July 31, 2002

# Chemical Warfare Agent (CWA) Simulant Program for Respirator Materials Resistance Testing

CWA simulant agents for testing of respirators and respirator systems are addressed separately for filtration and barrier materials. For filtration, the technologies governing use of simulants, mass transfer and absorbent capacity, are well understood. DMMP (dimethylmethylphosphate) is a good filtration simulant since it is relatively non-toxic, is easily detectable and has a volatility intermediate between GB and HD. Correlations between DMMP and GB or HD are well understood. Reports will be identified and made available to substantiate the use of DMMP as a filtration simulant for GB and HD. Additionally, Carbon Tetrachloride and Cyclohexane can be used as a GB and HD filtration simulant.

For barrier materials, the governing phenomenon relates to the chemical as well as physical interaction of materials. Because of this interaction, each barrier material needs to be considered individually to determine precise agents to simulant correlations. The ever expanding and evolving list of polymers and elastomers used as materials of construction for respirators makes a one on one correlation a never-ending task.

In order to address the requirement to identify simulant agents for test, manufacture and quality assurance uses with respirators, NIOSH has identified the following program activities:

1. Filtration:

a. DMMP is identified as a test simulant for test and evaluation of filter canisters and cartridges against GB and HD.

b. Correlation data for GB and HD testing with DMMP will be provided.

2. Barrier Materials:

a. A review of research and test information in Department of Defense databases has identified eleven simulants from both current and past work with GB and HD. As a result of the review and additional research, the SBCCOM and NIOSH personnel are considering the following list of candidates to be used as simulants for the GB and HD permeation study:

2-Chloroethyl phenyl sulfide
2-Chloroethyl cyclohexyl sulfide
Di-n-butyl sulfide
1,6-Dichlorohexane
Bis(4-chlorobutyl) ether

Diethyl methanephosphonate
Diethyl ethanephosphonate (DEEP)
Diisopropyl methylphosphonate (DIMP)
Dimethyl methanephosphonate (DMMP)
2,4-Dichlorophenol (DCP)
Triethly phosphate (TEP)

Additional simulants may be added or deleted from this list as information evolves from the study. When using these or any other simulants, respirator manufacturers must take into account the toxicity of the simulants.

b. A summary matrix derived from the military database has been developed by the SBCCOM Agent Simulant Knowledge Advisory Office, dated February 20, 2002, identifying various barrier materials versus simulant breakthrough information. The matrix can be used as a screening tool to determine the overall protective characteristics of a barrier material. The matrix is attached as an enclosure.

c. Accessible publications used in compiling the data matrix will be identified for technical review. The publications combined with the matrix will in some cases provide useful information in screening and evaluating relative performance of barrier materials.

d. Specific CWA versus barrier material data, currently with restricted access, will be reviewed with an objective to make the information obtainable for general use. This will provide meaningful data concerning the protective properties of specific barrier materials against GB and HD.

e. A project has been initiated by NIOSH and SBCCOM to identify chemical compounds that can be used as simulants for GB and HD and a corresponding laboratory procedure using simulants that can be used by manufacturers for estimating GB and HD permeation through elastomeric materials. Investigations with military scientists will be continued in an effort to develop additional useable simulant information.

| | A | B | C | D | E |
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| 1 | **Reference 1. *Permeation Measurements of Chemical Agent Simulants Through Protective Clothing Materials,* Taransankar Pal, Guy D. Griffin, Gordon H. Miller, Annetta P. Watson, Mary Lou Daugherty, and Tuan Vo-Dinh, Journal of Hazardous Materials, 33, (1993) 123-141 * Unclassified - unlimited distribution** | | | | |
| 2 | | | | | |
| 3 | **Material Composition*** | **HD Simulant*** | **HD Comments*** | **GB Simulant*** | **GB Comments*** |
| 4 | Teflon/fiberglass/Teflon (10 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 24 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP> 24 hr; MAL > 24hr |
| 5 | Teflon Kevlar Teflon(Force Field) (17 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 100 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP>100hr; MAL > 100hr |
| 6 | THf/Mws/Thf (First Team) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 24 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP> 24hr; MAL > 24 hr |
| 7 | Butyl/polyester/chloroprene(Chempruf II) (19 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 24 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP> 24hr; MAL > 24hr |
| 8 | Butyl/nylon/butyl (16 mil) (305 B/BA, 306 B/BA) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 24 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP> 24hr; MAL >24hr |
| 9 | Duct Tape (10 mil): Special Type For Hazardous Materials | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 7 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 210 min; MAL > 24hr |
| 10 | Viton polyester/Viton (9 mil) (305 B/BA, 306 B/BA) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time > 100 hr | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 140min; MAL > 100hr |
| 11 | Tyvek QC, Polyethylene-coated (6 Mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 30 min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 105min; MAL 30min |
| 12 | Barricade Chemical Barrier Fabric (21 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 60min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 50 min; MAL 90 min |
| 13 | Butyl Nitrile glove (Pioneer Gatorhide) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 55min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 60min; MAL 50 min |
| 14 | Tyvek (Saranex-coated) (8 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 90min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 30 min; MAL 12 min |
| 15 | Neoprene Plastic Glove | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 10min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 45min; MAL 10 min |
| 16 | PVC/nylon/PVC (305 PVC/BA) (17 mil) | Dibutyl Sulfide (DBS) | Ref 1: Breakthrough Time 4min | Diisopropylmethyl phosphonate (DIMP); Malathion (MAL) | Ref 1: Breakthrough Time: DIMP 10min; MAL 3min |

