	3.4
	Cyclohexane	D0301-91	0.0607	>1350	<0.12	--	--
	Toluene	D0301-78	0.0574	52	210	6.6 x 10^{-8}	4.3

[a]The minimum permeation rates that could be detected were: 0.47 µg/(cm^2·min) for acetone, 0.12 µg/(cm^2·min) for cyclohexane, and 0.11 µg/(cm^2·min) for toluene.

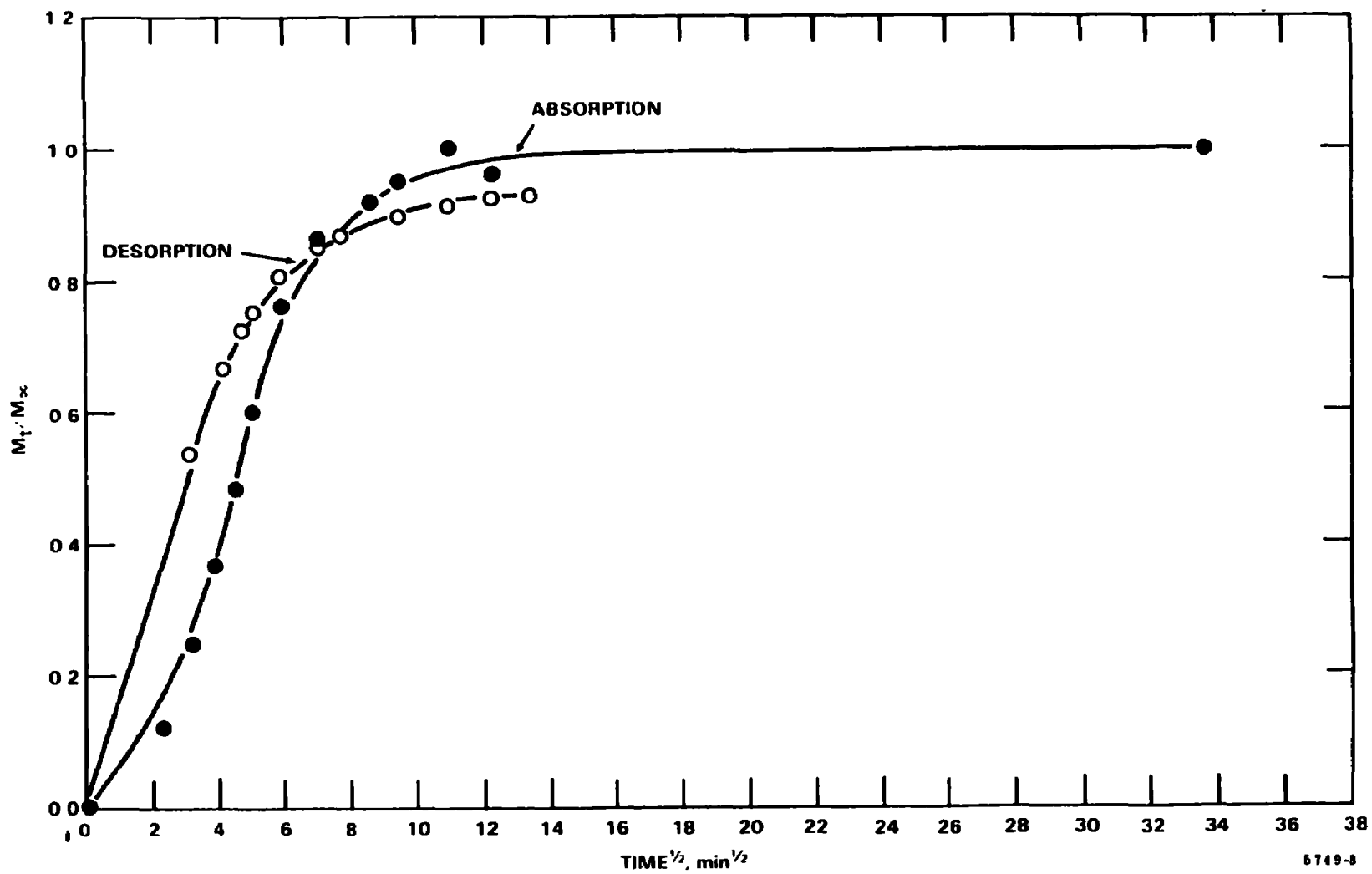[b]The symbol "--" means that the calculation could not be performed.

