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Project Summary

Improvement of PMN Review Procedures to Estimate Protective Clothing Performance; Executive Summary Report

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Through a five-year program performed with the EPA Office of Research and Development, the Chemical Engineering Branch (CEB) of the EPA Office of Toxic Substances (OTS) has developed state-of-the-art tools for assessing the effectiveness of rubber and plastic protective clothing materials as barriers to chemicals. These tools were developed for use by CEB to conduct more thorough assessments of the potential for occupational exposures to new chemicals as required in the Premanufacture Notification (PMN) review process. The tools include:

- **a computerized model for predicting the permeation of chemicals through common clothing materials using Fickian diffusion theory and the physical property data typically available from a PMN submission,**
- **guidelines for specifying permeation testing and interpreting the results of such tests, including development of a new, intermittent chemical contact permeation test method, and**
- **a manual that guides the assessment of protective clothing permeation on the basis of published data, data from CEB-prescribed testing, and the output of the predictive model.**

The report summarized here describes the development of these tools and lists the products delivered under this project from October 1985 through September 1990.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Section 5 of the Toxic Substances Control Act (Public Law 94-469) requires prospective manufacturers or importers of new chemicals to submit PMNs, which are reviewed by OTS, before the chemicals are manufactured or imported. Although many substances are not subjected to all aspects of the review process, those that are judged to pose health or environmental risks require detailed assessments of the potential for releases or exposures during manufacture, processing, and end use. When the PMN submitter recommends the use of protective clothing to limit dermal exposures, OTS needs a rapid and well-substantiated approach to assess the ability of protective clothing to act as a barrier to the PMN chemical.

The approach developed in this program centers on assessing the effectiveness of protective clothing materials as a barrier to chemical permeation. Permeation resistance is an important measure of the effectiveness of protective clothing in reducing or limiting dermal exposures. As illustrated in Figure 1, however, the performance of protective clothing as a chemical barrier is only one of many important considerations required for the proper specification of protective clothing. Proper selection and, as importantly, proper use of protective clothing requires multiple considerations starting with the definition of the hazard and ending with disposal of the used clothing.

The main objectives of this program were to develop a computer model for predicting permeation — one that would