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| 17 | **Reference 2. *Chemical Agent Simulants for Testing Transparent Materials,* CRDEC-CR-88069, Lewis, Randall, Liebman, Shirley A., and Isaccson, Louis, Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423, AD A197138 * Unclassified unlimited distribution** | | **Ref 2: Possible problem: the simulant can roll-off the transparent material or evaporate at a non-uniform rate.** | | |
| 18 | **Material Composition*** | **HD Simulant*** | **HD Comments*** | **GB Simulant*** | **GB Comments*** |
| 19 | Polycarbonates | 2-chloroethyethyl sulfide (CEES), 2-chloroethylmethyl sulfide (CEMS); 1,5dichloropentane | Ref 2: All caused crazing | Diisopropylmethyl phosphonate (DIMP); DiethylethylPhosphonate(DEEP); DimethylHydrogen Phosphonate(DMHP) | Ref 2: All caused crazing |
| 20 | Cast PMMA | 2-chloroethyethyl sulfide (CEES), 2-chloroethylmethyl sulfide (CEMS); 1,5dichloropentane | Ref 2: All caused crazing | Diisopropylmethyl phosphonate (DIMP); DiethylethylPhosphonate(DEEP); DimethylHydrogen Phosphonate(DMHP) | Ref 2: All caused crazing |
| 21 | Stretched PMMA | 2-chloroethyethyl sulfide (CEES), 2-chloroethylmethyl sulfide (CEMS); 1,5dichloropentane | Ref 2: All caused crazing | Diisopropylmethyl phosphonate (DIMP); DiethylethylPhosphonate(DEEP); DimethylHydrogen Phosphonate(DMHP) | Ref 2: All caused crazing |
| 22 | Polyurethane | 2-chloroethyethyl sulfide (CEES), 2-chloroethylmethyl sulfide (CEMS); 1,5dichloropentane | Ref 2. CEES and CEMS caused crazing; 1,5 dichloropentane had no crazing. | Diisopropylmethyl phosphonate (DIMP); DiethylethylPhosphonate(DEEP); DimethylHydrogen Phosphonate(DMHP) | Ref 2: DIMP induced crazing: DEEP and DMHP did not induce crazing. |
| 23 | **Reference 3. *Determination of Permeation Breakthrough Times by Droplet and Minicams Testing,* Bodnar, Stephen C., Sloan, James M., Gabriel, Karim M. Proceedings of the 1992 ERDEC Scientific Conference on Chemical Defense Research, 17-20 November 1992, AD 269-728, 799-803 * Unclassified- unlimited distribution** | | | | |
| 24 | **Material Composition*** | **HD Simulant*** | **HD Comments*** | | |
| 25 | Butyl Rubber | 2-chloroethyethyl sulfide (CEES), 2-chloroethylmethyl sulfide (CEMS); 3-chloropropylthiolacetate(CPTA) | Ref 3: Breakthrough Times of 2-chloroethylmethyl (CEMS) more consistent to that of HD; 2-chloroethylethylsulfide (CEES) slightly shorter than HD; 3-chloropropylthioacetate longer than HD | | |