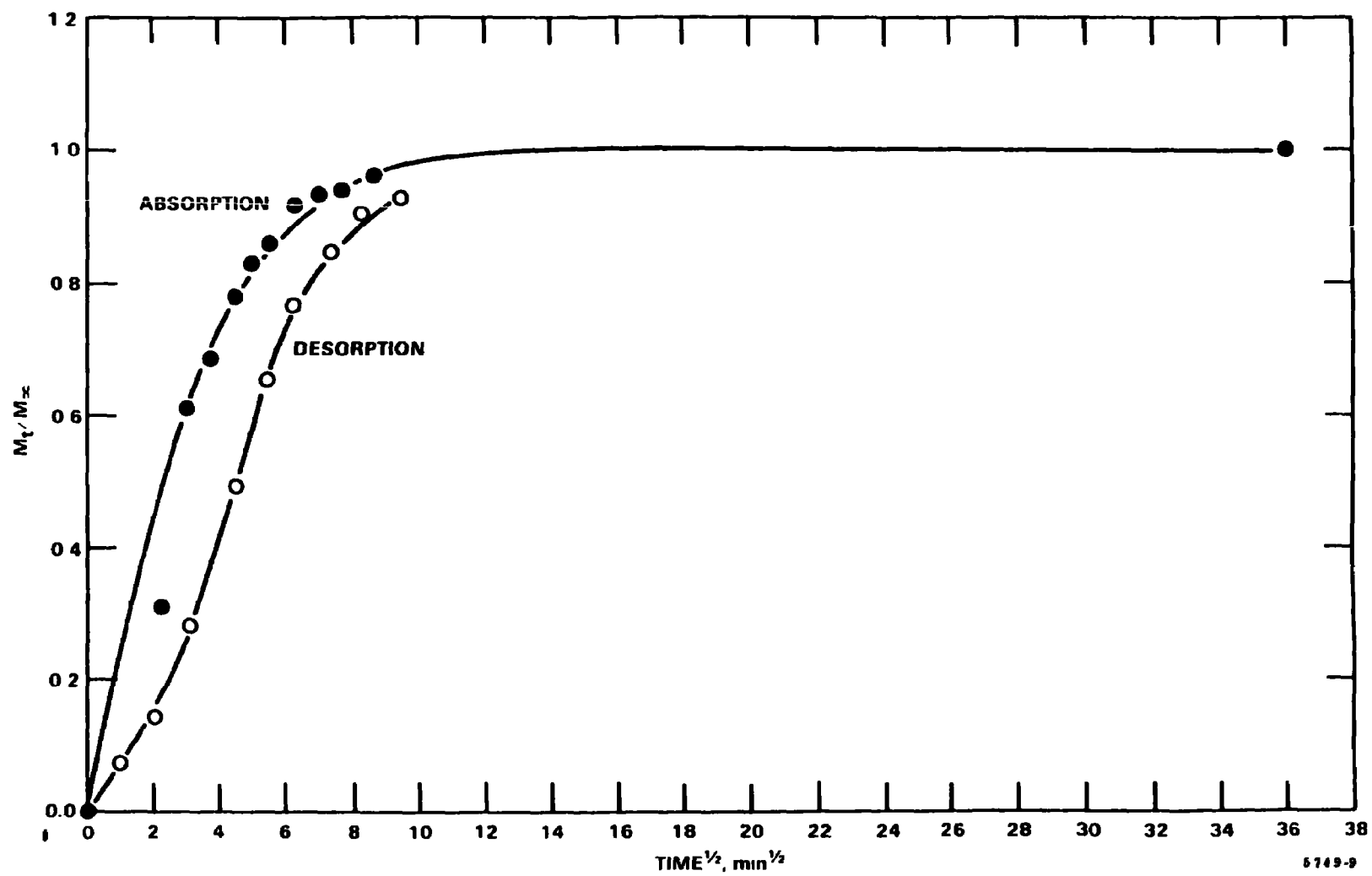Figure 11. Absorption and desorption curves for cyclohexane in butyl rubber

