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Preparation of composite materials which have high strength in compression. Scientific approach is to prepare novel polymeric coupling agents. These will permit formation of multiple flexible covalent bonds between fibers as well as to matrix materials. In addition, these new coupling agents will possess elastomeric properties which may increase matrix toughness to fracture.

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FINAL TECHNICAL REPORT
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COMPOSITE MATERIALS WITH IMPROVED PROPERTIES IN COMPRESSION

Professor William P. Weber
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FINAL TECHNICAL REPORT (Period: May 1, 1989 to September 30, 1993)

PART I

Papers Published (Since May 1, 1989)

1. Copolymerization of 1,1-Dimethyl-1-silacyclopent-3-ene and 1,1-Diphenyl-1-silacyclopent-3-ene. Characterization of Copolymer Microstructures by ^{1}H, ^{13}C and ^{29}Si NMR Spectroscopy, Q. Zhou and W.P. Weber, **Macromolecules,** 23, 1583 (1990).
2. Anionic Ring Opening Polymerization of 1,1,3-Trimethyl-1-silacyclopent-3-ene. Effect of Temperature on poly(1,1,3-Trimethyl-1-sila-*cis*-pent-3-ene) Microstructures, Y.T. Park, G. Manuel and W.P. Weber, **Macromolecules,** 23, 1911 (1990).
3. Anionic Polymerization of 1-Methyl-1-silacyclopent-3-ene. Characterization of poly(1-Methyl-1-sila-*cis*-pent-3-ene) by ^{1}H, ^{13}C and ^{29}Si NMR Spectroscopy. Mechanism of Polymerization, S.Q. Zhou and W.P. Weber, **Macromolecules,** 23, 1915 (1990).
4. Anionic Ring Opening Polymerization of 3,4-Benzo-1,1-dimethyl-1-silacyclopentane. Properties of poly(3,4-benzo-1,1-dimethyl-1-silapentene), Y.T. Park, Q. Zhou and W.P. Weber, **Polymer Bulletin,** 22, 349 (1989).
5. Anionic Ring Opening Polymerization of 2-methyl-2-silaindan. Characterization of the polymer and mechanism of polymerization, S.Q. Zhou and W.P. Weber, **Makromol. Chem. Rapid Commun.,** 11, 19 (1990).
6. Anionic Ring Opening Polymerization of 1-Silacyclopent-3-ene. Characterization of poly(1-sila-*cis*-pent-3-ene) by ^{1}H, ^{13}C and ^{29}Si NMR Spectroscopy, S.Q. Zhou, Y.T. Park, G. Manuel and W.P. Weber, **Polymer Bulletin,** 23, 491 (1990).
7. Synthesis of 3-Methylene-1,1-Dichloro-1-Silacyclobutane and 1,1-Dichloro-1-Silacyclopent-3-ene, R. Damrauer, A. Laporterie, G. Manuel, Y.T. Park, R. Simon and W.P. Weber, **J. Organometal. Chem.,** 391, 7 (1990).
8. Synthesis and Anionic Ring Opening Polymerization of 1-Germa-1,1-Dimethyl-[3,4-c]-thienocyclopentene, S.Q. Zhou, P. Mazerolles, C. Laurent and W.P. Weber, **Polymer Bulletin,** 23, 583 (1990).
9. Cyclopropanation of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene). Synthesis and Characterization of poly(1-methyl-3,4-methylene-1-phenyl-1-sila-*cis*-pent-3- ene), X. Liao, H.S.J. Lee and W.P. Weber, **Die Makromoleculare Chemie,** 191, 2173 (1990).

10. Addition of Difluorocarbene to Poly(1-Methyl-1-Phenyl-1-sila-*cis*-pent-3- ene). Characterization of Microstructures by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR Spectroscopy, H.S.J. Lee and W.P. Weber, **Polymer Preprints, 31,** 424 (1990).
11. Synthesis and Dimerization 2,3-Dimethyl-5-Silaspiro[4.4]nano-2,7-diene, Y.T. Park, S.Q. Zhou, D. Zhao, G. Manuel, R. Bau and W.P. Weber, **Organometallics, 9,** 2811 (1990).
12. Synthesis and Microstructure of poly(1-Phenyl-1-sila-*cis*-pent-3-ene), X. Liao, Y.H. Ko, G. Manuel and W.P. Weber, **Polymer Bulletin, 25,** 63 (1990).
13. Chemical Modification of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) by Addition of Dichloroketene, H.S.J. Lee and W.P. Weber, **Polymer Preprints, 32,** 621 (1991).
14. Preparation and Properties of High Molecular Weight poly(1-germa- or 1-sila- *cis*-pent-3-enes), S.Q. Zhou, L. Wang, X. Liao, G. Manuel and W.P. Weber, **J. Inorg. and Organometal. Polymers, 1,** 199 (1991).
15. Synthesis and Polymerization of 5-Silaspiro[4.4]-nona-2,7-dienes, Y.T. Park, S.Q. Zhou, G. Manuel and W.P. Weber, **Macromolecules, 24,** 3221 (1991).
16. Partial and Complete Chemical Modifications of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) by Addition of Dichloroketene, H.S.J. Lee and W.P. Weber, **Macromolecules, 24,** 4749 (1991).
17. Bromide Ion Catalyzed Dimerization of 6-oxa-3,3-diphenyl-3-silabicyclo[3.1.0]- hexane. Structure Determination and Ring Substitution of 1,5-Dioxa-2,2,6,6-tetraphenyl-1,6-disila-4,8-divinylcyclooctane. Synthesis of 1,3-dioxa-2,2,4,4-tetraphenyl-2,4-disila-6-vinylcyclohexane, Y.T. Park, G. Manuel, R. Bau, D. Zhao and W.P. Weber, **Organometallics, 10,** 1586 (1991).
18. Ring Opening Metathesis Polymerization of 1,1-Diphenyl-1-silacyclopent-3-ene, D.A. Stonich and W.P. Weber, **Polymer Bulletin, 25,** 629 (1991).
19. Synthesis and Reactions of Poly(1-methyl-1-phenyl-1-silapentane) by Chemical Reduction of Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) with Diimide, X. Liao and W.P. Weber, **Polymer Bulletin, 25,** 621 (1991).
20. Synthesis and Characterization of Poly(3,4-benzo-1-phenyl-1-silapentane) and Poly(3,4-benzo-1-silapentene), Y-H. Ko and W.P. Weber, **Polymer Bulletin, 26,** 487 (1991).
21. Synthesis and Characterization of Poly[(2-trimethylsilyl-2-cyclopentene-1,4-diyl)-vinylene], D.A. Stonich and W.P. Weber, **Polymer Bulletin, 26,** 493 (1991).

22. Synthesis and Characterization of Poly[(3,4,c)furano-1-germa-1,1-dimethylpentane], X. Liao, W.P. Weber, P. Mazerolles, C. Laurent and A. Faucher, **Polymer Bulletin**, 26, 499 (1991).
23. Anionic Ring Opening Polymerization of 1-Phenyl-1-vinyl-1-silacyclopent-3-ene. Synthesis and Characterization of Poly(1-phenyl-1-vinyl-1-sila-*cis*-pent-3- ene), X. Liao, R.T. Liebfried and W.P. Weber, **Polymer Bulletin**, 26, 625 (1991).
24. Synthesis and Characterization of Poly(2-Dimethylsilyl-2-cyclopentene-1,4- diylvinylene), D.A. Stonich and W.P. Weber, **Polymer Bulletin**, 27, 243 (1992).
25. Synthesis and Characterization of Poly(1-methyl-1-vinyl-1-silabutane), poly(1-phenyl-1-vinyl-1-silabutane) and poly(1,1-divinyl-1-silabutane), X. Liao and W.P. Weber, **Macromolecules**, 25, 1699 (1992).
26. Synthesis and Microstructure of Poly(1-phenyl-1-sila-cis-pent-3-ene), X. Liao, Y-H. Ko, G. Manuel and W.P. Weber, **Polymer Bulletin**, 25, 63 (1991).
27. Synthesis and Characterization of Poly(1-vinyl-1-silabutane), X. Liao and W.P. Weber, **Polymer Preprints**, 33, 1052 (1992).
28. Anionic Dimerization/Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene, S.J. Sargeant, S.Q. Zhou, G. Manuel and W.P. Weber, **Polymer Preprints**, 33, 1054 (1992).
29. Synthesis and Characterization of Poly(1-Methyl-1-vinyl-1-silabutane), X. Liao and W.P. Weber, **Macromolecules**, 25, 1639 (1992).
30. Synthesis and Characterization of Telechelic Oligocarbosilanes with Terminal Si-H or Vinyl Functional Groups, S.Q. Zhou and W.P. Weber, **Polymer Preprints**, 33, 1103 (1992).
31. Dimerization and Polymerization of 2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene, L. Wang, Y.H. Ko and W.P. Weber, **Polymer Preprints**, 33, 1050 (1992).
32. Partial and Complete Chemical Modifications of Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) by Addition of Dichloroketene, H.J.S. Lee and W.P. Weber, **Polymer**, 33, 1748 (1992).
33. Addition of Difluorocarbene to Poly(1-methyl-2-phenyl-1-sila-*cis*-pent-3-ene). Characterization of Microstructure by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR Spectroscopy, H.S.J. Lee and W.P. Weber, **Polymer**, 33, 4299 (1992).
34. Dimerization and Polymerization of 2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene, L. Wang, Y-H. Ko and W.P. Weber, **Macromolecules**, 25, 2828 (1992).

35. Anionic Dimerization and Ring Opening Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene, S.J. Sargeant, S.Q. Zhou, G. Manuel and W.P. Weber, **Macromolecules**, 25, 2832 (1992).
36. Stereoselective Anionic Ring Opening Polymerization of 1,1-Dimethyl-1-silacyclobutene. Characterization of Poly(1-1-dimethyl-1-sila-*cis*-but-2-ene), M. Theurig and W.P. Weber, **Polymer Bulletin**, 28, 17 (1992).
37. Anionic Ring Opening Polymerization of 2,3-Benzo-1-silacyclobutene Characterization of Poly(2,3-Benzo-1-silabutenes), M. Theurig, S.J. Sargeant, G. Manuel and W.P. Weber, **Macromolecules**, 25, 3834 (1992).
38. Synthesis and Characterization of Poly(1-methyl-1-silabutane), Poly(1-phenyl-1-silabutane) and Poly(1-silabutane), C.X. Liao and W.P. Weber, **Polymer Bulletin**, 28, 281 (1992).
39. Synthesis of Carbosilane Monomers and Polymers with Mesogenic Pendant Groups, S.J. Sargeant and W.P. Weber, **Polymer Preprints**, 34, 290 (1993).
40. Synthesis and Properties of Novel Functionally Substituted Carbosilane Polymers, C.X. Liao and W.P. Weber, **Macromolecules**, 26, 563 (1993).
41. Addition of Chlorofluorocarbene to Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) and Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene). Characterization of Chlorofluoro- cyclopropanated Polymer Microstructures by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy, L. Wang, C.X. Liao and W.P. Weber, **J. Polymer Science Part A, Polymer Chemistry**, 31, 1789 (1993).
42. Synthesis and Properties of Novel Carbon Polymers-Unsaturated Carbosilane Polymers with Pendant Oligo(oxyethylene) Groups, L. Wang and W.P. Weber, **Macromolecules**, 26, 969 (1993).
43. Synthesis, Characterization and Platinum Catalyzed Crosslinking of Copoly(1-silacyclobut-1-ylidene 1,4-phenylene). Properties of Aromatic Carbosilane Thermoset, C.X. Liao, M.W. Chen and W.P. Weber, **Polymer Preprints**, 34, 230 (1993).
44. Bulk Anionic Ring Opening Polymerization of Silacyclopent-3-enes, S.J. Sargeant, M.A. Tapsak and W.P. Weber, **Polymer Bulletin**, 30, 127 (1993).
45. The Synthesis of Carbosilane Monomers and Polymers with Mesogenic Pendant Groups. Preparation and Characterization of Aryloxy Substituted poly[1-sila-*cis*-pent-3-enes], S.J. Sargeant and W.P. Weber, **Macromolecules**, 26, 2400 (1993).

46. Anionic Ring Opening Copolymerization of 1,1-dimethyl-1-silacyclopent-3-ene and 1-methyl-1-phenyl-1-silacyclopent-3-ene, S.J. Sargeant, J.B. Farahi and W.P. Weber, **Macromolecules**, 26, 4729 (1993).
47. Synthesis, Characterization and Platinum Catalyzed Crosslinking of 1,4-bis(1-methyl-1-silacyclobutyl)benzene, Co-oligo(1-silacyclobut-1-ylidene/1,4-phenylene) and Co-oligo(1-silacyclobutylidene/4,4'-biphenylene), C.X. Liao, M.W. Chen, L. Sun and W.P. Weber, **J. Inorganic and Organometallic Polymers**, 3, 231 (1993).
48. Synthesis, Characterization and Platinum Catalyzed Hydrosilation Crosslinking of Copoly(methylsilylene/1,4-phenylene/methylvinylsilylene). Properties of Aromatic Carbosilane Thermosets, M.W. Chen, C.X. Liao and W.P. Weber, **J. Inorganic and Organometallic Polymers**, 3, 241 (1993).

Papers In Press or Submitted for Publication:

1. Synthesis, Characterization and Platinum Catalyzed Hydrosilation Crosslinking of Unsaturated Si-H Carbosilanes - Random 2:1:1 and 2:1:3 Copoly(methylsilylene/*cis* and *trans*-1,4-but-2-enylene/1,2-but-3-enylene). Physical Properties of Aliphatic Carbosilane Thermosets, Carbosilane/Carbon and Carbosilane/Glass Composites, G-H. Wang, M- W. Chen and W.P. Weber, **J. Chem. Materials**, in press (1993).
2. Partial and Complete Hydrogenation of Poly(1-methyl-1-phenyl-1-sila-*cis*- pent-3-ene). Synthesis and Characterization of poly(1-methyl-1-phenyl-1-silapentane) and Block Copoly(1- methyl-1-phenyl-1-sila-*cis*-pent-3-ene/1-methyl-1-phenyl-1-silapentane), C.X. Liao and W.P. Weber, **Polymer Bulletin**, in press (1993).
3. Stress-Strain Behavior and Dynamic Mechanical Properties of Poly(1,1-dimethyl-1- sila-*cis*-pent-3-ene), Poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) and of these Polymers After Crosslinking with Sulfur, M-W. Chen, C.X. Liao and W.P. Weber, **Polymer Engineering Science**, in press (1994).
4. Poly(carbosilanes) - Polymers with Backbone Variability, W.P. Weber, Trends in **Polymer Science**, in press (1993).
5. The Synthesis and Characterization of a Mesomorphic Brush Type Polycarbosilane: poly[1,1-bis-(4'-Biphenyl)silabutane], S.J. Sargeant, L. Bean, M.A. Tapsak and W.P. Weber, **Polymer Bulletin**, in press (1993).