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| **26** | **Reference 4. *Interpretations of Simulant Breakthrough Time With Laminates of Rubber Materials*, Anthony F. Wilde and Stephen C. Bodner, Proceedings of the 1994 ERDEC Scientific Conference on Chemical Defense Research, 15-18 November 1994, AD 313-080, 311-317. * Unclassified- unlimited distribution** | | | | |
| **27** | **Material Composition*** | **HD Simulant*** | **HD Comments*** | | |
| 28 | Silicone/Silicone (45.6 mil avg) | 2-chloroethyethyl sulfide (CEES) | Ref 4: Average Breakthrough times: 6.6 min | | |
| 29 | Butyl/Silicone (44.0 mil avg) | 2-chloroethyethyl sulfide (CEES) | Ref 4: Average Breakthrough times: 34.1 min | | |
| 30 | Butyl/Butyl (33.4 mill avg) | 2-chloroethyethyl sulfide (CEES) | Ref 4: Average Breakthrough times: 76.6 min | | |
| 31 | Nitrile/Butyl (43.1 mil avg) | 2-chloroethyethyl sulfide (CEES) | Ref 4: Average Breakthrough times: 106.7 min (3 tests) 88.8 min (7 tests) | | |
| 32 | Nitrile/Nitrile (41.9 mil avg) | 2-chloroethyethyl sulfide (CEES) | Ref 4: Average Breakthrough times: 48.5 min | | |
| **33** | **Reference 5. *Prediction of Polymer-Liquid Interaction Based on Polymer Phase Diagrams: Bis(2-Chloroethyl)Sulfide Cohesion Parameter Predictions For Over One Hundred Materials,* ERDEC-TR-306, Wendel J. Shuely, Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423, AD A310604* Unclassified- unlimited distribution** | **Ref 5. Very few commercial polymeric materials are predicted to be HD resistant.** | | | |
| **34** | **Material Composition*** | **Predicted Solubility in HD*** | | | |
| 35 | Isobutylene Butyl Rubber | insoluble | Ref 5. Interaction of solubility/miscibility; a familiar resistant/protective polymer for HD. | | |
| 36 | Teflon | insoluble | Ref 5. Interaction of solubility/miscibility; a familiar resistant/protective polymer for HD. | | |
| 37 | Poly (vinylidene fluoride), TEDLAR | insoluble | Ref 5. Interaction of solubility/miscibility; a familiar resistant/protective polymer for HD. | | |
| 38 | Polyvinyl Chloride( Vipla KR | not soluble in all proportions | Ref 5. Interaction of solubility/miscibility; tested and prediction affirmed. | | |
| 39 | Nylon, Versamid 930 | insoluble | Ref 5. | | |
| 40 | Polyisoprene Cariflex IR305 | not soluble in all proportions | Ref 5. Interaction of solubility/miscibility; tested and prediction affirmed. | | |
| 41 | Chlorosulfonated polyethylene ( Hypalon | insoluble | Ref 5. | | |

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| | 20,30,40) | | | | |
| 42 | 93 other materials | soluble in all proportions | Ref 5. | | |

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| **43** | **Reference 6. *Currently Available Permeability and Breakthrough data characterizing Chemical Warfare Agents and Their simulants in Civilian Protective Clothing Materials,* Mary Lou Daugherty, Annetta P. Watson, and Tuan Vo-Dinh, Journal of Hazardous Materials, 30 (1992) 2343-267 open literature** | | **Ref 6. There is a paucity of simulant permeability and breakthrough times data available. It is recommended to obtain this report as a document that gives some agent versus manufacturer trade name material data.** | | |
| **44** | **Material Composition*** | **HD Simulant*** | **HD Comments*** | **GB Simulant*** | **GB Comments*** |
| 45 | Chemrel | | | Malathion, 10% | Ref 6. Breakthrough Time; >360 min |
| 46 | Chemrel | | | Malthion, 60% | Ref 6. Breakthrough Time; > 240 min |
| 47 | Chemrel | | | Methyl Parathion,10 % | Ref 6. Breakthrough Time; > 360 min |
| 48 | Chemrel | | | Methyl Parathion,57 % | Ref 6. Breakthrough Time; >120 min |
| 49 | Teflon (ChemFAB Challenge 5100) | | | Naled | Ref 6. Breakthrough Time; >288 min |
| 50 | Teflon (ChemFAB Challenge 5100) | | | Ethion | Ref 6. Breakthrough Time; >204 min |
| 51 | Teflon (ChemFAB Challenge 5100) | | | Parathion | Ref 6. Breakthrough Time; >180 min |
| 52 | Natural Rubber (Edmont 36-124) (.51 mm) | | | Guthion | Ref 6. Breakthrough Time; >190 min |
| 53 | Neoprene (Edmont 29-865) (.51 mm) | | | Guthion | Ref 6. Breakthrough Time; >510 min |
| 54 | Nitrile (Edmont 37-175) (.46 mm) | | | Guthion | Ref 6. Breakthrough Time; >510 min |
| 55 | PVC (Edmont Canada) | | | Guthion | Ref 6. Breakthrough Time; >250 min |
| **56** | **Reference 7. *Sorption of Sulfur Mustard and its Oxygen Analog in Black and Nonblack-Filled Butyl Rubber Membranes,* Vinita Dubey, N.B.S. Rao, S.N. Maiti, A.K. Gupta, Journal of Applied Polymer Science, 69: 503-511, 1998 open literature** | | | | |
| 57 | Butyl Rubber Membranes | bis(2-chloroethyl) ether | Ref 7. Gravimetric method for permeation studies. | | |
| **58** | **Reference 8. *Diffusion and Sorption of Sulfur Mustard and Bis(2(chloroethyl)ether in Elastomers: A Comparative Study,*Vinita Dubey, A. K Gupta, Vinita Dubey,S.N. Maiti,** | | | | |