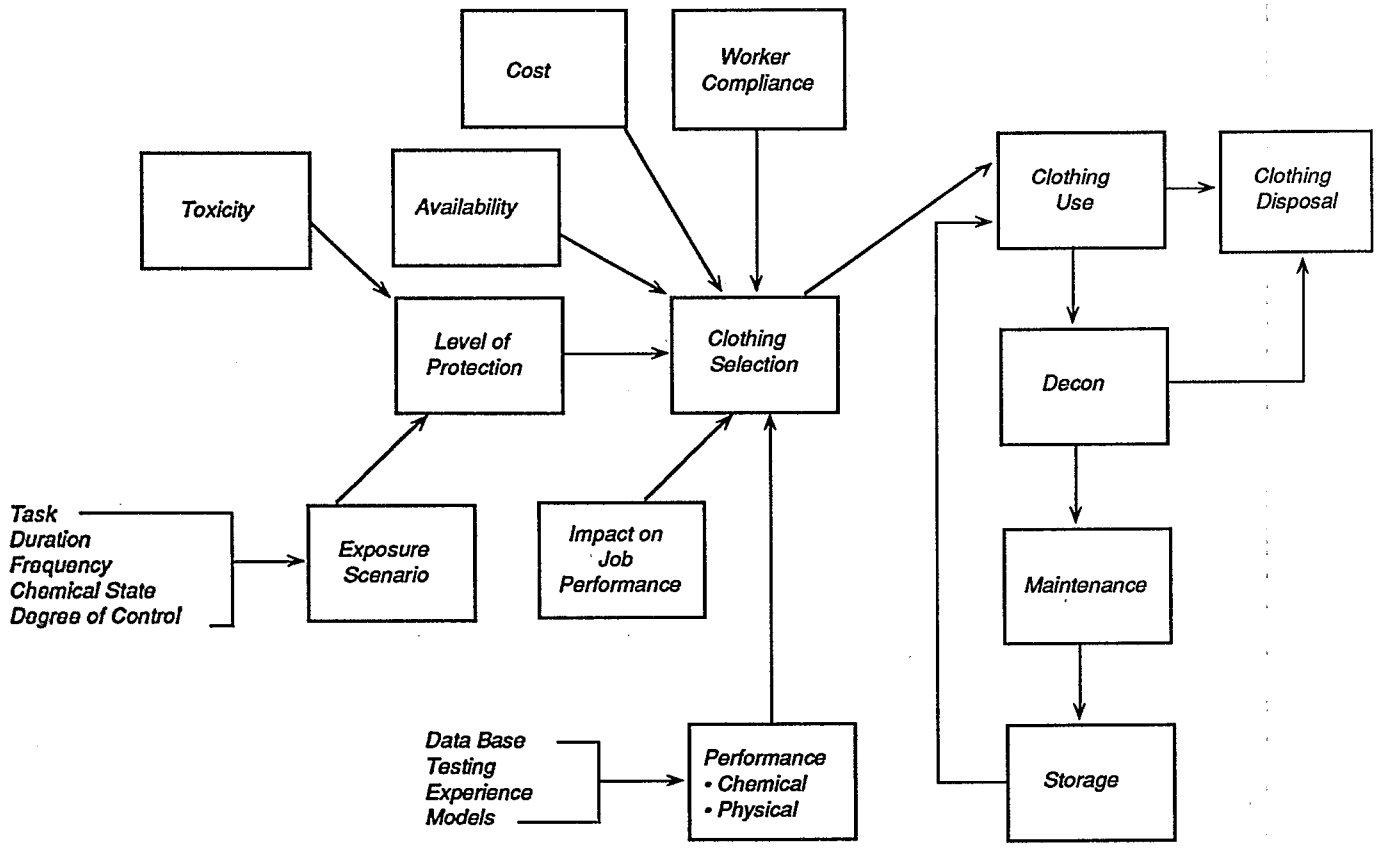

Figure 1. Selection and use of protective clothing.

meet OTS' needs and operational requirements — and to develop an integrated system for assessing the permeation resistance of protective clothing materials — one that would be part of the PMN review process. To guide in developing the computer model, OTS established the following criteria: the model should:

- be easy to use,
- be applicable to a wide range of chemicals and protective clothing materials,
- be applicable to chemicals not used to develop the model,
- not require data other than those typically supplied in PMN submissions or readily estimated using established techniques,
- predict the cumulative mass of chemical that permeates the clothing material as a function of time, and
- enable the prediction of breakthrough times at specified permeation rates or cumulative amounts permeated.

Accuracy requirements for the model outputs were not specifically defined. The criteria for evaluating chemical resistance test methods included the types of data that are generated, cost to perform the tests, skill level required to run the tests, and the limitations of the tests.

To assess the resistance of protective clothing materials to chemical permeation, four integrated approaches were developed to estimate permeation which involve a predictive model, test specification, and test data review. The three tools developed from this program— a permeation model, guidelines for specifying test methods and interpreting data, and a user manual — are discussed below.

Permeation Prediction Model

Theory and Initial Development

The permeation prediction model was developed using diffusion theory and Fick's law mathematical relationships to estimate the permeation rate and cumulative amount of chemical that permeates a polymeric material at any time following the initiation of the chemical contact. The relationships require two fundamental parameters: the diffusion coefficient, D, and the solubility, S, of the permeant in the polymer of interest. The Fick's law approach was selected because it was judged to provide the best opportunity to satisfy OTS' criteria. Although other methods (e.g., statistical correlation methods) may be more accurate in some cases, such methods often cannot predict permeation behavior as a function of time and lack sufficient theoretical basis for extrapolation to new chemicals.

A prototype model was developed in 1988. The prototype estimated the permeation of pure chemicals through five clothing materials: butyl rubber, LDPE, natural rubber, neoprene, and nitrile rubber. Two approaches to estimate S were developed: one using a group contribution approach, UNIFAP S, and the second using an equation of state approach, EOS S. One approach to estimate D, CORR D, was developed. The model was designed to run on a personal computer, was easy to use, required minimal data

inputs, and predicted permeation behavior as a function of time including breakthrough times. The validation of the prototype was limited by the availability of reliable data that described permeation as a function of time. It was concluded that further testing of the model was required and that the approach to estimate diffusion coefficients should be refined.

Permeation Model Refinement

The permeation model was refined through the analysis of an additional, larger set of permeation data that became available in 1989. The data set included breakthrough time and steady-state permeation rate data for approximately 200 chemical/material combinations, although few data pertained to LDPE. The effort to refine the permeation estimation model focussed on improving the procedure to estimate diffusion coefficients. The effort was twofold: to undertake a preliminary investigation of the importance of the concentration dependence of D and to improve the estimation of constant D values.