Patents - Issued:

1. "Crosslinkable Saturated and Unsaturated Carbosilane Polymers and Formulations," William P. Weber and Xiagao Liao, U.S. Patent 5,130,390, July 14, 1992.
2. "Crosslinkable Poly (Unsaturated Carbosilane) Polymers and Methods of Making Same," William P. Weber and Stephen Q. Zhou, U.S. Patent 5,169,916, December 8, 1992.
3. "Crosslinkable Poly (Unsaturated Carbosilane) Copolymers and Methods of Making Same," William P. Weber and Stephen Q. Zhou, U.S. Patent 5,171,810, December 15, 1992.
4. "Crosslinkable Saturated and Unsaturated Carbosilane Polymers and Formulations", W.P. Weber and Xiagao Liao, U.S. Patent 5,171,792, December 15, 1992.

Seminars Presented:

"Synthesis and Reactivity of Unsaturated Silyl Substituted Polymers," presented at:
Rhone Poulenc, Lyon, France, May 18-19, 1989
Universite Paul Sabatier, France, May 23, 1989
Universite of Bordeaux, France, May 26, 1989
California State University, San Diego, February 26, 1990
Ato Chem, Elf Aquataine, Sommerville, NJ, March 15, 1990
Non-Metallic Materials Laboratory, Wright Patterson Air Force Base, October 25,1990
Hercules Research Center, Wilmington, Delaware, October 26, 1990

"Ring Opening Polymerization of Silacyclopentenes," presented at:
Universite Paul Sabatier, May 14, 1991
Universite Montepellier, May 16, 1991
Institute for Organic Chemistry, Chinese Academy of Sciences, Shanghai, PRC, July 16, 1991
Fudan University, Shanghai, PRC, July 18, 1991
Peking University, July 22, 1991
Institute for Chemistry, Chinese Academy of Sciences, Beijing, July 23.
Tsing Hua University, Beijing, July 25, 1991
Naval Weapons Laboratory, China Lake, August 8, 1991

Meetings Attended:

Attended the Pacifichem Conference '89 sponsored by the American Chemical Society from December 17-21, 1989 in Honolulu, HI.

Attended the "Recent Advances in Polyimides and Other High Performance Polymers" meeting sponsored by the Division of Polymer Chemistry of the American Chemical Society held in San Diego, CA from January 22-25, 1990.

Attended the XXIII Silicon Symposium, Midland, MI from April 20-21, 1990.

Attended the 199th National American Chemical Society Meeting, Boston, MA from April 23-27, 1990.

Attended the 200th National American Chemical Society Meeting, Washington, D.C., August 26-30, 1990.

Attended the Second International Workshop on Advances in Silicon Based Polymer Science, Makaha, Oahu, HI, December 16-20, 1990.

Attended the XXIV Silicon Symposium, University of Texas, El Paso, TX, April 12-13, 1991. Dr. Y-H. Ko also attended this meeting.

Dr. H. Lee attended the 201st National American Chemical Society Meeting, Atlanta, GA from April 17-19, 1991.

Attended XXV Silicon Symposium, University of Southern California, Los Angeles, CA, April 3-4, 1992.

Attended 203rd National American Chemical Society Meeting, San Francisco, CA, April 5-10, 1992.

Attended the 204th National American Chemical Society Meeting, Washington, D.C., August 23-28, 1992.

Attended the XXVI Silicon Symposium, Indianapolis, IN, March 25-26, 1993.

Attended the 205th National American Chemical Society Meeting, Denver, CO, March 27-29, 1993.

Papers Presented at Meetings by Dr. Weber Unless Otherwise Noted:

"Synthesis and Polymerization of 5-silaspiro[4,4]nona-2,7-dienes," Poster presented at Silicon Symposium XXIII, Midland, MI, April 20-21, 1990.

"Polymerization of 1-Silacyclopent-3-ene Polymer. Characterization of Microstructures by End Group Analysis by ^1H, ^{13}C and ^{29}Si NMR. Pyrolysis of poly(1-silapent-3- ene)," Lecture presented at Silicon Symposium XXIII, Midland, MI, April 20-21, 1990.

"Mechanism of Anionic Ring Opening Polymerization of Silacyclopent-3-enes," Invited Lecture Ring Opening Polymerization Symposium at the 199th National American Chemical Society Meeting, Boston, MA, April 22-27, 1990.

"Addition of Difluorocarbene to Poly(1-Methyl-1-Phenyl-1-sila-*cis*-pent-3-ene). Characterization of Microstructures by ^1H, ^{13}C, ^{19}F and ^{29}Si NMR Spectroscopy," Invited Lecture at the Chemical Modification of Polymers Symposium at the 200th National American Chemical Society Meeting, Washington, D.C., August 26-30, 1990.

"Synthesis and Microstructure, and Thermal Degradation of Poly(1-silapent-3-enes)," Invited Lecture at the Second International Workshop on Advances in Silicon Based Polymer Science, Makaha, Oahu, HI, December 16- 20, 1990.

"Addition of Chlorofluorocarbene to Poly(1-sila-*cis*-pent-3-enes)," by Liming Wang and William Weber. Poster presented at the Second International Workshop on Advances in Silicon Based Polymer Science, Makaha, Oahu, HI, December 16-20, 1990.

"Addition of Dichloroketene to Poly(1-sila-*cis*-pent-3-enes)," by Howard S.J. Lee and William Weber. Poster presented at the Second International Workshop on Advances in Silicon Based Polymer Science, Makaha, Oahu, HI, December 16-20, 1990.

"Bromide Ion Catalyzed Dimerization of 6-oxa-3,3-diphenyl-3-silabicyclo[3.1.0]hexane. Structure Determination and Ring Substitution of 1,5-Dioxa-2,2,6,6-tetraphenyl-1,6-disila-4,8-divinylcyclooctane. Synthesis of 1,3-dioxa-2,2,4,4-tetraphenyl-2,4-disila-6-vinylcyclohexane," Paper presented at the XXIV Silicon Symposium, University of Texas, El Paso, TX, April 13, 1991.

"Chemical Modification of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) by Addition of Dichloroketene." Paper presented by Dr. H. Lee at the 201st National American Chemical Society Meeting, Atlanta, GA, April 18, 1991.

"Synthesis and Characterization of Telechelic Oligocarbosilanes with Terminal Si-H or Vinyl Functional Groups," by S.Q. Zhou* and William P. Weber. Presented at the 203rd National American Chemical Society Meeting, San Francisco, CA, April 5-8, 1992.

"Dimerization and Polymerization of 2,3-Benzo-5- silaspiro[4.4]nona-2,7-diene," G. Wang*, Y.H. Ko and W.P. Weber. Presented at the 203rd National American Chemical Society Meeting, San Francisco, CA, April 5-8, 1992.

"Anionic Dimerization/Polymerization of 1,1-Divinyl-1- silacyclopent-3-ene," by S.J. Sargeant*, S.Q. Zhou, G. Manuel and W.P. Weber. Presented at the 203rd National American Chemical Society Meeting, San Francisco, CA, April 5-8, 1992.

"Synthesis and Characterization of Poly(1-vinyl-1-silabutane)," by X. Liao* and W.P. Weber. Presented at the 203rd National American Chemical Society Meeting, San Francisco, CA, April 5-8, 1992.

"Synthesis, Characterization and Platinum Catalyzed Hydrosilation Crosslinking of Copoly(methylsilylene/1,4-phenylene/methylvinylsilylene) Properties of Aromatic Carbosilane Thermosets," W.P. Weber*. Presented at the XXVI Silicon Symposium, Indianapolis, IN, March 25-26, 1993.

"Synthesis, Characterization and Platinum Catalyzed Crosslinking of Copoly(1-silacyclobut-1-ylidene/1,4-phenylene). Properties of Aromatic Carbosilane Thermosets", W.P. Weber*. Presented at the 205th National American Chemical Society Meeting, Denver, CO, March 27-29, 1993.

"Synthesis of Carbosilane Monomers and Polymers with Mesogenic Pendant Groups," S.J. Sargeant*. Presented at the 205th National American Chemical Society Meeting, Denver, CO, March 27-29, 1993.

"Anionic Polymerization of Trimethylvinylsilane and Phenyldimethylvinylsilane Towards the Synthesis of Well-Defined Polyfluorodimethylvinylsilane and Polyvinylalcohol," Y. Gan*. Presented at the 205th National American Chemical Society Meeting, Denver, CO, March 27-29, 1993.

Graduate Student Supported

Ralf Volkle, research assistant, 50% time, July 27, 1992 through April 30, 1993. Diplomarbeit, Universitat Hannover.

Mark Tapsak, first year graduate student, research assistant, 50% time, August 1-31, 1992; 50% time, June 1-August 31, 1993. He is a graduate of St. Cloud State University, Minnesota.

Hongjie Guo, first year graduate student, research assistant, 50% time, August 17, 1992 through August 31, 1993. She is a graduate of Nankai University (Tianjin, China).

Jian-Qing Lu, second year graduate student, research assistant, 50% time, June 1, 1992 through January 15, 1993; April 1, 1993 through August 31, 1993. He is a graduate of Peking University, B.S., and M.S. He has passed his Ph.D. qualifying examination.

Liming Wang, research assistant, 50% time, June 1 through August 31, 1991; 25% time, September 1-30, 1991; 25% time, January 1992 through May 31, 1992; 50% time, June 1 through August 31, 1992. She completed her Ph.D. in August 1992 and is now a postdoctoral research fellow with Professor M. Goodman, Univ. of Calif., San Diego.

Steve Sargeant, third year graduate student, research assistant, 50% time, June 27, 1990 thorough July 31, 1990; 66% time, June 1 through July 30, 1991; 50% time, June 1 through June 30, 1992; June 1-15, 1993. He has completed his Ph.D. in May 1993. He is currently a postdoctoral research associate with Professor J. Frechet, Cornell University.

Julia Z. Xu, research assistant, 50% time, June 1 through August 31, 1991. She has completed the M.S. degree and is now employed with ISIS Pharmaceuticals, Calabasas, CA.

Marcus Theurig, fellowship holder, was a research assistant, 50% time, July 1 through September 30, 1991. He has returned the University of Braunschweig, Germany.

Harry Hai Hong, research assistant, 50% time, June 1 through August 31, 1991. He completed his Ph.D. in December 1991 and is now employed with Shin-Etsu Technical Services in Torrance, CA.

Derek Stonich, research assistant, 50% time, June 1, 1989 through June 30, 1991. He completed his Ph.D. in May 1991 and is now employed with ICI Americas in Richmond, CA.

Howard Lee, research assistant, 50% time, September 1-30, 1990. He completed his Ph.D. in December 1990 and following a brief postdoctoral research appointment with my group he is an Assistant Professor at Fu-Jen Catholic University, Taiwan.

Bing Ai, graduate student in physics, research assistant, 25% time, September 1-30, 1990.

Pascale Nouchi, graduate student in physics, research assistant, 25% time, September 1-30, 1990.

Postdoctoral Research Associate Supported

Dr. G. Wang, postdoctoral research associate, 100% time, April 1, 1992 through February 1, 1993. He is a graduate of the Chinese Academy of Sciences, Institute of Organic Chemistry, Shanghai, China.

Dr. Liqing Sun, postdoctoral research associate, 50% time, January 1 through August 31, 1992. Dr. Sun received his Ph.D. under the direction of Professor Ron Salovey at the University of Southern California. He is currently employed by Monsanto Chemical Company.

Dr. Min-Wei Chen, visiting scholar, 85% time, October 31, 1991 to June 30, 1993. Dr. Chen is an Associate Professor at the East China Institute of Chemical Technology, Shanghai, China. She is an expert at the measurement of physical properties of polymers.

Dr. Xiagao Liao, postdoctoral research associate, 100% time, July 1 through September 30, 1991; Senior Postdoctoral Research Associate, January 1 through October 9, 1992. He received his Ph.D. at the Chinese Academy of Sciences, Institute of Organic Chemistry, Shanghai, China. He is now employed as a research scientist at Pharmacia in Monrovia, CA.

Dr. Howard Lee, postdoctoral research associate, 100% time, July 1 through September 30, 1991. He is now an Assistant Professor at Fu-Jen Catholic University, Taiwan.

Dr. Georges Manuel, Visiting Scientist from the Universite Paul Sabatier, Toulouse, France, 100% time, July 1 through August [illegible], 1991; July 13 through August 12, 1992.

Dr. Stephen Qingzhan Zhou, postdoctoral research associate, 100% time, June 1 through October 31, 1989. Dr. Zhou received his Ph.D. under the direction of Professor William Weber at the University of Southern California. Dr. Zhou was promoted to Senior Postdoctoral Research Associate, 100% time, November 1, 1989. He held this position from November 1, 1989 through July 12, 1990; and May 1 through September 30, 1991. He is now employed as a research scientist at Pharmacia in Monrovia, CA.

Dr. Young Tae Ko, postdoctoral research associate, 100% time, October 31, 1989 through April 30, 1991. Dr. Ko did his doctoral studies at the Universite Paul Sabatier in Toulouse, France working with Professor Satge. He is now employed with Kumho Petrochemical Company in South Korea.

Dr. Judah Farahi, postdoctoral research associate, 100% time, November 3, 1990 through August 31, 1991. Dr. Farahi received his doctoral training with Professor Kenneth Doxsee at USC and the University of Oregon. He is now employed with Veterans Administration Hospital, Los Angeles, CA.

Principal Investigator Supported

Professor William Weber, principal investigator, worked full-time on this project July 1, 1990 through August 31, 1990; July 1 through August 31, 1991; June 1 through August 31, 1992; June 1-30 and August 1-31, 1993 and 28% time July 1-31, 1993; in addition to 10% of time during the year.

PART II

a. Principal Investigator: Professor William P. Weber

b. Cognizant ONR Scientific Officer: Dr. JoAnn Milliken
Chemistry Division, Code 1113; Office of Naval Research; 800 N.
Quincy Street, Arlington, VA 22217-5000

c: Current telephone number: (213) 740-5961.

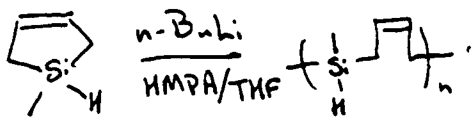
d. Description of Project:

Preparation of composite materials which have high strength in compression. Scientific approach is to prepare novel polymeric coupling agents. These will permit formation of multiple flexible covalent bonds between fibers as well as to matrix materials. In addition, these new coupling agents will possess elastomeric properties which may increase matrix toughness to fracture.

e. Scientific Achievements:

The major goal of this contract was to prepare new unsaturated Si-H carbosilane materials which could be coated on carbon and glass fabric and crosslinked by a platinum catalyzed hydrosilation chemistry to yield novel composite materials with high strength in compression. Composite materials are generally made up of matrix, fibers and coupling agents. The crosslinked carbosilane material constitutes **both** the matrix and the coupling agents in these novel composite materials.