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| | **N.B.S. Rao, Journal of Applied Polymer Science, Vol 77, 2472-2479 (2000) open literature** | | | | |
| 59 | Various Elastomers | bis(2-chloroethyl) ether | Ref 8. Diffuses faster than sulfur mustard. | | |
| 60 | | | | | |

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| 61 | **GB Simulant*** | | **HD / GB Simulant*** | | |
| 62 | **9. Diisopropylfluorophosphonate (DFP) has been used as a vapor simulant for GB.*** | | **10. Methyl Salicylate (MS, MES) has been used as a vapor simulant for HD and GB.*** | | |
| 63 | | | | | |
| 64 | *** Disclaimers and Comments** | | | **Comments** | |
| 65 | **Disclaimer: While the Edgewood Chemical Biological Center, Department of the Army believes that the data contained herein are factual and the opinions expressed are those of qualified experts regarding the results of the tests conducted, the data is not to be taken as warranty or representation for which the Department of Army or Edgewood Chemical Biological Center assumes legal responsibility. They are offered solely for your consideration, investigation, and verification. Any use of this data and information must be determined by the user to be in accordance with applicable Federal, State, and Local law regulations. The simulant information provided is not to be used as a recommendation of any simulant. The data is for informational use only. The findings are not to be construed as an official Department of the Army position unless so designated by other authorizing documents. We make no warranty of merchantability or any other warranty, express or implied, with respect to such information, and we assume no liability resulting from its use.** | **Disclaimer: Users should make their own investigations to determine the suitability of the information for their particular purposes. In no way shall the Department of the Army or Edgewood Chemical Biological Center be liable for any claims, losses, or damages of any third party or for lost profits or any special, indirect, incidental, consequential or exemplary damages, howsoever arising, even if the Department of the Army or Edgewood Chemical Biological Center has been advised of the possibility of such damages.** | **Disclaimer: Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.** | a. There is no better simulant than the agent itself.<br>b. There is very little (HD) (GB) simulant data versus materials available. Because the US government had neat agent testing facilities, there was no need to use simulants for materials testing. The agents were tested directly against the materials; and data is available on the effects of HD and GB versus materials. However, this information has limited distribution. c. The experimental testing procedures used in the above references are different than those in the NIOSH SMARTMAN Test. | d. CEES and CEMS evaporate more quickly than HD. Therefore, if one used CEES or CEMS as a HD liquid droplet simulant, a barrier may be needed to prevent CEES and CEMS evaporation.<br>e. It may be necessary to use more than one simulant for an agent: one simulant for the vapor challenge and another simulant for the liquid challenge. |
| 66 | | | | | |
| 67 | **Simulant** | **CAS Registry Number** | **Simulant** | **CAS Registry Number** | |
| 68 | | | | | |
| 69 | CEES | 693-07-2 | DIMP | 1445-75-6 | |
| 70 | DBS | 544-40-1 | MAL | 121-75-5 | |
| 71 | DEEP | 78-38-6 | MS, MES | 119-36-8 | |
| 72 | DFP | 55-91-4 | | | |
| 73 | | | | | |