Papers 1–6
Protective Clothing and Equipment

1

PENETRATION OF LIQUID THROUGH SMALL HOLES USING A STANDARD TEST METHOD D.J. Hewett, S.P. Berardinelli, G.P. Noonan and R.C. Hall, National Institute for Occupational Safety and Health, 944 Chestnut Ridge Road, Morgantown, West Virginia 26505.

The American Society for Testing and Materials (ASTM) Penetration Test Method F903-87 is regarded as a standard method to qualitatively test chemical protective clothing (CPC) for pinholes. The method uses atmospheric (zero gauge) and 6.9 kPa (1.0 psig) pressure tests. The purpose of this study was to determine to what degree hole diameter and surface tension variables affect the determination of a pass/fail result. An additional pressure test of 13.8 kPa (2.0 psig) was added to the protocol for this study. (The 13.8 kPa test was discontinued and replaced by the 6.9 kPa pressure test in the 1987 revision of ASTM F903.) Four challenge liquids were selected to represent a wide range of surface tensions encompassing those typical of blood and body fluids: 73.4, 45.3, 29.9 and 19.4 dynes/cm. A Mylar® polyester film served as a barrier. Holes were melted through the film and were measured by electron microscopy in the range of 4 to 232 /u/m. Regression analysis shows that surface tension and hole size are significant ($p < .0001$) predictors of test outcomes (pass/fail) at atmospheric pressure. At atmospheric pressure, liquids with low surface tensions were more likely to penetrate smaller size Mylar® film holes than higher surface tension liquids. The 6.9 kPa pressure test results (99% failures) and 13.8 kPa results (100% failures) were not dependant upon hole diameter and surface tension effects. This indicated that a 6.9 kPa test provides the same level of utility as the discontinued 13.8 kPa test, for a Mylar® barrier challenged by the range of hole sizes and surface tensions used in this study.

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SOLUBILITY PARAMETERS AND CHEMICAL PROTECTIVE CLOTHING PERMEATION PART 2. MODELLING DIFFUSION COEFFICIENTS, BREAKTHROUGH TIMES AND STEADY-STATE PERMEATION RATES E. T. Zellers and G. Z. Zhang, University of Michigan, School of Public Health, Department of Environmental and Industrial Health, 1420 Washington Heights, Ann Arbor, MI 48109-2029

A new approach to modelling the permeation of solvents through chemical protective clothing (CPC) polymers using solubility parameters is described. Three-dimensional (3-D) solubility parameters are used in separate models of the solvent-CPC equilibrium solubility, S, and diffusion coefficient, D. Modelled values of these variables are then combined in Fickian diffusion equations to estimate solvent breakthrough times (BT) and steady-state permeation rates (SSPR). Published data on the permeation of 18 solvents through North Viton® gloves are used to test the accuracy of the approach. Estimates of S are determined based on a solubility parameter model described previously. Of several empirical correlations investigated to model D, best results are achieved using the product of the solvent molar volume, V_1, and either the weighted solvent- Viton® 3-D solubility parameter difference, A_w, or the Flory interaction parameter, χ, also calculated from 3-D solubility parameters. To account for the change in the value of D over the course of the permeation test, D values are evaluated at breakthrough and steady state. Modelled BT values within a factor of three of experimental values (typically within a factor of two) are obtained for the 15 solvents for which analytical detection limits were reported. Modelled SSPR values within a factor of six of experimental values (typically within a factor of four) are obtained for the 15 solvents with valid SSPR measurements. This is the first report of a permeation modelling approach employing solubility parameters that is consistent with accepted permeation theory based on Fick's Laws. Although semi-empirical, the results presented demonstrate the potential for broad application.

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RECOMMENDED TEST METHODS FOR MEASURING PROTECTIVE CLOTHING PERFORMANCE AGAINST LIQUIFIED GAS HAZARDS J.O. Stull, C.R. Dodgen, and T.C. Greimel, TRI/Environmental, Inc., 9063 Bee Caves Road, Austin, TX 78733.

A series of test methods were developed to assess the performance of chemical protective clothing materials for protection against liquified gases. Liquified gases represent a unique set of hazards to industrial workers or emergency responders, and require protection strategies that may be different than those used for conventional liquid chemicals due to their extremely low temperatures. Other than toxicity, these chemicals at their liquid temperatures present additional haz-

ards to the wearer. Protective clothing materials may freeze or crack at these temperatures, leading to exposure, and contact with the cold liquid can cause injury to the wearer, such as frostbite.