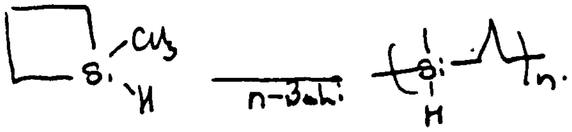
Low molecular weight unsatratued Si-H carbosilane polymers have been prepared by anionic ring opening polymerization of Si-H silacyclopent-3-enes. See #3, 5, 6, 12, 26.



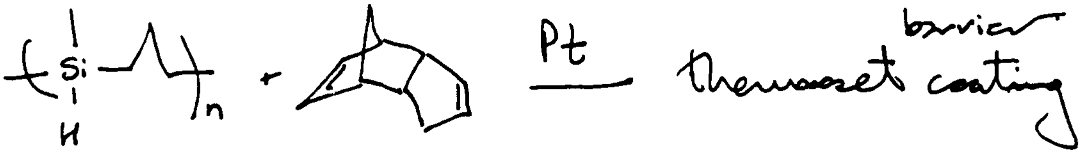
Similar high molecular weight systems have been prepared by ring opening metathesis polymerization (ROMP). See #12 and patent #4.

These are low viscosity (~100 centistates) low T_g (-80°C) materials. These are one component systems which have mutually reactive Si-H and C=C double bonds which undergo Pt crosslinking to thermoset materials with T_g greater than 150°C.

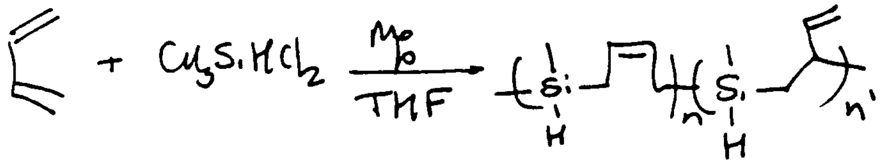
Two component systems with greater shelf life in which the Si-H and C=C are separated have been prepared by anionic ring opneing polymerzation of appropriate Si-H silabutane or Si-vinyl silacyclopent-3-ene systems. See #23, 25, 27, 28, 29, 30, 35, 38.



These undergo Pt catalyzed hydrosilation crosslinking with unsaturated monomers and/or polymers, such as 1,2-polybutadiene, to yield low dielectric (2.3), low moisture absorption (0.01%) corrosion resistant coatings.



Of greatest significance a one step procedure for the preparation of Si-H unsaturated low molecular weight carbosilane polymer directly from 1,3-butadiene and dihalosialne has been developed. This procedure eliminates the need to prepare cyclic monomers.



These new polymers has an appreciable fraction of pendant vinyl groups. Both 1:1 and 2:1, butadiene to silylene polymers have been prepared. The pendant vinyl groups permit particularly facile Pt catalyzed crosslinking cure to thermoset materials. These materials have been coated on carbon fabric, crosslinked and their physical properties measured (short beam shears, flexure, tensile strength and compression strength). They are weaker than exposy composites at this stage of development (see papers #43, 47 and 48, and paper in press #1).

HERCULES

Hercules Incorporated
Research Center
500 Hercules Road
Wilmington, DE 19808-1599
(302) 995-3000
Fax: (302) 995-3694

September 21, 1993

Dr. William P. Weber
Loker Hydrocarbon Institute
University of Southern California
University Park
Los Angeles, CA 90089-1661

Dear Bill:

Enclosed please find our report for the ARPA electronics packaging contract.

Please call me with any questions or comments.

Sincerely,

R T Leibfried

Raymond T. Leibfried
Materials Research Division
Hercules Incorporated

RTL:dlbv
m:\leibfried\weber.993

Enclosure

RELIABLE, COST EFFECTIVE PACKAGING FOR MILITARY ELECTRONICS

The US military is reconsidering its position on electronic packaging and is currently revising Mil-I-38535, the specification detailing hermetic protection for semiconductor chips. Packaging is a preponderant cost in devices that must now be packaged in molded compounds or gels and housed in expensive ceramic boxes which are then sealed hermetically. The military will follow the lead of industry into new materials and lower cost advanced production methods for packaging. The term packaging is used in the limited sense of encapsulating devices in a protective barrier for the prevention of physical damage and corrosion. The overall design of the device must be accommodated with the approach to long term reliability under service conditions.

Resin transfer molding is the major process for plastic packaging of chips. Highly filled epoxy resins have proven their reliability and they are continually improved. Dexter-Hysol has been a leader in this continued advancement and have marketed some formulations for glob top packaging which are deposited over the chip and leads. Other formulations are used to mount chips and to protect wire bonds and connectors. One of the challenges is to minimize the volume of packaging needed so the electronic devices can continue to shrink. The proliferation of hand held electronics grows from this trend toward miniaturization.

Coating technology is advancing to the point where extremely thin coatings could replace the mass of material used in molded or globbed packages. The materials can resist vibration, shocks, thermal cycling and high humidity conditions. This report covers a new approach to protective coatings from potentially economical polycarbosilane formulations that can be easily applied and cured on semiconductor chips and other electronic devices.

Carbosilane Polymer Research

Prof. William Weber and his group at the Loker Hydrocarbon Institute have advanced the technology of carbosilane polymers. The government sponsored research has produced practical results since the polymers can be readily produced commercially and applied as electronic packaging. The polymers and their formulations are the subject of numerous papers and US Patents (US 5,171,792; 5,130,390; 5,169,916; 5,171,810). This strong patent coverage increases the potential for industrial production of these materials.

Platinum catalyzed hydrosilation has been used as the cure mechanism in the carbosilane polymer formulations since it has been proven that platinum will not migrate to the conducting surfaces of electronic devices during use. Also, this chemistry has no by-products that would promote thermal or hydrolytic deterioration of the packaging.

New Electronic Encapsulants

Previous reports indicated that carbosilane polymers synthesized at the Loker Hydrocarbon Institute could be formulated to produce excellent electronic encapsulants. The materials have a low dielectric constant (2.55), low dissipation factor (0.0007) and low water absorption (0.01%). Coatings of these materials passed preliminary tests in boiling water without changing the dielectric properties around the test circuits (gold lines on alumina) under the coatings.

This report covers the successful performance of an economical packaging concept where 3μm thick carbosilane polymer coatings protect AT&T triple track test substrates in a 300 hour pressure cooker test (120°C, 15 psi steam). The test protocol and resistance determinations were carried out at the Sherman Fairchild Laboratory at Lehigh University. The resistance at the test surface remains high (10^{14} ohms/□) after 300 hours showing that water has not permeated or penetrated the coating or its interface with the test device. Also, it appears the extraction methods used to purify the carbosilane polymer candidates were effective. The presence of salts would adversely effect the achievement of high resistance throughout the test.

The carbosilane polymer coatings on AT&T triple tracks also passed a severe thermal cycling test carried out at National Technical Systems (Boxboro, MA). The temperature transitions from -65°C to 125°C and back took under two minutes and the pause was 12 minutes at each temperature. After 100 cycles the coatings showed no significant low density spots under an acoustic microscope at Sonoscan, Inc. Only pre-existing small flaws are indicated by the images (see attached). The mismatch in thermal expansion (100/7) of the coating and substrate did not decrease the adhesion of the coating to the substrate during expansion and contraction cycles or soak periods. This may be partially attributed to the presence of an effective silane coupling agent (1% methacryloxypropyl triethoxysilane) in the coating and the low modulus of the coating itself. The low mass of the thin coating is also a factor in this test. Experience has shown that surviving 100 cycles predicts good service performance for packaging.

The new carbosilane coatings can be applied by practical means such as spinning onto chips or large numbers of mounted chips can be quickly dip coated in properly diluted coating formulations and cured in hot air ovens. The coatings provide optimum electrical properties such as low dielectric constants and dissipation factors, with high dielectric breakdown and resistivity, leading to good performance in the chips as well as protection against water and corrosion. Physical protection is provided by the relatively tough coatings but vibration tests should be performed if this program continues. This concept of chip encapsulation is potentially low cost compared to hermetic sealing or even transfer molding.

It is very likely that the methylsilapentene polymers detailed by Weber can be scaled up into commercial production. There is a one step synthetic method that uses common low cost starting materials (butadiene $0.19/lb, methyldichlorosilane $1.80/lb, and magnesium ($1.40/lb).

Coating Formulations

The carbosilane resins with desirable coating properties are MSB, poly(1-methylsilabutane) and MSP, poly (1-methylsilapentene). These oligomeric resins (MW ~2000) are formulated with dicyclopentadiene (DCPD) or polycyclic aliphatic hydrocarbons (PCAH) to make coatings that are cured by the hydrosilation reaction using a platinum catalyst. Coupling agents are added to promote adhesion to the test circuits.

Test Circuits/Standard Coating

The test devices were AT&T triple tracks which are gold circuits on alumina. The spacing between the gold lines is 0.75μm and the 1.00μm lines form a continuous labyrinth connected to outside leads. The coating entirely covers the 1/4" x 3/8" gold grid. The resistance between the lines in an indicator of the dielectric properties of the coating. Any condensed water will short the circuit, so gross penetration is easily spotted. Higher resistance indicates the quality of the coating. The best coatings are silicone gels which give 10^{14} - 10^{16} ohm/□ after 300 hours at 120°C (15 psi steam). The silicone (DC 6550 RTV) is applied at a thickness of >500µm (>20 mil). This is to provide some physical protection as well as a water barrier.

Pressure Cooker Test

The coated triple tracks are exposed to steam (120°C) without exposure to condensed water. The carbosilane formulations show a decrease in resistance early in the test which then improves later. This indicates curing during the test possibly promoted by water.

Pressure Cooker Test (120°C, 15 psi steam)

Coating	**Resistance (Ohms/Square)**	
	Hr	**3.0µm**
MSB/DCPD	0	2×10^{15}
	100	10^{12}
	200	10^{13}
	300	2×10^{13}

Coating	**Resistance (Ohms/Square)**	
	Hr	**2.8μm**
MSB/PCAH	0	2x 10^{16}
	100	10^{13}
	200	10^{14}
	300	10^{14}

Silicone	**Resistance (Ohms/Square)**		
	Hr	**525μm**	**375μm**
6550 RTV	0	10^{17}	10^{16}
	100	10^{16}	10^{16}
	200	5 x 10^{14}	10^{14}
	300	10^{16}	10^{14}

The excellent performance demonstrates the integrity of the low polarity coatings, their water repellent nature and their adhesion to the substrate. The probable route for moisture vapor or condensed water is at low density (poor adhesion) areas of the coating on the gold/alumina substrate. The coatings are cooled to room temperature seven times during the test to determine the resistance at the test surface. These thermal cycles provide further opportunities for condensed water to penetrate the interface if it is degraded by heating and cooling stresses due to the thermal expansion mismatch between the coating and the substrate [coating (100μm/m/°C, R.T. → 100°C), alumina (7μm/m/°C, R.T. → 100°C)]. If the evaluation of these materials is continued in the future, the pressure cooker test should be carried out on coated test circuits that have survived thermal cycling (-65 ↔ 150°C, 1000 cycles). The prognosis for the polycarbosilane coatings surviving such a test is excellent.

An organosilicon package under development by Hercules (SYCAR™ Resin Encapsulant) was applied as a glob top to AT&T triple tracks. The cured resin also performed well in the pressure cooker test comparing favorably with the silicone RTV coating.

	Developmental SYCAR™ Resin	**Silicon RTV 6550**
	ohms/□	ohms/□
hr 0	2 x 10^{15}	10^{17}
100	2 x 10^{14}	10^{16}
200	2 x 10^{14}	2 x 10^{14}
300	10^{15}	2 x 10^{15}

The acoustic imaging of coatings that were cycled from -65°C to 125°C and back 100 times is in the attachment. There is an explanation of the microscopic technique. The images show only small spots of low density that will not change the good performance of the coatings.

Acoustic Imaging

Coating	**Composition**	**Thickness (µm)**
#9	SYCAR™ Resin	775
#10	MSP(2.5)/PCAH	5.0
#11	MSB/DCPD	3.0
#12	MSP/PCAH	2.8

Summary

Effective packaging of electronic devices have been demonstrated using thin coatings of new carbosilane polymer formulations. The high temperature steam test and thermal cycling test shows that the coatings provide effective protection under severe environmental conditions. The degree of physical protection provided by the coatings is yet to be demonstrated.

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Lehigh University Research Report

Microelectronics Research Program to Evaluate Hercules' Polymeric Coatings

June 21, 1993

Submitted by :

Ramesh Kodnani
Research Associate

Dr. Donald Jaffe
Principal Investigator

EXECUTIVE SUMMARY

This report presents the results of testing carried out at Lehigh University to evaluate and characterize the moisture protection and other characteristics of Hercules' polymeric coatings for Microelectronics. Five developmental coatings, and commercial Sycar coatings were evaluated in this preliminary test program. The developmental coatings were designated by Hercules as: MSB/DCPD(t,z), MSB/DCPD(z,t), MSP/PCAH, MSP/PCAH(z), and MSP(2.5)/PCAH. In addition, a commercial Dow Corning silicone rubber coating designated in this report as RTV-6550 was evaluated for comparison purposes.

The experiments were carried out using AT&T triple track testers (TTTs). The TTTs consist of a patterned gold metallization on a 99.5% alumina (Al_2O_3) substrate. The TTTs were cleaned at Lehigh chemically and in UV-O_3. The cleaned devices were subsequently coated with the above coatings at Hercules. In addition, a group of TTTs was coated at Lehigh with RTV-6550. Sycar, MSB/DCPD(t,z) and RTV-6550 were applied drop-top, and rest of the coatings were spin coated on the test substrate (TTT). MSP(2.5)/PCAH was spin coated at two thicknesses and the thin coating was discontinued from testing after 12 hours of PCT. On an average five to eight test devices were tested per coating type, with the exception of MSP(2.5)/PCAH and MSP/PCAH. Additional details on number of samples, coating type are provided in the experimental section of this report.

All coatings were evaluated in a Pressure Cooker Test (PCT) at 121°C and 100% relative humidity (RH) for 300 hours. The PCT evaluates the hydrolytic stability of the coatings and coating/TTT interface. Leakage current measurements were made on the TTTs before and periodically during the test. The value of surface resistance of the coatings, which is inversely proportional to the leakage current, was calculated and used as the main parameter to rank the relative moisture protection performance of the coatings. The higher the surface resistance values and lesser the change in surface resistance during the test, better the moisture protection performance of the applied coating.

Finally, the adhesion of some of the coatings, to the TTT substrate, after 300 hours of PCT aging was characterized as per ASTM D3359-87 (Scotch) Tape Test - Method B.

The major conclusions are :

Moisture Protection Performance of Hercules' Coatings and Comparison with Silicone RTV: The surface resistance values, measured on TTTs after 300 hours of PCT exposure, for the five developmental coatings are in the range of 10^{12} - 10^{14} Ohms/square, whereas for Sycar they are about 10^{15} Ohms/square. The higher surface resistance values of Sycar are comparable to the surface resistance values of silicone RTV-6550, and are indicative of Sycar as a good encapsulation material with regards to it's moisture protection properties. The surface resistance values for developmental coatings are similar, or marginally lower, to those of commercial polyimides tested at Lehigh in the past, and are 2-3 orders of magnitude lower than silicone RTV-6550 with the exception of MSP/PCAH. This coating exhibited improvement in it's moisture protection performance after 125 hours of PCT aging and was comparable to RTV (HER) at 300 hours of PCT. Although this result is encouraging, it is statistically weak due to a small sample size (two samples) of MSP/PCAH, and would require further analysis for reproducibility of the test results.