5149-8

Figure 12. Absorption and desorption curves for toluene in butyl rubber
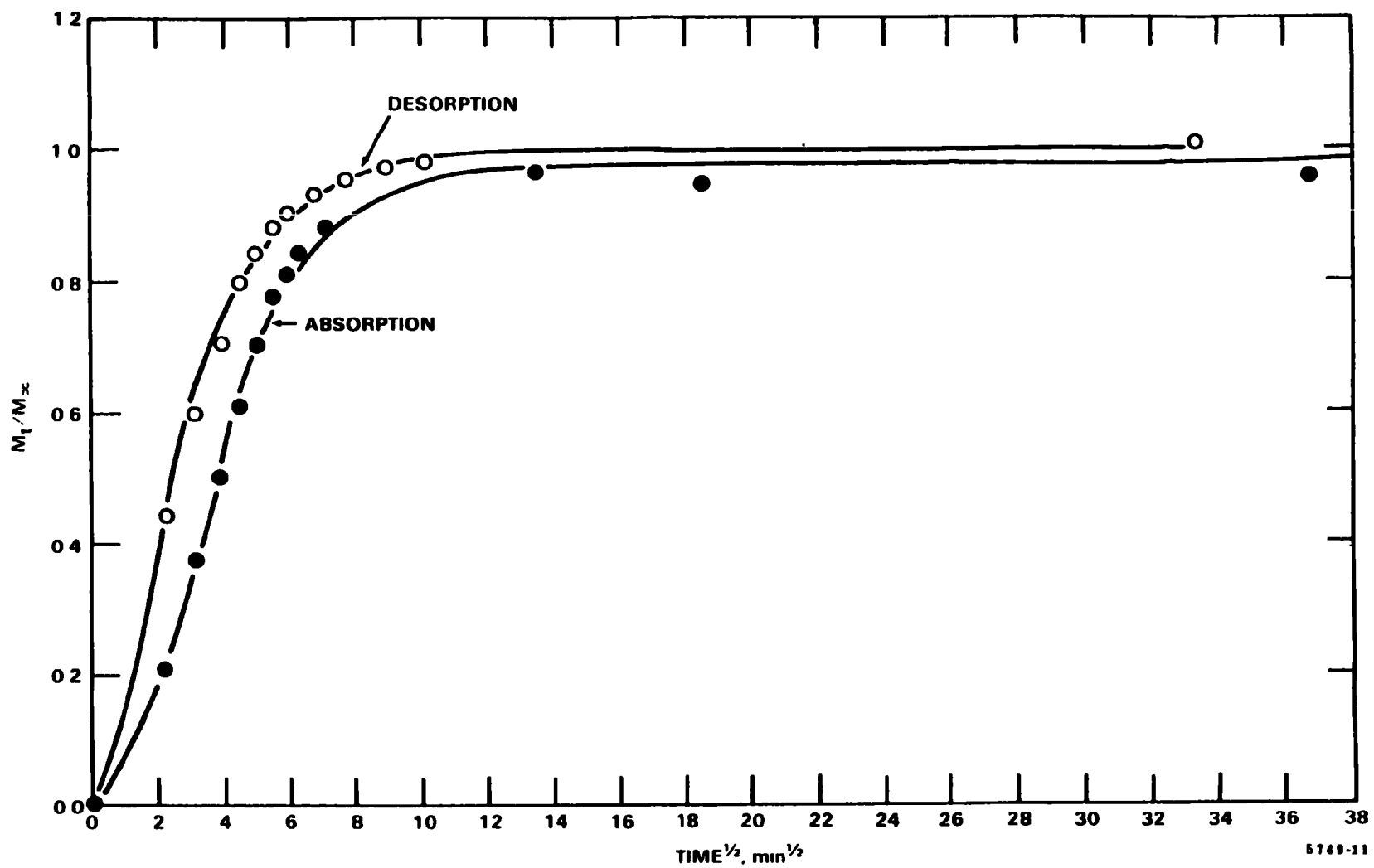
133