Concentration Dependent Diffusion Coefficients

The investigation of concentration dependent diffusion coefficients used numerical methods to calculate permeation-time profiles for general cases of concentration dependent behavior. A finite difference numerical analysis technique was developed, and for 15 of 31 chemical/polymer combinations analyzed, the permeation-time data could be more accurately described using a concentration dependent D. The permeation-time data set was too small, however, to develop predictive correlations for D. Consequently, the permeation estimation model still uses the assumption of a constant D. The correlation equations, initially developed to estimate constant D values, were refined by analyzing the larger set of "average" D values now available.

Prediction Accuracy

To test the accuracy of the revised model, the model predictions were compared with the available permeation data. Overall, the accuracy of the model is fair for predicting the permeation of organic chemicals through butyl rubber, natural rubber, neoprene, and nitrile rubber. The model predicts the permeation behavior within an order of magnitude for 70% to 80% of the chemical/polymer combinations evaluated, which is often within the range of experimental values reported in the literature. The UNIFAP S/CORR D was found to be more accurate than the EOS S/CORR D approach, which tends to underestimate the permeation behavior. The UNIFAP S/CORR D approach cannot be applied in all cases, however, because required input parameters are not available for several chemical functional groups.

Computer System

The permeation estimation model was coded in FORTRAN to run on IBM or compatible personal computers. The data input requirements depend upon the method selected to estimate S:

- UNIFAP S/CORR D
  - -structure defined using UNIFAP group designations,
  - -molecular weight (daltons), and
  - -liquid density (g/cm^3)
- EOS S/CORR D
  - -molecular weight (daltons),
  - -liquid density (g/cm^3), and
  - -vapor pressure (mm Hg)

On-screen instructions are provided for the selection of menu options and the input of the required data. The permeation model output is automatically directed to the computer screen. Options are provided to print, plot, or save the results to a disk file.

External Peer Review

The permeation prediction model was externally peer reviewed in June 1989 for ease of use, clarity, utility of output, and accuracy of predictions compared with experimental data. In general, their review comments were positive, particularly regarding ease of use and utility of output. In some cases, the reviewers believed that the prediction accuracy warranted improvement, particularly regarding the prediction of breakthrough times.

Guidelines for Specifying Test Methods and Interpreting Data

Review of Test Methods

In developing test methods and data analysis procedures, the applicability and limitations of existing chemical resistance test methods were reviewed: methods for measuring permeation resistance, degradation resistance, liquid immersion weight change, and chemical sorption/desorption of protective clothing materials. Although physical property test methods were also reviewed, they were not pursued in this project. The ASTM Method F739 permeation test method was recommended as the best method for assessing the barrier effectiveness of protective clothing materials to liquids, gases, and multicomponent solutions.

ASTM F739 Reporting Requirements

ASTM F739 was reviewed in detail to identify limitations of the data generated and to develop specific guidelines for data interpretation. Although the permeation test is straightforward in concept, a range of results can be obtained under different testing conditions for the same chemical/material combination. Breakthrough detection time is often reported as the measured parameter by which to characterize barrier effectiveness. Breakthrough detection time, however, is not an intrinsic property of the chemical/material pair and can be strongly affected by the experimental parameters.

Permeation data measured and reported as a function of time are recommended as most useful to the exposure assessments required in the PMN review process. Revised reporting requirements were recommended to the ASTM F23 Committee in 1987. As a result, the data reporting section of ASTM F739 was revised and the ASTM F23 Committee promulgated the ASTM F1194 Standard Guide for Documenting the Results of Chemical Permeation Testing on Protective Clothing Materials in 1989.

Intermittent Contact Permeation Test Method

A preliminary method was developed in 1988 to measure chemical permeation under intermittent chemical contact conditions. Because the ASTM F739 method specifies continuous chemical contact, the results may overestimate permeation resulting from "splash" or intermittent chemical contacts typical in the manufacturing environment. The proposed method involves repeated cycles in which the clothing material is alternately exposed to the chemical and then to a stream of air. Measured breakthrough detection times were comparable with those measured by the ASTM F739 method, but permeation rates were greatly reduced and oscillated with the exposure cycle. The intermittent contact permeation method was the subject of an ASTM inter-laboratory evaluation in 1989, and the results were positive. Efforts are now in progress to promulgate this method as an ASTM standard method.