Adhesion of Hercules' Coatings on the TTT (Al_2O_3) Surface: Adhesion of the spin coated films on TTTs was characterized with ASTM (scotch) Tape-Test. Although, these coatings performed differently in the PCT test, they could not be distinguished from one another in the ASTM Tape Test. On a scale of 0-5, with 0 being a complete loss of adhesion and 5 being a strong adhesion, all the spin coated coatings ranked 3-4.

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EXECUTIVE SUMMARY

APPENDIX-1 - Leakage Current Test Data

APPENDIX-2 - ASTM Test Standard (D3359-87)

1.0 INTRODUCTION

The use of conformal polymeric coatings in microelectronics is becoming more widespread due to their lower cost when compared to their hermetic equivalents and due to improvements in the polymeric coatings themselves. The major concern relative to the use of polymeric coated devices remains that of reliability. Reliability studies of polymer coated devices have identified corrosion as one of the most significant failure mechanism. Corrosion in micro-electronic devices occurs in presence of ionic impurities and moisture at the polymer/substrate interface. Improvements in polymeric coatings have lessened the influence of ambient moisture thus retarding the corrosion process. To evaluate and characterize coatings for microelectronic applications in a short period, a variety of accelerated stress tests are used .

This report presents the results of testing carried out at Lehigh University to evaluate and characterize the moisture protection and other characteristics of Hercules' polymeric coatings for Microelectronics. Five developmental coatings, and commercial Sycar coatings were evaluated in this preliminary test program. The developmental coatings were designated by Hercules as: MSB/DCPD(t,z), MSB/DCPD(z,t), MSP/PCAH, MSP/PCAH(z), and MSP(2.5)/PCAH. In addition, a commercial Dow Corning silicone rubber coating designated in this report as RTV-6550 was evaluated for comparison purposes.

The experiments were carried out using AT&T triple track testers (TTTs). The TTTs consist of a patterned gold metallization on a 99.5% alumina (Al_2O_3) substrate. The TTTs were cleaned at Lehigh chemically and in UV-O_3. The cleaned devices were subsequently coated with the above coatings at Hercules. In addition, a group of TTTs was coated at Lehigh with RTV-6550. Sycar, MSB/DCPD(t,z) and RTV-6550 were applied drop-top, and rest of the coatings were spin coated on the test substrate (TTT). MSP(2.5)/PCAH was spin coated at two thicknesses and the thin coating was discontinued from testing after 12 hours of PCT. On an average five to eight test devices were tested per coating type, with the exception of MSP(2.5)/PCAH and MSP/PCAH. Additional details on number of samples, coating type are provided in the experimental section of this report.

All coatings were evaluated in a Pressure Cooker Test (PCT) at 121°C and 100% relative humidity (RH) for 300 hours. The PCT evaluates the hydrolytic stability of the coatings and coating/TTT interface. Leakage current measurements were made on the TTTs before and periodically during the test. The value of surface resistance of the coatings, which is inversely proportional to the leakage current, was calculated and used as the main parameter to rank the relative moisture protection performance of the coatings. The higher the surface resistance values and lesser the change in surface resistance during the test, better the moisture protection performance of the applied coating.

2.0 EXPERIMENTAL

2.1 Experimental Plan

The following chart summarizes sample preparation, and testing operations and locations for the evaluation of Hercules' coatings.

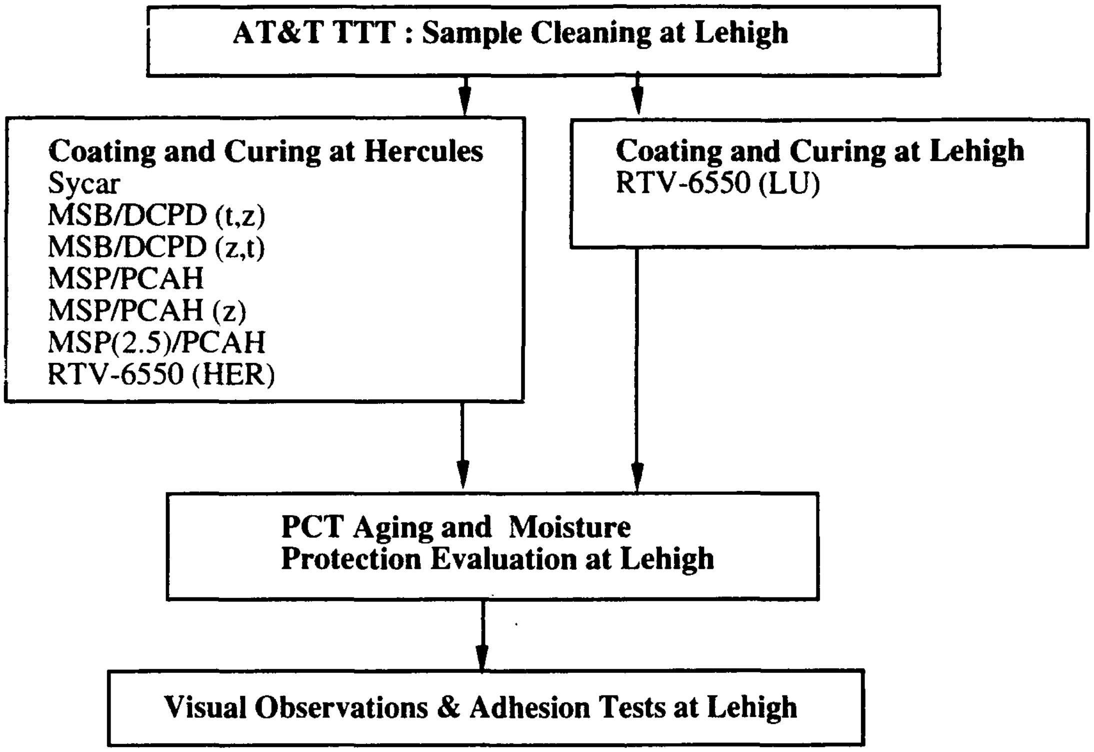


Figure 1: Sample Preparation, and Testing Operations and Locations.

2.2 Cleaning and Coating Preparation

AT&T TTTs, prior to coating, were cleaned at Lehigh as per the following cleaning schedule:

1. SC-1[1] cleaning: H_2O_2:NH_4OH:H_2O 1:1:5 75°C, 10 min.
2. Rinse with de ionized (DI) water
3. Dry at 150°C, 1/2 hour
4. UV/Ozone cleaning, 5 min.

The cleaned TTTs were subsequently coated and cured at Hercules within 12 hours of cleaning. A group of freshly cleaned TTTs was also coated with Silicone RTV-6550 at Lehigh as controls. The RTV was cured at room temperature (RT) for 24 hours followed by one hour at 180°C, both at Lehigh and Hercules. The curing conditions for the coatings applied at Hercules were not reported to Lehigh.

Five to eight TTTs were coated for each coating evaluated, with the exception of MSP/PCAH for which only two coated parts were tested. MSP(2.5)/PCAH was applied in two thicknesses with ten parts coated thin (~ 5 μm) and one part coated thick (~ 35 μm). The following table summarizes the coating procedures, coating thicknesses, and additional remarks for the coatings tested in the test plan.

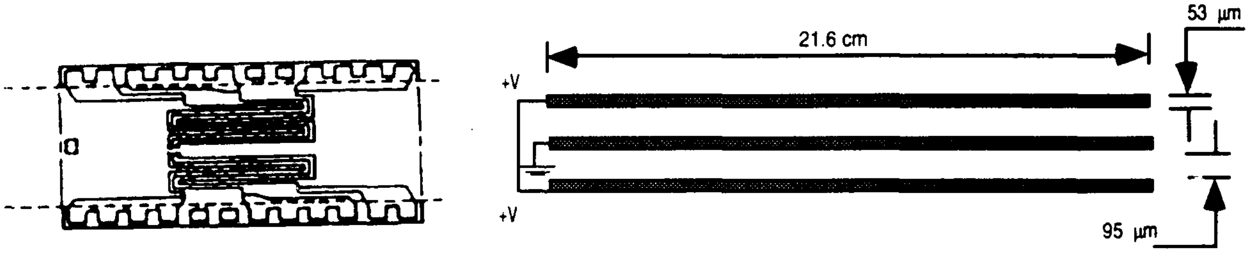
Table 1: Description of Coatings Evaluated in PCT

Coating	Coating Procedure	Measured[†] Thickness	TTTs Tested	Remarks
SYCAR	Drop-Top	~ 775 µm	6	Filled Commercial Coating
MSB/DCPD (t,z)	Drop-Top	~ 750 µm	6	Filled Coating
MSB/DCPD (z,t)	Spin-Coat	3±0.2 µm	5	
MSP/PCAH (z)	Spin-Coat	2.8±0.2 µm	6	
MSP/PCAH	Spin-Coat	12±2 µm	2	Non-uniform Coverage on TTTs
MSP(2.5)/PCAH	Spin-Coat	5±1 µm	10	
MSP(2.5)/PCAH(R)	Spin-Coat	35±5 µm	1	
RTV-6550 (LU)	Drop-Top	~ 525 µm	8	Only Group Coated & Cured at L.U.
RTV-6550 (HER)	Drop-Top	~ 375 µm	6	

[†]: The thicknesses for drop-top coatings were measured with vernier calipers and for the spin-coated films were measured with Tencor Aplha Step 200 Profilometer.

2.3 Test Devices

In this investigation, AT&T triple track testers (TTTs) were used as test devices. These testers consist of three parallel gold conductors 21.6 cm long, 53 µm wide and 95 µm apart, in a meander pattern on a 99.5% Al_2O_3 ceramic substrate. A schematic of this test structure is shown in Figure 2.



(a) (b)

Figure 2 : A schematic of an AT&T Triple-Track Tester showing (a) metallization pattern on a 24-pin ceramic substrate (b) geometry and biasing configuration of the test structure.

2.4 Pressure Cooker Test (PCT) Conditions

The Pressure Cooker Test (PCT) was used to evaluate the moisture protection performance of the Hercules and RTV-6550 coatings on TTTs. The PCT stress conditions were 121°C and saturated steam at 2 atmospheres pressure, for times to 300 hours. At regular intervals, the devices were removed from test chambers for leakage current measurements.

2.5 Leakage Current Measurements

Leakage currents on the coated TTTs were measured, off-line, periodically at 0, 12, 50, 90, 125, 160, 215, and 300 hours of exposure in PCT as follows :

1. TTTs were first equilibrated for one hour at room temperature in a controlled atmosphere of 90-95 % RH inlet air, saturated by percolation through water at a flow rate of 5-7

cc/min.

2. Testers were then plugged into 24-pin zero-insertion force sockets, in the same controlled atmosphere, at 180 volts bias. At this stage the testers were also equilibrated for a period of 1 hour under bias. The center track of the triple track structure was connected to the ground potential and the 2 outer tracks were shorted and were applied a positive 180 V bias, as shown in Figure 2 (b).

3. After the testers were equilibrated the leakage currents between the oppositely biased conductors on TTTs were measured using a Kiethley-617 digital electrometer.

The degradation in coatings, loss in their capability of moisture protection performance, is reflected by increase in the leakage current of the coated devices throughout the tests.

2.6 Surface Resistance Calculations

Leakage currents in the test devices (TTTs) are dependent on the applied voltage and the geometry of the test structure, specifically, the spacing and length of the conducting tracks. To allow a more convenient comparison with other test results, the leakage current data was converted into surface resistance values, which is a fundamental measure and independent of the applied voltage (assuming Ohm's law) and the geometry of the test device. The relationship between surface resistance and leakage current is:

$$SR = \frac{V}{(I * n)} \quad \text{, where,}$$

n is the number of squares of insulator (0.00022 squares for TTT), SR is the surface resistance of the test device in "Ohms/square", V is the applied bias in "Volts", and i is the measured value of leakage current in "Amperes".

These calculated surface resistance values are a measure of the relative moisture protection performance of the coatings. The higher the surface resistance values and the lesser the change in surface resistance during the tests, better is the moisture protection performance.

2.7 Adhesion Test

To evaluate the adhesion of coatings to the TTT surface, adhesion tests were carried out on the representative TTTs after 300 hrs of PCT aging. The adhesion test as per ASTM D3359-87 Tape Test - Method B was used to characterize the adhesion of these coatings to TTTs. This test is used to primarily establish the adequacy of adhesion, and the procedure of testing involves applying and removing pressure-sensitive tape over the cuts made in the film. For detailed description on the test procedure and adhesion ratings, a copy of the test standard is enclosed in Appendix 2.

3.0 RESULTS

3.1 Leakage Current and Surface Resistance as a Function of PCT Time

The measured values of leakage currents in TTTs for Hercules' coatings, as a function of PCT time to 300 hours are provided in Table 1 through Table 7 in Appendix-1. For comparison, results for Dow Corning silicone rubber, RTV-6550, coated TTTs are also included. The calculated values of surface resistance as a function of PCT time are plotted in Figures 3 and 4.

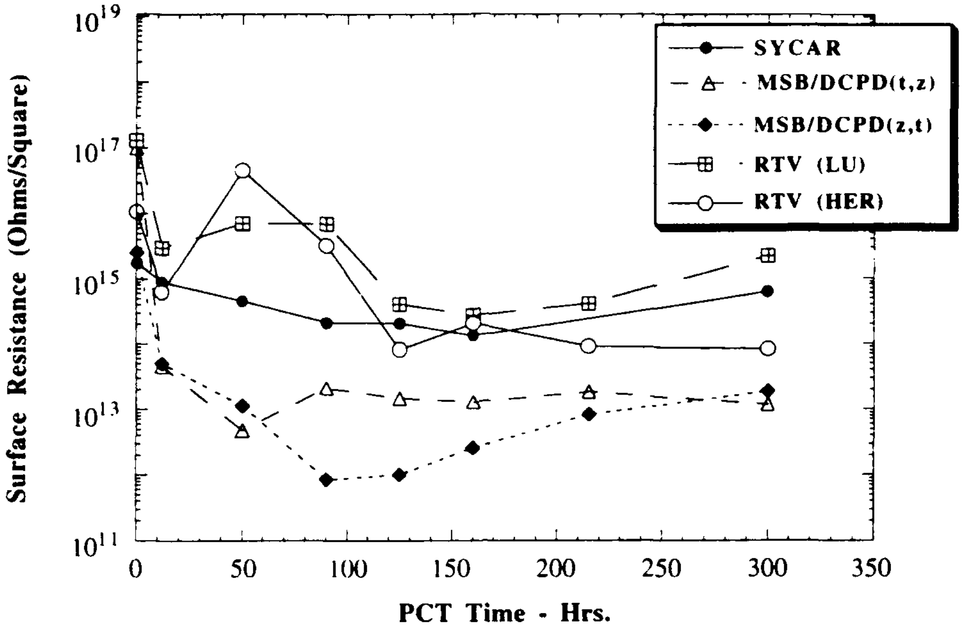


Figure 3: PCT Evaluation of Hercules' coatings - MSB/DCPD and Sycar. Surface resistance of coated AT&T TTTs vs. PCT Time.