Figure 13. Absorption and desorption curves for cyclohexane in natural rubber
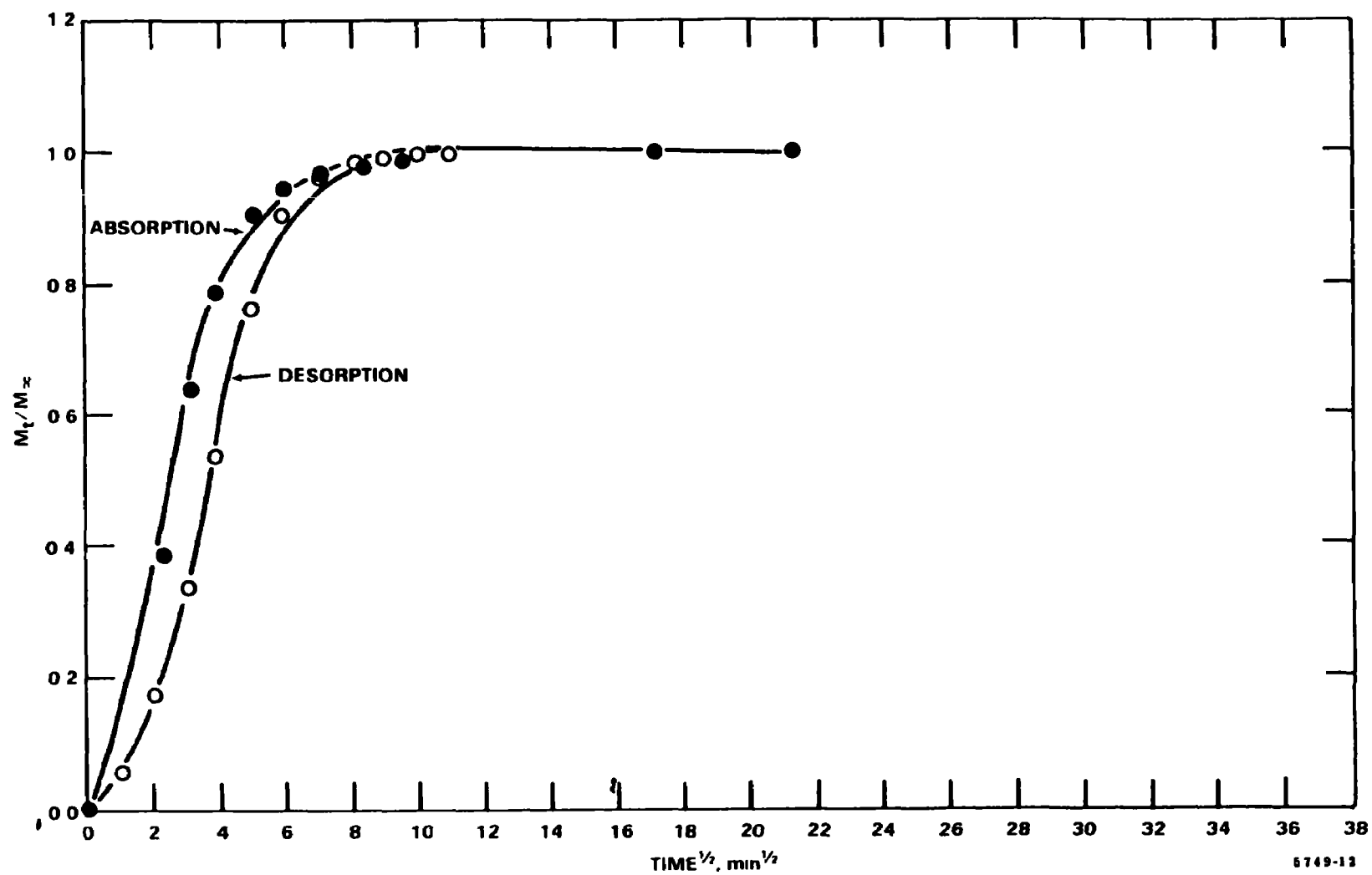
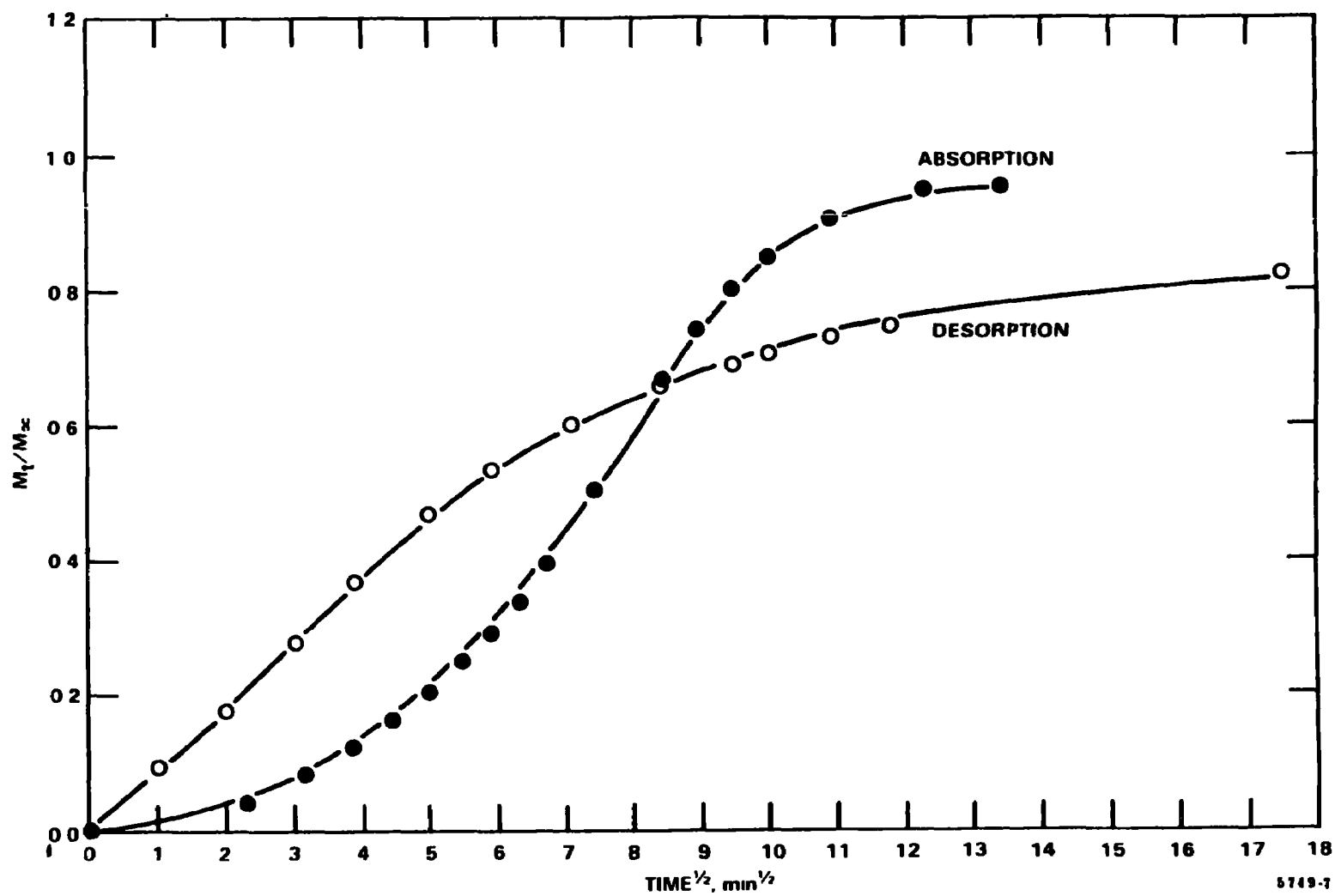*Figure 14. Absorption and desorption curves for toluene in natural rubber*