Permeation of Multifunctional Acrylates

In 1989, OTS' specific need for permeation data for the general class of compounds known as multifunctional acrylates was addressed. Performing permeation tests for these compounds is not routine,

however, because of their low vapor pressure and low water solubility. Silicone rubber sheeting was selected as the collection medium for the ASTM F739 Method because of its favorable performance in other projects performed under this contract. Permeation tests were conducted with trimethylolpropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (HDDA), and two mixtures of 1,6-hexanediol diacrylate with 2-ethylhexyl acrylate (EHA) at 20°C with butyl, nitrile, and natural rubber glove materials. None of the acrylate compounds nor the mixtures were detected to permeate the butyl or nitrile rubber at the conditions and sensitivity of the method. Pure HDDA, a 50% HDDA/50% EHA mixture, and a 25% HDDA/75% EHA mixture permeated the natural rubber material. TMPTA permeation through the natural rubber was also detected but only in one of the triplicate tests after 360 min. Comparison of these results with those reported in the literature shows that the multifunctional acrylates permeate the glove materials (in this case natural rubber) at much lower rates than those measured for simple, low molecular weight acrylate compounds.

User Manual

A User Manual was prepared in 1990 to document the integrated approach recommended for using the procedures developed to assess protective clothing material permeation in an instructive and concise format. The manual was prepared as a supplement to the *CEB Manual for the Preparation of Engineering Assessments.* The user manual outlines four approaches to assess the permeation of chemicals through protective clothing materials based on the technical developments described above:

- review existing permeation data for the PMN chemical
- review existing permeation data for structural analogues of the PMN chemical
- use the permeation prediction model
- specify permeation testing

Selecting the approach, or approaches, depends on the types of information available for the chemical under review and the desired accuracy of the assessment. No one approach is recommended and using multiple approaches may be appropriate. The types of permeation estimates range from specific estimates of potential dermal exposure due to permeation, to materials recommendation for further testing, to the identification of materials not suitable for use.

Conclusions

In a five-year program, the OTS/CEB developed state-of-the-art tools for assessing chemical permeation of rubber and plastic protective clothing materials. OTS developed these tools to conduct more thorough assessments of the potential for occupational exposure to new chemicals as required in the PMN review process. The tools include:

- a computerized model for predicting the permeation of chemicals through common clothing materials,
- guidelines for specifying permeation testing and interpreting the results of such tests, and
- a user manual that guides the assessment of protective clothing permeation on the basis of published data, data from CEB-prescribed testing, and the permeation model predictions.

Consequently, OTS now has a documented and substantiated approach to assess the potential for protective clothing permeation by PMN chemicals, one of several important factors to consider in the overall assessment of dermal exposures. This capability will enable more thorough assessments of occupational exposures in the PMN review process and better compliance with the mandate of Section 5 of TSCA.

Recommendations

The primary recommendation is that OTS incorporate the permeation assessment procedures into its standard dermal exposure assessment process. Not only will this result in more thorough assessments, but the procedures can be validated and areas requiring further development can be identified through application to actual PMN cases. Recommendations regarding further refinement of the tools reported here follow.

Permeation Prediction Model

Before further efforts are undertaken to refine or extend the predictive model, OTS should reevaluate its requirements, specifically those regarding prediction accuracy. Acceptable model accuracy must be defined and prioritized relative to broad applicability, ease of use, and cost of development. At present, the model is useful for order of magnitude estimates. No efforts to improve this accuracy can be undertaken until a larger set of well documented, permeation-time data is obtained.

If such data are obtained, specific recommendations are:

- to further test the accuracy and applicability of the present model for LDPE and consider expanding the model to other clothing materials, in particular the newer, multilayer plastic materials,
- to pursue approaches to predict the concentration dependence of the diffusion coefficient and to expand the applicability of the UNIFAP group contribution approach to predict S.
- to develop a model to estimate chemical mixture permeation.

Guidelines for Specifying Test Methods and Interpreting Data

OTS should continue its involvement with the efforts of ASTM Committee F23 on Protective Clothing. To date, this involvement has improved and better defined permeation test methods for specification. Also, OTS should support the continued development of the EPA *Guidelines for the Selection of Chemical Protective Clothing* manual and chemical resistance database, the use of which is an integral part of the assessment procedures developed here. Specific recommendations are:

- to pursue the promulgation of the intermittent contact permeation test method as an ASTM method.
- to maintain an awareness of developments by the ASTM and other EPA program offices regarding test methods for measuring the physical properties and the particulate penetration of clothing — areas that may warrant the development of assessment procedures.

Integration of Procedures into PMN Review Process

When applicable, the permeation assessment methods developed in this project should be incorporated as part of the standard procedure for assessing dermal exposures. OTS should also consider other important aspects of clothing selection and use (i.e., physical performance of clothing, effect on job performance, clothing reuse, and disposal issues, etc.) and judge whether these areas warrant development of assessment procedures.

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The complete report, entitled "Improvement of PMN Review Procedures to Estimate Protective Clothing Performance; Executive Summary Report," (Order No. PB92-105 691AS; Cost: $17.00, subject to change) will be available only from:
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