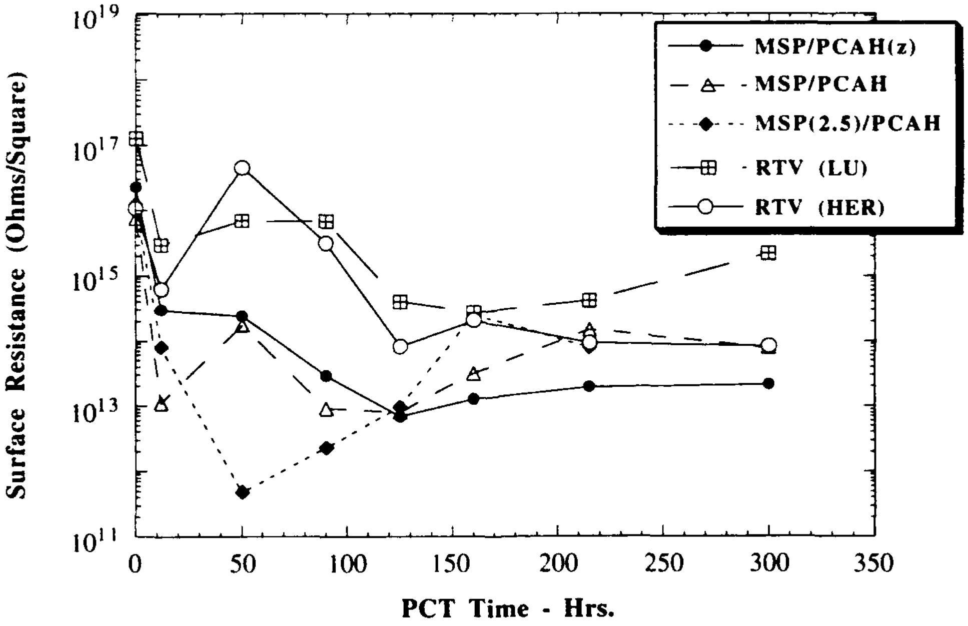


Figure 4: PCT Evaluation of Hercules' coatings - MSP/PCAH. Surface resistance of coated AT&T TTTs vs. PCT Time.

3.2 Adhesion Following 300 Hours of PCT

The adhesion ratings following 300 hours of PCT for spin coated films, MSP/PCAH, MSP/PCAH(z), MSP(2.5)/PCAH, MSB/DCPD(z,t), are given in Table 1.

Table 2: Adhesion of spin coated Hercules films after 300 hours of PCT.

Coating	Adhesion Rating on a scale of 0-5*
MSB/DCPD(z,t)	4B
MSP/PCAH(z)	4B
MSP/PCAH	3B
MSP(2.5)/PCAH (R)	3B-4B

* - coatings were rated on a scale of 0 to 5, with 0 being the poor (complete delamination) and 5 being a very good adhesion. The classification B indicates that test method B was used for the adhesion characterization. The details of test procedure and evaluation are as per Appendix-2.

3.3 Summary of Results

The following table summarizes the moisture protection performance and adhesion test results of the Hercules' coatings after 300 hours of PCT.

Table 3: Summary of Results Following 300 hours of PCT

Coating	Coating Thickness	Sur. Res. (Ohms/Sq.)	Adhesion Rating	Remarks
SYCAR	~ 775 µm	6.1E+14	NM	
MSB/DCPD (t,z)	~ 750 µm	1.2E+13	NM	3 of the 6 TTTs Delaminated During PCT Test
MSB/DCPD (z,t)	3±0.2 µm	1.8E+13	4B	
MSP/PCAH (z)	2.8±0.2 µm	2.1E+13	4B	
MSP/PCAH	12±2 µm	7.6E+13	3B	
MSP(2.5)/PCAH	5±1 µm	9E+10*	NM	Group Discontinued After 12 hrs. of PCT due to Rapid Degradation
MSP(2.5)/PCAH(R)	35±5 µm	7.6E+13**	3B-4B	Took Up Water in PCT and Came Out Wet (only 1 sample tested-see text)
RTV-6550 (LU)	~ 525 µm	2.2E+15	NM	
RTV-6550 (HER)	~ 375 µm	8.7E+13	NM	

NM: Not measured
* : PCT tested for only 12 hours
**: PCT tested for 215 hours

4.0 OBSERVATIONS AND DISCUSSION

4.1 Relative Moisture Protection Performance

Among the coatings tested, Sycar exhibited good moisture protection performance comparable to commercial silicone RTV. The good encapsulation properties exhibited by Sycar could be on account of good adhesion of the material to the test substrate. This would further be enhanced by the presence of the filler in the coating in reducing the CTE of the resin resulting in lower interfacial stresses at high temperatures in PCT.

MSP/PCAH exhibited improvement in it's moisture protection performance after 125 hours of PCT aging and was comparable to RTV (HER) at 300 hours of PCT. Although this result is encouraging, it is statistically weak due to a small sample size (two samples) of MSP/PCAH, and would require further analysis for reproducibility of the test results.

The MSP(2.5)/PCAH coating was prepared at two thicknesses. The TTTs coated with a thin coat of MSP(2.5)/PCAH exhibited a significant rise in the measured values of leakage current in the first 12 hours of PCT. Subsequently, on Hercules' directive, these thin coated parts were removed form the PCT. The leakage current data for these discontinued parts is also provided in the appendix. The results plotted in Figure 4 are for the (one) thick coated part of MSP(2.5)/PCAH.

The performance of other developmental coatings, though moderate, was comparable to some commercial polyimide coatings. A relatively high scatter in the measure of leakage currents was observed for these coatings and this could be reduced by improvements and control in processing of these films.

4.2 Comparison of RTV-6550 - Coated at Lehigh and Hercules

Two groups of RTV coated TTTs, one coated at Lehigh immediately after cleaning of the test specimens and one prepared at Hercules within 12 hours of cleaning, were tested to evaluate a possible contamination during transportation. Although these two groups exhibited similar surface resistance values up to 160 hours of PCT, the RTV-6550 (HER) deviated in the remainder of the test and finished at ~ 1 order of magnitude lower surface resistance than RTV-6550 (LU). Part of this difference in PCT performance of the two RTV groups may possibly be attributed to the difference in their average coating thickness, but this is speculative. In any case, due to the similarity in behavior of the two RTV groups up to 160 hours of PCT , it is our opinion that the TTTs were not significantly contaminated during transportation from Lehigh to Hercules.

4.3 Visual Inspection Following 300 Hours of PCT

All Hercules coatings with the exception of filled MSB/DCPD (t,z) adhered to the TTT surface through the PCT testing. Three of the six test devices (T13-T15) coated with the above coating exhibited complete delamination during the test. This coating was prepared in two groups of three parts each at separate occasions. A possible cause of difference in their adhesion to the test substrate could be due to a difference in the processing or curing of the coating at these separate occasions. Also, if the T_g of the material was exceeded during the PCT aging, it could result in release of residual (frozen) stresses and thus explain the coating delamination from the test surface.

The two parts spin coated with MSP/PCAH exhibited a non uniform coverage of the test surface. These "open" spots on the test substrate could be due to the presence of local organic impurities on the substrate, or poor mixing of the catalyst/curing agent in the resin causing localized difference in surface tension and poor wetting of the test substrate.

The MSP(2.5)/PCAH coating was prepared at two thicknesses. This coating, both thicknesses, took up water in the test and came out wet from the test chamber. This observation indicates that the coating is hydrophilic.

4.4 Adhesion Following 300 Hours of PCT

The four spin coated films exhibited good adhesion to TTTs in the ASTM Tape-Test. It should be noted that this test is useful for analyzing adequacy of adhesion and does not effectively distinguish coatings with good adhesion. The fact that these coatings exhibited good adhesion also indicates that other coating parameters, such as high levels of ionic impurities, high water and/or ion permeation through the coatings, are possibly influencing the poor moisture protection performance.

5.0 CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Moisture Protection Performance of Hercules' Coatings and Comparison with Silicone RTV: The surface resistance values, measured on TTTs after 300 hours of PCT exposure, for the five developmental coatings are in the range of 10^{12} - 10^{14} Ohms/square, whereas for Sycar they are about 10^{15} Ohms/square. The higher surface resistance values of Sycar are comparable to the surface resistance values of silicone RTV-6550, and are indicative of Sycar as a good encapsulation material with regards to it's moisture protection properties. The surface resistance values for developmental coatings are similar, or marginally lower, to those of commercial polyimides tested at Lehigh in the past, and are 2-3 orders of magnitude lower than silicone RTV-6550 with the exception of MSP/PCAH. This coating exhibited improvement in it's moisture protection performance after 125 hours of PCT aging and was comparable to RTV (HER) at 300 hours of PCT. Although this result is encouraging, it is statistically weak due to a small sample size (two samples) of MSP/PCAH, and would require further analysis for reproducibility of the test results.

Adhesion of Hercules' Coatings on the TTT (Al_2O_3) Surface: Adhesion of the spin coated films on TTTs was characterized with ASTM (scotch) Tape-Test. Although, these coatings performed differently in the PCT test, they could not be distinguished from one another in the ASTM Tape Test. On a scale of 0-5, with 0 being a complete loss of adhesion and 5 being a strong adhesion, all the spin coated coatings ranked 3-4.

5.2 Future Work

Further characterizations of the developmental coatings are required to understand the differences in their moisture protection performance. Sycar performed similarly to RTV in it's moisture protection characteristics evaluated in PCT. Based on this, Sycar is a good candidate for microelectronic encapsulation applications. Additional characterizations of this coating would be of interest. These include: (1) protection of Al test devices in environmental tests, (2) effect of temperature cycling on thermo-mechanical stresses induced in the substrate, (3) adhesion of the coating to typical substrates and metallizations such as Al, Au, Si/SiO_2, and Al_2O_3, and (4) level of ionic impurities in the material etc.

References:

[1] Werner Kern, *J. of Electrochem Society,* Vol. 137, No. 6, June 1990

APPENDIX-1

TABLE 1: PCT Evaluation of HERCULES - SYCAR
Coated AT&T Triple-Track Testers
Coating Thickness (μm): ~ 775

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
SYCAR-1	1.26E-09	2.07E-09	8.24E-07	8.50E-07	7.90E-07	1.51E-06	1.43E-09	1.68E-08
SYCAR-2	2.90E-11	3.60E-11	1.11E-10	9.50E-11	1.20E-10	1.24E-10	3.30E-11	1.71E-09
SYCAR-3	7.20E-12	3.30E-11	5.13E-11	2.61E-10	3.80E-10	1.46E-09	6.00E-12	3.94E-11
SYCAR-4	8.10E-09	3.80E-08	4.80E-08	8.95E-09	1.14E-08	1.53E-08	1.36E-08	6.75E-08
SYCAR-5	2.60E-10	2.43E-10	5.90E-10	6.10E-10	3.10E-10	6.20E-10	2.02E-11	4.83E-10
SYCAR-6	2.35E-08	2.90E-08	3.02E-10	3.50E-08	3.64E-08	2.40E-08	3.30E-11	1.61E-10
SYCAR-1 (log)	-8.8996	-8.6840	-6.0841	-6.0706	-6.1024	-5.8210	-8.8447	-7.7747
SYCAR-2 (log)	-10.5376	-10.4437	-9.9547	-10.0223	-9.9208	-9.9066	-10.4815	-8.7670
SYCAR-3 (log)	-11.1427	-10.4815	-10.2899	-9.5834	-9.4202	-8.8356	-11.2218	-10.4045
SYCAR-4 (log)	-8.0915	-7.4202	-7.3188	-8.0482	-7.9431	-7.8153	-7.8665	-7.1707
SYCAR-5 (log)	-9.5850	-9.6144	-9.2291	-9.2147	-9.5086	-9.2076	-10.6946	-9.3161
SYCAR-6 (log)	-7.6289	-7.5376	-9.5200	-7.4559	-7.4389	-7.6198	-10.4815	-9.7932
Average (log)	-9.3142	-9.0302	-8.7328	-8.3992	-8.3890	-8.2010	-9.9318	-8.8710
Std. Dev. (log)	1.3726	1.3701	1.6613	1.4925	1.4828	1.4475	1.2883	1.2251
Average+SD	1.1E-08	2.2E-08	8.5E-08	1.2E-07	1.2E-07	1.8E-07	2.3E-09	2.3E-08
Average	4.9E-10	9.3E-10	1.9E-09	4.0E-09	4.1E-09	6.3E-09	1.2E-10	1.3E-09
Average-SD	2.1E-11	4.0E-11	4.0E-11	1.3E-10	1.3E-10	2.2E-10	6.0E-12	8.0E-11
Sur. Conductance	5.9E-16	1.1E-15	2.3E-15	4.9E-15	5.0E-15	7.7E-15	1.4E-16	1.6E-15
Sur. Resistance	1.7E+15	8.8E+14	4.4E+14	2.1E+14	2.0E+14	1.3E+14	7.0E+15	6.1E+14

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TABLE 2: PCT Evaluation of HERCULES - MCB/DCPD (T,Z)
Coated AT&T Triple-Track Testers
Coating Thickness (μm): ~ 750

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours 0	12	50	90	125	160	215	300
MCB/DCPD(t,z)-1	1.05E-11	Significant increase in leakage currents, and coating delamination						
MCB/DCPD(t,z)-2	6.60E-12	Significant increase in leakage currents, and coating delamination						
MCB/DCPD(t,z)-3	2.20E-11	Significant increase in leakage currents, and coating delamination						
MCB/DCPD(t,z)-4	2.30E-11	4.43E-07	3.40E-07	4.20E-08	3.56E-08	5.30E-08	4.68E-07	9.60E-08
MCB/DCPD(t,z)-5	5.10E-12	2.54E-08	1.08E-06	7.50E-08	1.12E-07	1.38E-07	9.09E-09	9.40E-08
MCB/DCPD(t,z)-6	2.70E-12	5.46E-10	1.42E-08	2.01E-08	4.73E-08	3.75E-08	2.21E-08	3.80E-08
MCB/DCPD(t,z)-1 (log)	-10.9788							
MCB/DCPD(t,z)-2 (log)	-11.1805							
MCB/DCPD(t,z)-3 (log)	-10.6576							
MCB/DCPD(t,z)-4 (log)	-10.6383	-6.3536	-6.4685	-7.3768	-7.4486	-7.2757	-6.3298	-7.0177
MCB/DCPD(t,z)-5 (log)	-11.2924	-7.5952	-5.9666	-7.1249	-6.9508	-6.8601	-8.0414	-7.0269
MCB/DCPD(t,z)-6 (log)	-11.5686	-9.2628	-7.8477	-7.6968	-7.3251	-7.4260	-7.6556	-7.4202
Average (log)	-11.0675	-7.7372	-6.7609	-7.3995	-7.2415	-7.1873	-7.3423	-7.1549
Std. Dev. (log)	0.4083	1.4598	0.9741	0.2866	0.2592	0.2931	0.8978	0.2298
Average+SD	2.2E-11	5.3E-07	1.6E-06	7.7E-08	1.0E-07	1.3E-07	3.6E-07	1.2E-07
Average	8.6E-12	1.8E-08	1.7E-07	4.0E-08	5.7E-08	6.5E-08	4.5E-08	7.0E-08
Average-SD	3.3E-12	6.4E-10	1.8E-08	2.1E-08	3.2E-08	3.3E-08	5.8E-09	4.1E-08
Sur. Conductance	1.0E-17	2.2E-14	2.1E-13	4.9E-14	7.0E-14	7.9E-14	5.6E-14	8.6E-14
Sur. Resistance	9.6E+16	4.5E+13	4.7E+12	2.1E+13	1.4E+13	1.3E+13	1.8E+13	1.2E+13