135

Figure 15. Absorption and desorption curves for cyclohexane in neoprene rubber
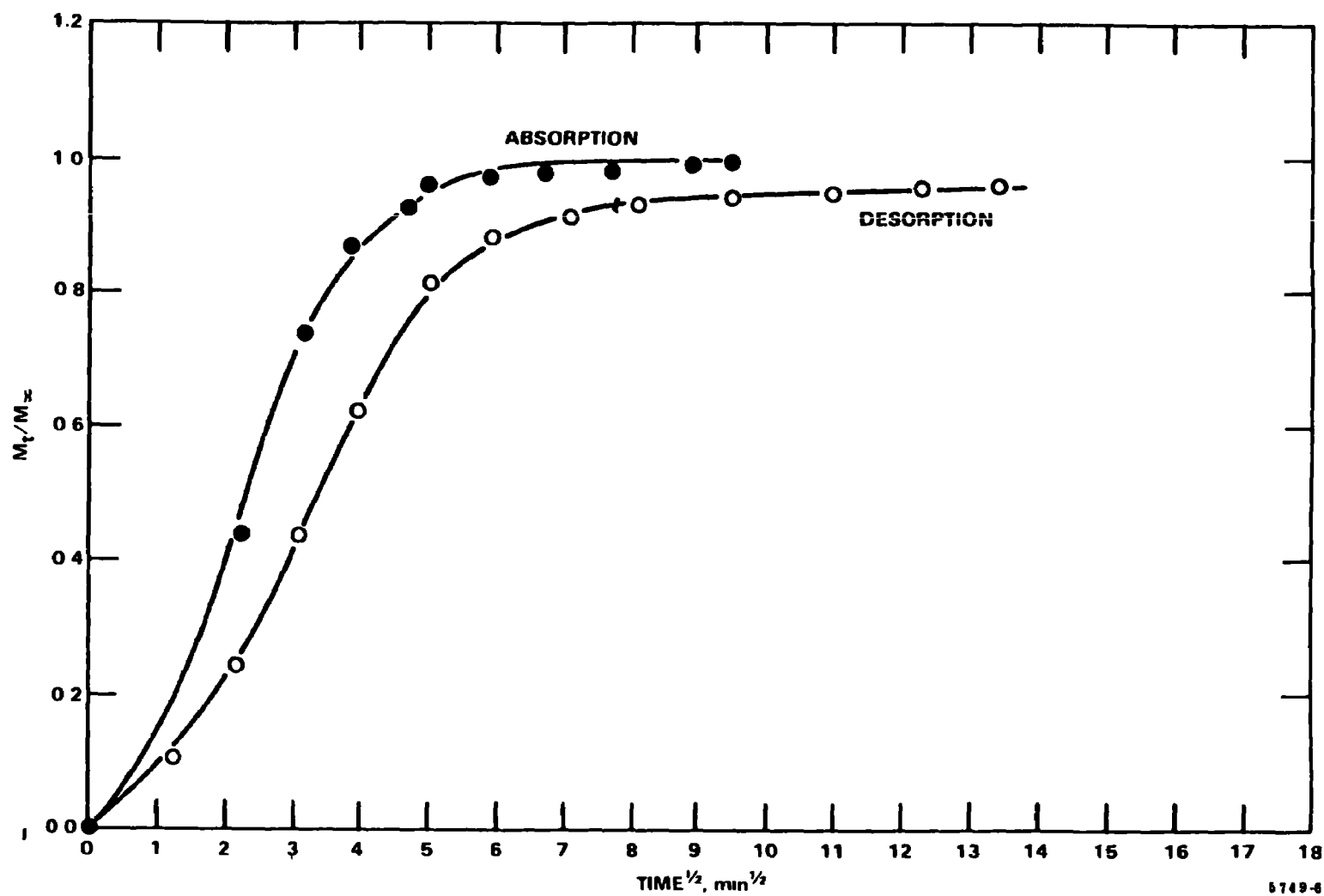