Procedures were developed to address the three material performance areas—permeation resistance, embrittlement, and insulation to cold temperatures. In each case, existing test methods were modified to provide information specific to liquified gas hazards. Simple modifications were made to ASTM F 739 for measuring permeation resistance to allow introduction of the liquified gas into the test cell and maintain the chemical as a liquid in contact with the material. Material embrittlement evaluations were based on a test involving a fixture specified in ASTM D 2136, which uses a rapid bending motion and contact with dry ice to simulate conductive heat transfer. Cold insulation tests entailed a modified form of ASTM D 1518 for measuring heat transfer. Each of these procedures was applied to a number of garment and glove materials against representative liquified gases. The results show a range of performance for the different materials tested.

Test methods developed as part of this study were incorporated into supplementary requirements in NFPA 1991, *Standard on Vapor-Protective Suits for Hazardous Chemical Emergencies*.

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PERMEATION TESTING OF TDI AND MDI: A COMPARISON OF TEST METHODS AND PERFORMANCE DATA C.R. Dodgen, J.O. Stull, TRI/Environmental, Inc., 9063 Bee Caves Rd., Austin, TX 78733; McBriarty, J.P., ICI Polyurethanes, 286 Mantua Grove Road, West Deptford, NJ 08066-1732.

The isocyanates, toluene diisocyanate (TDI) and polymethylene polyphenyl isocyanate (polymeric MDI), typically used in the manufacture of polyurethane foams and other elastomers, pose skin and respiratory hazards due to the sensitization potential and high inhalation toxicity of these compounds. Evaluation of the performance of various protective clothing materials via permeation testing poses several technical challenges in the laboratory due to the low volatility and high reactivity of TDI and MDI. At the request of an industrial research organization, a two-part study was undertaken to evaluate the permeation resistance of these isocyanates through protective clothing. In the first part of the study, the permeation of two commercial diisocyanate preparations was investigated using four different collection methods, in order to determine the most viable collection method for comparing the permeation resistance of protective clothing materials against these two diisocyanates. Three separate materials were initially evaluated against two chemical challenges: a commercial TDI mixture (80% 2,4-isomer, 20% 2,6-isomer) and a commercial polymethylene polyphenyl isocyanate (polymeric MDI). The collection methods investigated included continuous contact with organic solvent, intermittent contact with organic solvent, drawing a known volume of air through coated glass fiber filters (modified OSHA air sampling methods 42 and 47), and continuous contact with an aqueous collection medium (modified P&CAM Method Nos. 141 and 142). Each collection method was used in conjunction with ASTM F739-91, the standard procedure for measuring protective clothing permeation resistance. It was found that permeation testing using continuous contact with an aqueous collection media (a modification of the Marcali method), allowed broad comparisons of chemical protective clothing performance by isolating the effect of the collection solvent on the rate of permeation of the challenge chemical through the test material. In the second part of the study, performance data was collected on the permeation resistance of 45 commercially available protective clothing materials, separately challenged with TDI and polymeric MDI. This data showed wide variation in the permeation resistance of the different protective clothing materials to these chemicals.

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PERMEATION OF MALATHION FORMULATIONS THROUGH NITRILE GLOVES S.S. Que Hee and Y.W. Lin, Center for Occupational and Environmental Health, Department of Environmental Health Sciences, UCLA School of Public Health, 10833 Le Conte Avenue, Los Angeles, CA 90024-1772

Two emulsion concentrate formulations of the organophosphate insecticide malathion were investigated relative to permeation of malathion and the components of the formulations through Nitrile Sol-Vex gloves using an ASTM-type PTC-permeation cell using hexane and m-xylene as collection media. The two formulations were FMC Aqua Malathion 8 (80.5% malathion) and Prentox Malathion 50% Emulsifiable Insecticide. Pure liquid malathion was also used as a challenge agent. Since there was no literature on the effectiveness of Nitrile to malathion challenge, it was hoped that the resistance to xylenes, a known inert component of the formulations would confer protection also to malathion since it was also nonpolar. While malathion at a steady state rate of 0.41-1.37 mg/cm^2/min had a calculated lag time of 50-85 minutes, malathion in m-xylene permeated at 0.02-0.08 mg/cm^2/min with a calculated lag time of 73-80 minutes. Malathion at the same concentration as the latter in FMC and Prentox formula-

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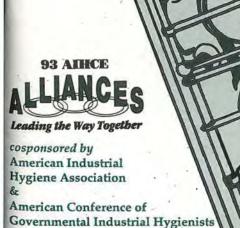
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