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TABLE 3: PCT Evaluation of HERCULES - MSB/DCPD (Z,T)
Uncoated AT&T Triple-Track Testers
Coating Thickness (µm): 3±0.2

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
MSB/DCPD(z,t)-1	1.06E-09	1.77E-09	8.20E-11	6.64E-08	2.36E-08	4.90E-08	4.52E-09	2.85E-09
MSB/DCPD(z,t)-2	2.05E-11	3.07E-07	8.20E-05	4.11E-07	1.41E-06	4.66E-08	5.50E-08	1.90E-08
MSB/DCPD(z,t)-3	3.96E-09	2.18E-08	1.94E-09	2.27E-06	1.54E-06	5.60E-07	2.55E-08	9.00E-09
MSB/DCPD(z,t)-4	5.18E-10	6.60E-09	2.20E-06	1.43E-05	8.90E-06	8.30E-06	1.60E-05	8.00E-06
MSB/DCPD(z,t)-5	9.60E-11	1.34E-09	6.08E-07	3.10E-06	1.18E-06	1.43E-06	2.03E-06	4.14E-07
MSB/DCPD(z,t)-1 (log)	-8.9747	-8.7520	-10.0862	-7.1778	-7.6271	-7.3098	-8.3449	-8.5452
MSB/DCPD(z,t)-2 (log)	-10.6882	-6.5129	-4.0862	-6.3862	-5.8508	-7.3316	-7.2596	-7.7212
MSB/DCPD(z,t)-3 (log)	-8.4023	-7.6615	-8.7122	-5.6440	-5.8125	-6.2518	-7.5935	-8.0458
MSB/DCPD(z,t)-4 (log)	-9.2857	-8.1805	-5.6576	-4.8447	-5.0506	-5.0809	-4.7959	-5.0969
MSB/DCPD(z,t)-5 (log)	-10.0177	-8.8729	-6.2161	-5.5086	-5.9281	-5.8447	-5.6925	-6.3830
Average (log)	-9.4737	-7.7767	-7.1355	-6.0132	-6.0852	-6.4935	-6.9985	-7.3523
Std. Dev. (log)	0.8949	0.9530	2.7492	0.9995	1.0920	1.0681	1.5369	1.5413
Average+SD	2.6E-09	1.5E-07	4.1E-05	9.7E-06	1.0E-05	3.8E-06	3.5E-06	1.5E-06
Average	3.4E-10	1.7E-08	7.3E-08	9.7E-07	8.2E-07	3.2E-07	1.0E-07	4.4E-08
Average-SD	4.3E-11	1.9E-09	1.3E-10	9.7E-08	6.6E-08	2.7E-08	2.9E-09	1.3E-09
Sur. Conductance	4.1E-16	2.0E-14	8.9E-14	1.2E-12	1.0E-12	3.9E-13	1.2E-13	5.4E-14
Sur. Resistance	2.4E+15	4.9E+13	1.1E+13	8.4E+11	1.0E+12	2.5E+12	8.2E+12	1.8E+13

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TABLE 4: PCT Evaluation of HERCULES - MSP/PCAH (Z)
Coated AT&T Triple-Track Testers
Coating Thickness (μm): 2.8±0.2

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
MSP/PCAH(z)-1	5.19E-09	5.81E-09	1.80E-05	4.70E-06	2.30E-05	3.40E-05	3.10E-05	2.90E-05
MSP/PCAH(z)-2	1.31E-11							
MSP/PCAH(z)-3								
MSP/PCAH(z)-4	1.91E-11	4.30E-09	2.70E-10	6.30E-09	1.06E-08	1.65E-08	1.22E-08	6.23E-09
MSP/PCAH(z)-5	5.20E-12	2.23E-09	1.47E-10	3.40E-09	7.10E-09	5.40E-09	4.60E-09	6.60E-09
MSP/PCAH(z)-6	1.06E-11	1.11E-09	1.99E-10	6.60E-09		6.02E-09	1.89E-09	1.88E-09
MSP/PCAH(z)-1 (log)	-8.2848	-8.2358	-4.7447	-5.3279	-4.6383	-4.4685	-4.5086	-4.5376
MSP/PCAH(z)-2 (log)	-10.8827							
MSP/PCAH(z)-3 (log)								
MSP/PCAH(z)-4 (log)	-10.7190	-8.3665	-9.5686	-8.2007	-7.9747	-7.7825	-7.9136	-8.2055
MSP/PCAH(z)-5 (log)	-11.2840	-8.6517	-9.8327	-8.4685	-8.1487	-8.2676	-8.3372	-8.1805
MSP/PCAH(z)-6 (log)	-10.9747	-8.9547	-9.7011	-8.1805		-8.2204	-8.7235	-8.7258
Average (log)	-10.4290	-8.5522	-8.4618	-7.5444	-6.9206	-7.1848	-7.3708	-7.4124
Std. Dev. (log)	1.2162	0.3196	2.4804	1.4835	1.9784	1.8239	1.9365	1.9329
Average+SD	6.1E-10	5.9E-09	1.0E-06	8.7E-07	1.1E-05	4.4E-06	3.7E-06	3.3E-06
Average	3.7E-11	2.8E-09	3.5E-09	2.9E-08	1.2E-07	6.5E-08	4.3E-08	3.9E-08
Average-SD	2.3E-12	1.3E-09	1.1E-11	9.4E-10	1.3E-09	9.8E-10	4.9E-10	4.5E-10
Sur. Conductance	4.6E-17	3.4E-15	4.2E-15	3.5E-14	1.5E-13	8.0E-14	5.2E-14	4.7E-14
Sur. Resistance	2.2E+16	2.9E+14	2.4E+14	2.9E+13	6.8E+12	1.3E+13	1.9E+13	2.1E+13

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TABLE 5: PCT Evaluation of HERCULES - MSP/PCAH
Coated AT&T Triple-Track Testers
Coating Thickness (μm): 12±2

	Leakage Current (amps)							
Sample	Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
MSP/PCAH-1	6.58E-10	2.53E-08	4.20E-10	2.37E-07	5.82E-07	1.74E-07	5.36E-09	1.08E-08
MSP/PCAH-2	1.91E-11	2.20E-07	5.40E-08	3.40E-08	1.81E-08	3.94E-09	6.00E-09	
MSP/PCAH-1 (log)	-9.1818	-7.5969	-9.3768	-6.6253	-6.2351	-6.7595	-8.2708	-7.9666
MSP/PCAH-2 (log)	-10.7190	-6.6576	-7.2676	-7.4685	-7.7423	-8.4045	-8.2218	
Average (log)	-9.9504	-7.1272	-8.3222	-7.0469	-6.9887	-7.5820	-8.2463	-7.9666
Std. Dev. (log)	1.0870	0.6642	1.4914	0.5963	1.0658	1.1632	0.0346	0.0000
Average+SD	1.4E-09	3.4E-07	1.5E-07	3.5E-07	1.2E-06	3.8E-07	6.1E-09	1.1E-08
Average	1.1E-10	7.5E-08	4.8E-09	9.0E-08	1.0E-07	2.6E-08	5.7E-09	1.1E-08
Average-SD	9.2E-12	1.6E-08	1.5E-10	2.3E-08	8.8E-09	1.8E-09	5.2E-09	1.1E-08
Sur. Conductance	1.4E-16	9.1E-14	5.8E-15	1.1E-13	1.3E-13	3.2E-14	6.9E-15	1.3E-14
Sur. Resistance	7.3E+15	1.1E+13	1.7E+14	9.1E+12	8.0E+12	3.1E+13	1.4E+14	7.6E+13

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TABLE 6: PCT Evaluation of HERCULES' - MSP(2.5)/PCAH - Thin Coating

Coated AT&T Triple-Track Testers

Coating Thickness (μm): 5±1

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
MSP(2.5)/PCAH	1.61E-08	2.10E-05	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	1.70E-08	2.60E-05	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	2.46E-08	9.10E-06	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	4.48E-09	1.79E-05	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	5.56E-08	4.80E-06	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	9.70E-10	2.94E-06	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	9.25E-10	5.50E-07	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	6.31E-08	2.07E-05	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	1.07E-08	1.53E-05	Discontinued due to a significant increase in leakage current					
MSP(2.5)/PCAH	3.40E-10	1.69E-05	Discontinued due to a significant increase in leakage current					

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TABLE 7: PCT Evaluation of HERCULES' - MSP(2.5)/PCAH(R) - Thick Coating

Coated AT&T Triple-Track Testers

Coating Thickness (μm): 35±5

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
MSP(2.5)/PCAH	6.90E-11	1.03E-08	1.71E-06	3.60E-07	8.60E-08	3.30E-09	1.07E-08	
Sur. Resistance	1.2E+16	7.9E+13	4.8E+11	2.3E+12	9.5E+12	2.5E+14	7.6E+13	

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TABLE 8: PCT Evaluation of Silicone RTV-6550 (LEHIGH)
Coated AT&T Triple-Track Testers
Coating Thickness (µm): ~ 525

	Leakage Current (amps)							
Sample	Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
RTV-6550(LU)-1	6.40E-12	8.10E-11	8.20E-12	6.60E-12	4.40E-11	6.10E-11	8.20E-11	7.70E-12
RTV-6550(LU)-2	8.40E-12	9.70E-09	3.90E-11	8.20E-12	4.07E-09	2.07E-08	9.50E-08	6.90E-08
RTV-6550(LU)-3	4.50E-12	1.44E-10	5.20E-12	4.10E-12	1.32E-10	3.83E-10	4.30E-10	9.70E-11
RTV-6550(LU)-4	3.70E-12	1.64E-11	3.70E-12	2.90E-12	1.51E-07	5.39E-09	4.20E-11	4.70E-12
RTV-6550(LU)-5	9.40E-12	3.15E-09	2.74E-09	6.90E-09	2.80E-09	2.10E-08	3.80E-08	2.00E-08
RTV-6550(LU)-6	1.46E-11	2.80E-10	1.20E-09	1.87E-09	1.46E-09	1.06E-09	2.50E-10	5.60E-11
RTV-6550(LU)-7	4.10E-12	3.80E-10	4.15E-09	4.80E-09	6.10E-09	2.17E-08	1.72E-08	8.20E-09
RTV-6550(LU)-8	7.40E-12	6.82E-11	5.40E-10	1.29E-09	3.90E-09	6.38E-09	1.21E-08	1.88E-10
RTV-6550(LU)-1 (log)	-11.1938	-10.0915	-11.0862	-11.1805	-10.3565	-10.2147	-10.0862	-11.1135
RTV-6550(LU)-2 (log)	-11.0757	-8.0132	-10.4089	-11.0862	-8.3904	-7.6840	-7.0223	-7.1612
RTV-6550(LU)-3 (log)	-11.3468	-9.8416	-11.2840	-11.3872	-9.8794	-9.4168	-9.3665	-10.0132
RTV-6550(LU)-4 (log)	-11.4318	-10.7852	-11.4318	-11.5376	-6.8210	-8.2684	-10.3768	-11.3279
RTV-6550(LU)-5 (log)	-11.0269	-8.5017	-8.5622	-8.1612	-8.5528	-7.6778	-7.4202	-7.6990
RTV-6550(LU)-6 (log)	-10.8356	-9.5528	-8.9208	-8.7282	-8.8356	-8.9747	-9.6021	-10.2518
RTV-6550(LU)-7 (log)	-11.3872	-9.4202	-8.3820	-8.3188	-8.2147	-7.6635	-7.7645	-8.0862
RTV-6550(LU)-8 (log)	-11.1308	-10.1662	-9.2676	-8.8894	-8.4089	-8.1952	-7.9172	-9.7258
Average (log)	-11.1786	-9.5466	-9.9179	-9.9111	-8.6824	-8.5119	-8.6945	-9.4223
Std. Dev. (log)	0.2034	0.9072	1.2749	1.5051	1.0770	0.9406	1.3056	1.5806
Average+SD	1.1E-11	2.3E-09	2.3E-09	3.9E-09	2.5E-08	2.7E-08	4.1E-08	1.4E-08
Average	6.6E-12	2.8E-10	1.2E-10	1.2E-10	2.1E-09	3.1E-09	2.0E-09	3.8E-10
Average-SD	4.1E-12	3.5E-11	6.4E-12	3.8E-12	1.7E-10	3.5E-10	1.0E-10	9.9E-12
Sur. Conductance	8.1E-18	3.5E-16	1.5E-16	1.5E-16	2.5E-15	3.8E-15	2.5E-15	4.6E-16
Sur. Resistance	1.2E+17	2.9E+15	6.8E+15	6.7E+15	3.9E+14	2.7E+14	4.0E+14	2.2E+15

APPENDIX-1

TABLE 9: PCT Evaluation of Silicone RTV-6550 (HERCULES)
Coated AT&T Triple-Track Testers
Coating Thickness (µm): ~ 375