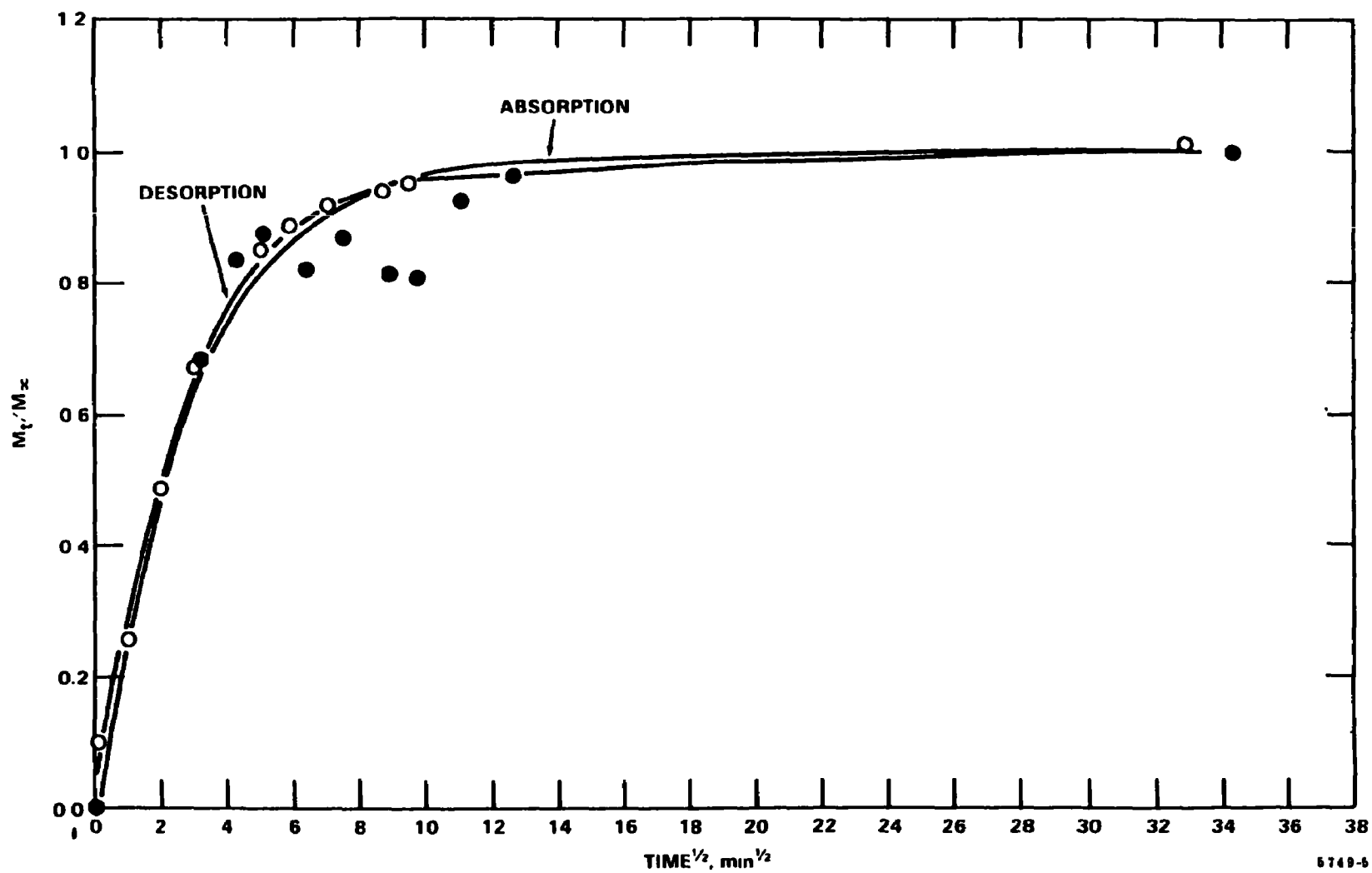Figure 16. Absorption and desorption curves for toluene in neoprene rubber.

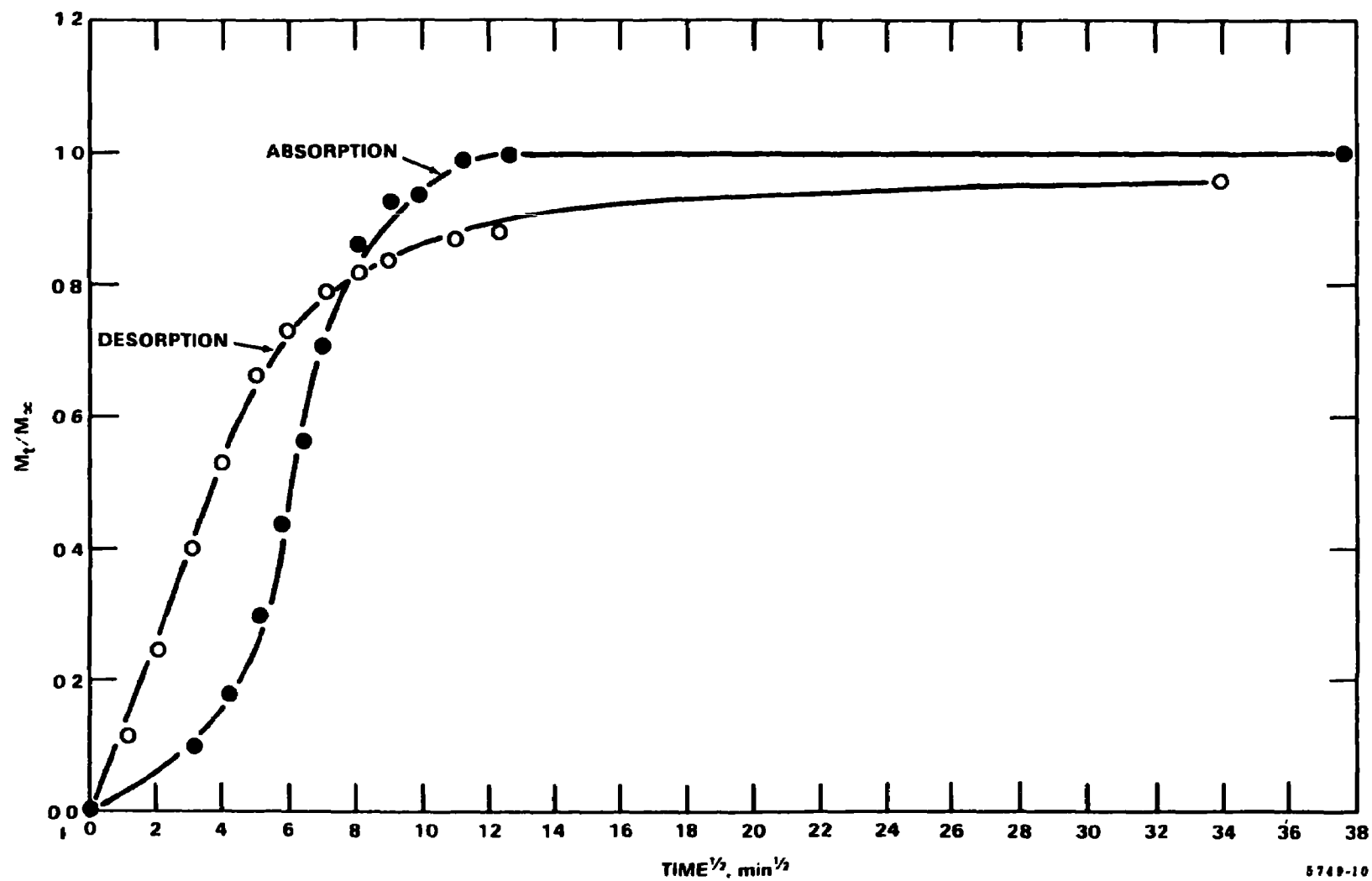Figure 17. Absorption and desorption curves for acetone in nitrile rubber