Sample	Leakage Current (amps) Time in Pressure Cooker (121°C, Saturated Steam) - Hours							
	0	12	50	90	125	160	215	300
RTV-6550(HER)-1	2.90E-12	1.15E-10	4.30E-12	3.20E-11	3.30E-09	6.60E-09	1.11E-08	2.80E-09
RTV-6550(HER)-2	6.40E-12	6.40E-10	1.14E-11	1.75E-10	3.73E-09	2.73E-09	1.21E-08	2.05E-07
RTV-6550(HER)-3	8.90E-08	9.20E-08	4.80E-10	1.02E-08	6.80E-08	1.01E-08	1.42E-08	3.84E-08
RTV-6550(HER)-4	4.10E-12	4.90E-10	5.20E-12	8.60E-11	1.31E-08	1.51E-09	3.63E-09	4.80E-10
RTV-6550(HER)-5	2.64E-10	3.16E-08	2.48E-08	3.02E-08	3.10E-08	9.41E-09	1.06E-08	5.10E-08
RTV-6550(HER)-6	1.33E-10	6.60E-09	4.20E-09	5.90E-09	1.77E-08	1.04E-08	1.73E-08	1.95E-08
RTV-6550(HER)-1(log)	-11.5376	-9.9393	-11.3665	-10.4949	-8.4815	-8.1805	-7.9547	-8.5528
RTV-6550(HER)-2(log)	-11.1938	-9.1938	-10.9431	-9.7570	-8.4283	-8.5638	-7.9172	-6.6882
RTV-6550(HER)-3(log)	-7.0506	-7.0362	-9.3188	-7.9914	-7.1675	-7.9957	-7.8477	-7.4157
RTV-6550(HER)-4(log)	-11.3872	-9.3098	-11.2840	-10.0655	-7.8827	-8.8210	-8.4401	-9.3188
RTV-6550(HER)-5(log)	-9.5784	-7.5003	-7.6055	-7.5200	-7.5086	-8.0264	-7.9747	-7.2924
RTV-6550(HER)-6(log)	-9.8761	-8.1805	-8.3768	-8.2291	-7.7520	-7.9830	-7.7620	-7.7100
Average (log)	-10.1040	-8.8698	-10.7281	-9.5772	-7.9900	-8.3902	-8.0399	-7.9939
Std. Dev. (log)	1.7053	1.2655	0.9573	1.0996	0.6115	0.3721	0.2704	1.1700
Average+SD	4.0E-09	2.5E-08	1.7E-10	3.3E-09	4.2E-08	9.6E-09	1.7E-08	1.5E-07
Average	7.9E-11	1.3E-09	1.9E-11	2.6E-10	1.0E-08	4.1E-09	9.1E-09	1.0E-08
Average-SD	1.6E-12	7.3E-11	2.1E-12	2.1E-11	2.5E-09	1.7E-09	4.9E-09	6.9E-10
Sur. Conductance	9.6E-17	1.6E-15	2.3E-17	3.2E-16	1.3E-14	5.0E-15	1.1E-14	1.2E-14
Sur. Resistance	1.0E+16	6.1E+14	4.4E+16	3.1E+15	8.0E+13	2.0E+14	9.0E+13	8.1E+13

APPENDIX - 2

Designation: D 3359 – 87

Standard Test Methods for Measuring Adhesion by Tape Test[1]

This standard is issued under the fixed designation D 3359; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

These methods have been approved for use by agencies of the Department of Defense and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 These test methods cover procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film.

1.2 Method A is primarily intended for use at job sites while Method B is more suitable for use in the laboratory. Also, Method B is not considered suitable for films thicker than 5 mils (125 μm).

NOTE 1—Subject to agreement between the purchaser and the seller, Method B can be used for thicker films if wider spaced cuts are employed.

1.3 These test methods are used to establish whether the adhesion of a coating to a substrate is at a generally adequate level. They do not distinguish between higher levels of adhesion for which more sophisticated methods of measurement are required.

NOTE 2—It should be recognized that differences in adherability of the coating surface can affect the results obtained with coatings having the same inherent adhesion.

1.4 In multicoat systems adhesion failure may occur between coats so that the adhesion of the coating system to the substrate is not determined.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 609 Methods for Preparation of Steel Panels for Testing Paint, Varnish, Lacquer, and Related Products[2]
D 823 Methods of Producing Films of Uniform Thickness of Paint, Varnish, and Related Products on Test Panels[2]
D 1730 Practices for Preparation of Aluminum and Aluminum-Alloy Surfaces for Painting[2]
D 2092 Practices for Preparation of Zinc-Coated Galvanized Steel Surfaces for Paint[2]
D 3330 Test Method for Peel Adhesion of Pressure-Sensitive Tape of 180° Angle[3]

3. Summary of Test Methods

3.1 *Test Method A*—An X-cut is made in the film to the substrate, pressure-sensitive tape is applied over the cut and then removed, and adhesion is assessed qualitatively on the 0 to 5 scale.

3.2 *Test Method B*—A lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure-sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

TEST METHOD A—X-CUT TAPE TEST

4. Apparatus and Materials

4.1 *Cutting Tool*—Sharp razor blade, scalpel, knife or other cutting devices. It is of particular importance that the cutting edges be in good condition.

4.2 *Cutting Guide*—Steel or other hard metal straightedge to ensure straight cuts.

4.3 *Tape*-One-inch (25-mm) wide semitransparent pressure-sensitive tape with an adhesion strength of 38 ± 5 oz/in. (43 ± 5.6 g/mm or N/100 mm) width when tested in accordance with Test Method D 3330. The adhesion shall not change by more than ± 6.5 % of its mean value within 12 months. The backing of the tape may consist of fiber-reinforced cellulose acetate,[4] unplasticized poly(vinyl chloride), or polyester film. Tape with different properties may be used subject to agreement between the purchaser and the seller. When results obtained in different laboratories do not agree, it is recommended that the test be repeated using tape from the same batch.

4.4 *Rubber Eraser*, on the end of a pencil.

4.5 *Illumination*—A light source is helpful in determining whether the cuts have been made through the film to the substrate.

5. Test Specimens

5.1 When this test method is used in the field, the specimen is the coated structure or article on which the

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and are the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

Current edition approved May 29, 1987. Published September 1987. Originally published as D 3359 – 74. Last previous edition D 3359 – 83.

[2] *Annual Book of ASTM Standards*, Vol 06.01.

[3] *Annual Book of ASTM Standards*, Vol 15.09.

[4] Permacel 99 manufactured by Permacel, New Brunswick, NJ 08903, and available from various Permacel tape distributors is reported to be suitable for this purpose. The manufacturer of the tape used in the interlaboratory study[5] has advised that as of September 1981 the properties of this tape are being changed. Users of its should, therefore, check whether current material gives comparable results to previous supplies.

adhesion is to be evaluated.

5.2 For laboratory use apply the materials to be tested to panels of the composition and surface conditions on which it is desired to determine the adhesion.

NOTE 3—Applicable test panel description and surface preparation methods are given in Methods D 609 and Practices D 1730 and D 2092.

NOTE 4—Coatings should be applied in accordance with Methods D 823, or as agreed upon between the purchaser and the seller.

NOTE 5—If desired or specified, the coated test panels may be subjected to a preliminary exposure such as water immersion, salt spray, or high humidity before conducting the tape test. The conditions and time of exposure will be governed by ultimate coating use or shall be agreed upon between the purchaser and seller.

6. Procedure

6.1 Select an area free of blemishes and minor surface imperfections. For tests in the field, ensure that the surface is clean and dry. Extremes in temperature or relative humidity may affect the adhesion of the tape or the coating.

6.2 Make two cuts in the film each about 1.5 in. (40 mm) long that intersect near their middle with a smaller angle of between 30 and 45°. When making the incisions, use the straightedge and cut through the coating to the substrate in one steady motion.

6.3 Inspect the incisions for reflection of light from the metal substrate to establish that the coating film has been penetrated. If the substrate has not been reached make another X in a different location. Do not attempt to deepen a previous cut as this may affect adhesion along the incision.

6.4 Remove two complete laps of the pressure-sensitive tape from the roll and discard. Remove an additional length at a steady (that is, not jerked) rate and cut a piece about 3 in. (75 mm) long.

6.5 Place the center of the tape at the intersection of the cuts with the tape running in the same direction as the smaller angles. Smooth the tape into place by finger in the area of the incisions and then rub firmly with the eraser on the end of a pencil. The color under the transparent tape is a useful indication of when good contact has been made.

6.6 Within 90 ± 30 s of application, remove the tape by seizing the free end and pulling it off rapidly (not jerked) back upon itself at as close to an angle of 180° as possible.

6.7 Inspect the X-cut area for removal of coating from the substrate or previous coating and rate the adhesion in accordance with the following scale:

5A	No peeling or removal
4A	Trace peeling or removal along incisions
3A	Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side
2A	Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side
1A	Removal from most of the area of the X under the tape
0A	Removal beyond the area of the X

6.8 Repeat the test in two other locations on each test panel. For large structures make sufficient tests to ensure that the adhesion evaluation is representative of the whole surface.

6.9 After making several cuts examine the cutting edge and, if necessary, remove any flat spots or wire-edge by abrading lightly on a fine oil stone before using again. Discard cutting tools that develop nicks or other defects that tear the film.

7. Report

7.1 Report the number of tests, their mean and range, and for coating systems, where the failure occurred that is, between first coat and substrate, between first and second coat, etc.

7.2 For field tests report the structure or article tested, the location and the environmental conditions at the time of testing.

7.3 For test panels report the substrate employed, the type of coating, the method of cure, and the environmental conditions at the time of testing.

8. Precision Test[5]

8.1 In an interlaboratory study of this test method in which operators in six laboratories made one adhesion measurement on three panels each of three coatings covering a wide range of adhesion, the within-laboratories standard deviation was found to be 0.33 and the between-laboratories 0.44. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

8.1.1 *Repeatability*—Provided adhesion is uniform over a large surface, results obtained by the same operator should be considered suspect if they differ by more than 1 rating unit for two measurements.

8.1.2 *Reproducibility*—Two results, each the mean of triplicates, obtained by different operators should be considered suspect if they differ by more than 1.5 rating units.

TEST METHOD B—CROSS-CUT TAPE TEST

9. Apparatus and Materials

9.1 *Cutting Tool*—Sharp razor blade, scalpel, knife or other cutting device having a cutting edge angle between 15 and 30° that will make either a single cut or several cuts at once. It is of particular importance that the cutting edge be in good condition.

9.2 *Cutting Guide*—If cuts are made manually (as opposed to a mechanical apparatus) a steel or other hard metal straightedge or template to ensure straight cuts.

9.3 *Rule*—Tempered steel rule graduated in 0.5 mm for measuring individual cuts.

9.4 *Tape*, as described in 4.3.

9.5 *Rubber Eraser*, on the end of a pencil.

9.6 *Illumination*, as described in 4.5.

9.7 *Magnifying Glass*—An illuminated magnifier to b used while making individual cuts and examining the tes area.

10. Test Specimens

10.1 Test specimens shall be as described in Section 5.

11. Procedure

11.1 Where required or when agreed upon, subject th specimens to a preliminary test before conducting the tap test (see Note 3). After drying or testing, select an area free o blemishes and minor surface imperfections.

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[5] Supporting data are available from ASTM Headquarters. Request RR D01-1008.

11.2 Place the panel on a firm base and under the illuminated magnifier make parallel cuts as follows:

11.2.1 For coatings having a dry film thickness up to and including 2.0 mils (50 μm) space the cuts 1 mm apart and make eleven cuts unless otherwise agreed upon.

11.2.2 For coatings having a dry film thickness between 2.0 mils (50 μm) and 5 mils (125 μm), space the cuts 2 mm apart and make six cuts. For films thicker than 5 mils use Method A.

11.2.3 Make all cuts about ¾ in. (20 mm) long. Cut through the film to the substrate in one steady motion using just sufficient pressure on the cutting tool to have the cutting edge reach the substrate. When making successive single cuts with the aid of a guide, place the guide on the uncut area.

11.3 After making the required cuts brush the film lightly with a soft brush or tissue to remove any detached flakes or ribbons of coatings.

11.4 Examine the cutting edge and, if necessary, remove any flat spots or wire-edge by abrading lightly on a fine oil stone. Make the additional number of cuts at 90° to and centered on the original cuts.

Classification of Adhesion Test Results

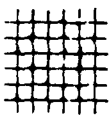
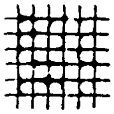
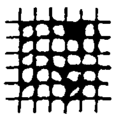
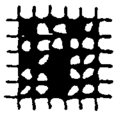
Classification	Surface of cross-cut area from which flaking has occurred. (Example for six parallel cuts)
5B	None
4B	
3B	
2B	
1B	
0B	Greater than 65%

FIG. 1 Classification of Adhesion Test Results

11.5 Brush the area as before and inspect the incisions for reflection of light from the substrate. If the metal has not been reached make another grid in a different location.

11.6 Remove two complete laps of tape and discard. Remove an additional length at a steady (that is, not jerked) rate and cut a piece about 3 in. (75 mm) long.

11.7 Place the center of the tape over the grid and in the area of the grid smooth into place by a finger. To ensure good contact with the film rub the tape firmly with the eraser on the end of a pencil. The color under the tape is a useful indiction of when good contact has been made.

11.8 Within 90 ± 30 s of application, remove the tape by seizing the free end and rapidly (not jerked) pulling it off at as close to an angle of 180° as possible.

11.9 Inspect the grid area for removal of coating from the substrate or from a previous coating using the illuminated magnifier. Rate the adhesion in accordance with the following scale illustrated in Fig. 1:

5B	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
4B	Small flakes of the coating are detached at intersections; less than 5 % of the area is affected.
3B	Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.
2B	The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.
1B	The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65 % of the lattice.
0B	Flaking and detachment worse than Grade 1.

11.10 Repeat the test in two other locations on each test panel.

12. Report

12.1 Report the number of tests, their mean and range, and for coating systems, where the failure occurred, that is, between first coat and substrate, between first and second coat, etc.

12.2 Report the substrate employed, the type of coating and the method of cure.

13. Precision[5]

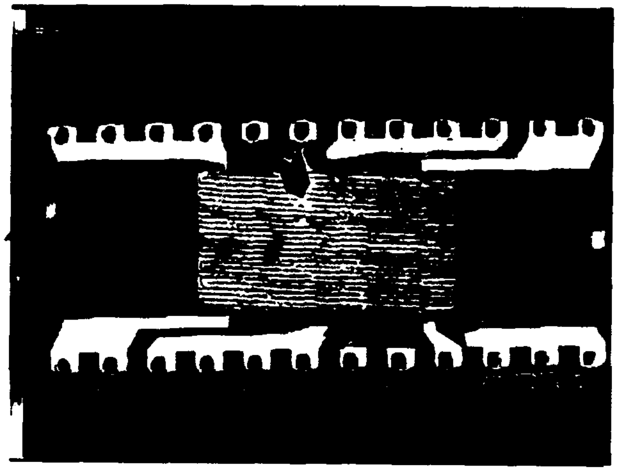
13.1 On the basis of two interlaboratory tests of this test method in one of which operators in six laboratories made one adhesion measurement on three panels each of three coatings covering a wide range of adhesion and in the other operators in six laboratories made three measurements on two panels each of four different coatings applied over two other coatings, the pooled standard deviations for within- and between-laboratories were found to be 0.37 and 0.7. Based on these standard deviations, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

13.1. *Repeatability*—Provided adhesion is uniform over a large surface, results obtained by the same operator should be considered suspect if they differ by more than one rating unit for two measurements.