138

6749-5

Figure 18. Absorption and desorption curves for toluene in nitrile rubber

5749-10

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1 REPORT NO. EPA/600/2-86/055	2. PB86-209087/AS	3. RECIPIENT'S ACCESSION NO.
4 TITLE AND SUBTITLE Predicting the Effectiveness of Chemical-Protective Clothing: Model and Test Method Development		**5. REPORT DATE** September 30, 1986
		6. PERFORMING ORGANIZATION CODE
7 AUTHOR(S) Abhoyjit S. Bhown, Elizabeth F. Philpot, Donald P. Segers, Gary D. Sides, Ralph B. Spafford		**8. PERFORMING ORGANIZATION REPORT NO.** SoRI-EAS-85-835 5749-F
9 PERFORMING ORGANIZATION NAME AND ADDRESS Southern Research Institute 2000 Ninth Avenue South Birmingham, Alabama 35255-5305		**10. PROGRAM ELEMENT NO.**
		11. CONTRACT/GRANT NO. 68-03-3113
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Water Engineering Research Laboratory 26 W. St. Clair Street Cincinnati, OH 45268		**13. TYPE OF REPORT AND PERIOD COVERED** Project Report (1/85- 9/85)
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A predictive model and test method were developed for determining the chemical resistance of protective polymeric gloves exposed to liquid organic chemicals. The prediction of permeation through protective gloves by solvents was based on theories of the solution thermodynamics of polymer/solvent systems and the diffusion of solvents in polymers. These models and test methods were further developed to estimate the solubility, S, and the diffusion coefficient, D for a solvent in a glove polymer. Given S and D, the permeation of a glove by a solvent can be predicted for various exposure conditions using analytical or numerical solutions to Fick's Laws.

The model developed for estimating solubility is based on group-contribution methods for predicting phase equilibria, while that for estimating diffusion coefficients versus concentration is based on free-volume theory. The predictive test method developed is a liquid-immersion/desorption method that provides estimates of S and D.

Limited confirmation of the developed models and test method was secured by comparing estimated values of S and D with reported experimental data and by using the estimated values to predict instantaneous permeation rates, breakthrough times, and steady-state permeation rates for comparison with experimental permeation data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18 DISTRIBUTION STATEMENT	19 SECURITY CLASS *(This Report)*	21 NO. OF PAGES
	20. SECURITY CLASS *(This page)*	22. PRICE

EPA Form 2220-1 (9-73)