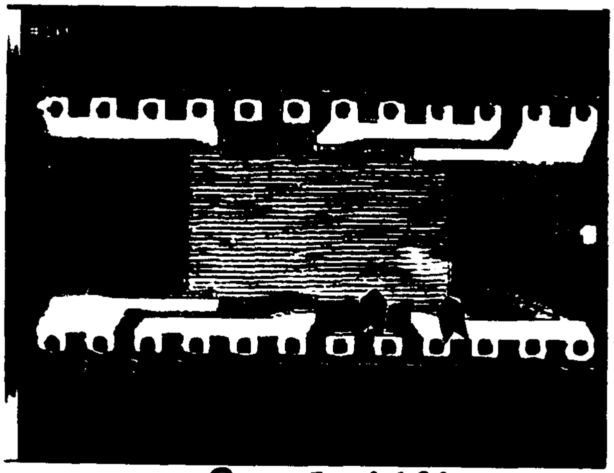
13.1.2 *Reproducibility*—Two results, each the mean of duplicates or triplicates, obtained by different operators should be considered suspect if they differ by more than two rating units.

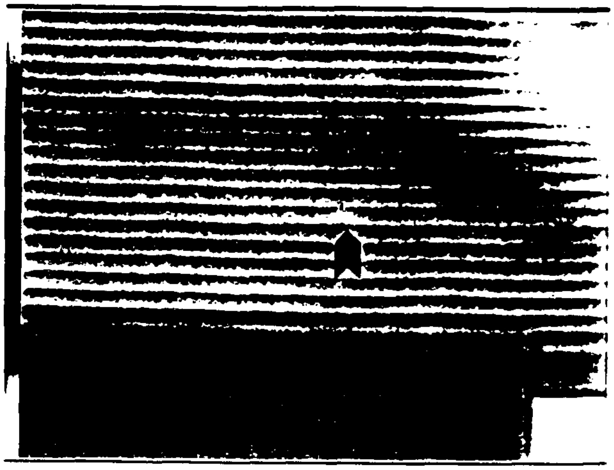
The following images show the triple track samples. The images were made at 100 MHz, focusing through the back of the ceramic substrate to the metalization/resin interface. Detail of the metalization can be seen as well as the lead bond sites at the edges of the substrates. Some small flaws are seen which are indicated by arrows. Increased magnification views of some of the flaw areas are included for each sample. No large cracks were observed in the samples. Some diagonal line type features are present in the samples which result from tilt of the sample surface.

Sycar
175
4mm



MSP2.5
PCAH
Table 1
5mm

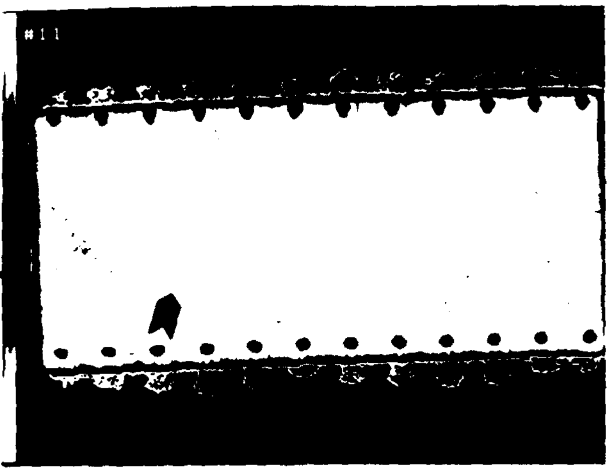


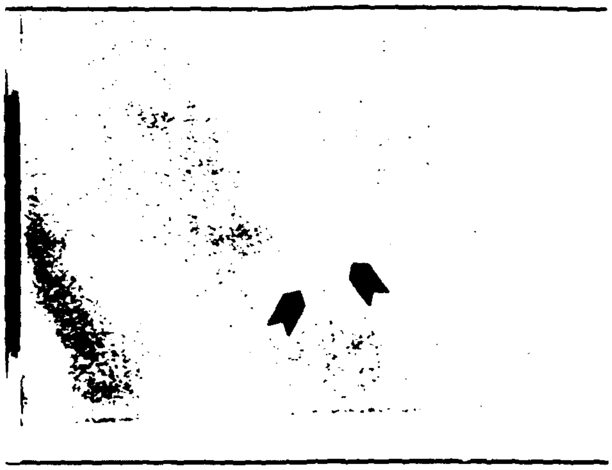


BLUE ARROW
INDICATES EXCESS MATERIAL ON SURFACE

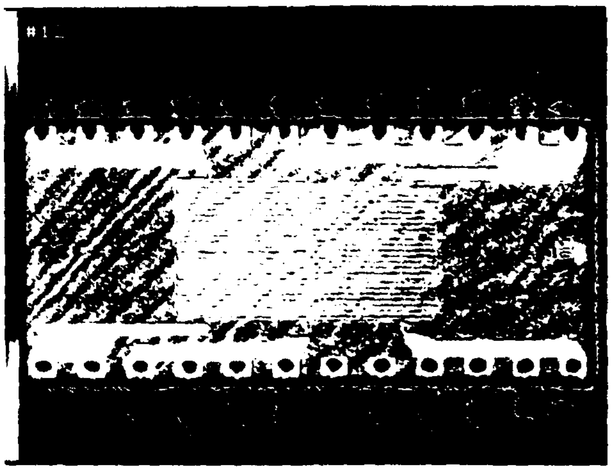
See Tables

MS8/
DCPD
3 μm





MSP/
PCAH
2.8
μm



No flaws
on the circuit!

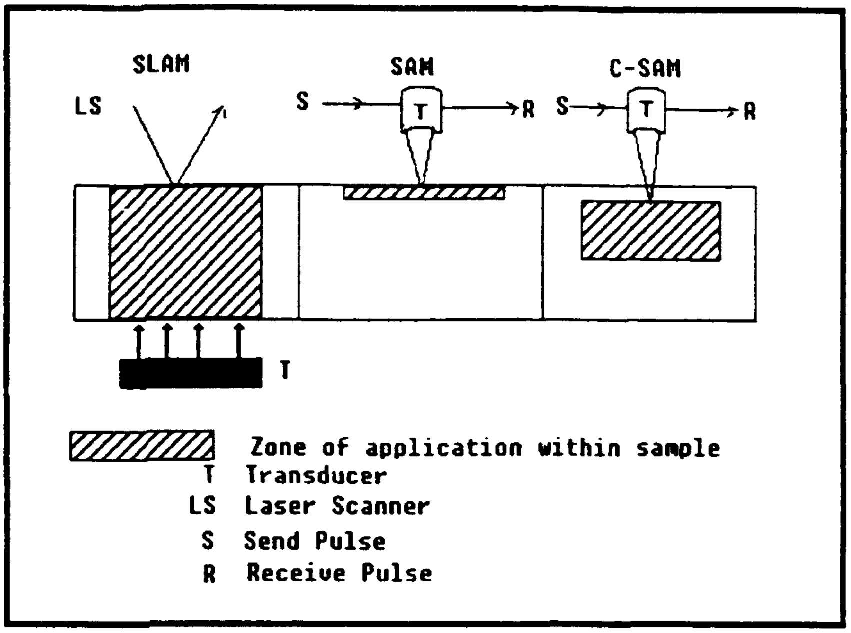
Three Types of Acoustic Microscopes

There are three intrinsically different types of acoustic microscopes. The first one is a transmission mode instrument that generates images of a sample throughout its entire thickness. The "SLAM", or Scanning Laser Acoustic Microscope operates using a continuous plane wave of ultrasound introduced on one side of the sample. The amount of transmitted ultrasound is detected on the opposite side by a rapidly scanning, finely focused laser beam. The amount of transmitted ultrasound is directly related to the amount of bond quality or material homogeneity present in the sample.

The other two types of acoustic microscopes are reflection mode tools that use a pulse-echo transducer focused at or below the sample surface. The focused transducer (ultrasound spot) is mechanically moved across the sample in raster fashion to create the image. A typical image may consist of tens of thousands of individual data points.

These two systems are known as "SAM" (Scanning Acoustic Microscope) and "C-SAM" (C-Mode Scanning Acoustic Microscope) and are designed for very high resolution imaging of the surface and subsurface regions of a sample.

The respective penetration zones or "application" areas within a sample are indicated in the figure above. Both SLAM and C-SAM are described in greater detail later in this report.



Sounding Out Material Defects

In an ordinary light microscope an image of a specimen is produced because of interaction between light waves and the specimen's surface. Analogously, images can be made with non-light sources such as ultrasound. The difference however, is that ultrasound will transmit through a specimen which is naturally optically opaque.

Ultrasound in the range of 10-500 MHz is typically employed to characterize internal discontinuities such as voids, delaminations, inclusions, porosity and cracks. Therefore, imaging based upon acoustic wave analysis reveals defects deep within and at the surface of most dense materials. Perhaps the most important characteristic is that these techniques are entirely nondestructive!

Why Ultrasound ?

When an opaque material is viewed the two primary choices for flaw detection and material characterization are X-ray and ultrasound. X-ray's are affected by the amount of molecular mass the ray's must pass through. X-ray's are also unchanged by internal discontinuities unless these discontinuities constitute significant variation in the sample's structure, usually greater then 20%.

Ultrasound, unlike X-ray, will not transmit across an air gap. Even a submicron gap is enough to stop its transmission. This unique property makes the acoustic microscope the first choice for detecting internal flaws that are "air space" related. Because X-Ray and Acoustic Micro Imaging provide uniquely distinct information they tend to be complementary analytical techniques rather then competitive.

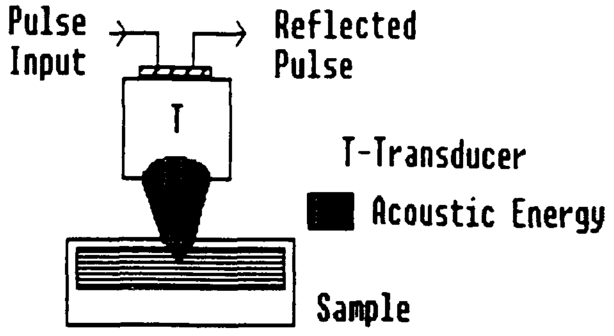
Sonoscan, Inc.

C-SAM
Principles

The C-Mode Scanning Acoustic Microscope is a pulse-echo (reflection type) microscope that generates images by mechanically scanning a transducer in a raster pattern over the sample. A focused spot of ultrasound is generated by an acoustic lens assembly at frequencies typically ranging from 10-100 MHz. The ultrasound is brought to the sample by a coupling medium, usually deionized water or an inert fluid. The transducer alternately acts as sender and receiver, being electronically switched between the transmit and receive modes.

A very short acoustic pulse enters the sample and return echoes are produced at specific interfaces within the part. The return times are a function of the distance from the interface to the transducer. An oscilloscope display of the echo pattern, known as the A-Scan, clearly shows these levels and their time/distance relationships. This provides a basis for investigating anomalies at specific levels within a part.

An electronic gate is positioned in time and controlled to open for a defined duration allowing only the information from a specific level to be imaged while excluding all other echoes. The "gated" echo modulates a CRT which is synchronized with the transducer's position. In this way images are produced in raster fashion on the CRT. Complete images are produced in about 10 seconds.

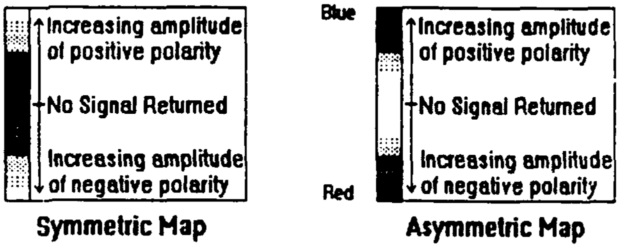


C-Mode Scanning Acoustic Microscope (C-SAM)

C-SAM Color Map Interpretation

In C-SAM images the contrast changes compared to the background constitute the important information. Voids, cracks, disbonds and delaminations provide high contrast and are easily distinguished from the background. Combined with the ability to "gate" and "focus" at specific levels, C-SAM is a powerful tool for analyzing the nature of any defect within a sample.

C-SAM Color Maps



The diagram above is for reference in interpreting the color maps of the C-SAM images. In general, the central portion of the color bar for all maps indicates little of no signal return (good material continuity). The top and bottom ends of the color bar indicate larger amplitudes of the returned signal pulses. Some of the maps, Asymmetric types, contain information about the polarity of the pulse. A negative echo is indicated by the colors at the lower end of the color bar and are typically associated with a disbond. A positive echo is indicated by the colors at the upper end of the color bar and associated with well bonded regions. In this "Asymmetric Map" example blue indicates a positive echo (bond) and red indicates a negative echo (disbond). In all cases, the original images are obtained as 256 grey levels and then pseudo colored to highlight specific details.

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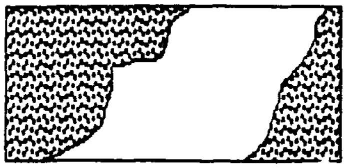
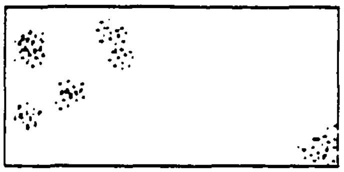
C-DIA
Quantification
and
MIL-STD-883C,
Method 2030
Die Attach
Evaluation

Mil Standard 883C, Method 2030, Ultrasonic Inspection of Die Attach

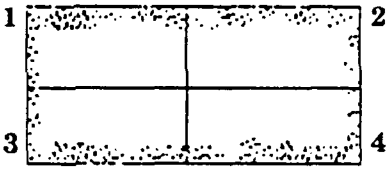


Reject... void greater than 15% intended contact area, or corner void greater than 10%



Accept... no single void greater than 15% of intended contact area, corner void less than 10%

Reject... quadrant 70% disbonded



Accept... all quadrants less than 70% disbonded

Quantitative analysis is performed on the SLAM and C-SAM acoustic microscope series using the C-DIA (Computer Digital Image Analysis) feature. During any quantitative analysis a window is placed around the region to be analyzed and the 256 level color scale is reduced to contain binary information (two levels). This results in a percentage of the pixel values being placed in the "bonded" region and some in the "disbonded" region.

The image print that coincides with the quantized result displays the thresholded (two level) information in the upper left corner. The grey level histogram or the actual grey level image (analyst's choice) is displayed to its right.

If the histogram is displayed the graph shows the pixel frequency distribution for 128 intensity levels within the windowed area. The histogram statistics, including the percent bond (range # - #) and the percent disbond (range # - #), are displayed in the lower section.

Any interface can be quantized. The one most typically done is the die attach for ceramic or multi chip module integrated circuit. During this analysis customized algorithms, developed exclusively by Sonoscan, automatically calculate the percentage bond/disbond within a specified area (white box).

If the MIL-STD-883C, Method 2030 specification is applied, four separate calculations are performed. The predetermined Accept/Reject criteria has been outlined above for your reference.

What results after processing is a calculated value that is classified according to the established criteria. If the attach meets the criteria it is considered "Accepted" and labeled as so, if "Rejected" it will be labeled accordingly. The cause(s) for rejection are noted by an asterick on the quantized C-DIA image.

Various statistical calculations are continually being added to support the measurement of void size and frequency distribution. One or several of these calculations may appear in the image(s) contained in your report.