Corrosion Ability and the Chemistry of Mercuric Chloride and Related Compounds

1986

Martin R. Kruger
University of Central Florida

Find similar works at: https://stars.library.ucf.edu/rtd

University of Central Florida Libraries http://library.ucf.edu

Part of the Operations Research, Systems Engineering and Industrial Engineering Commons

STARS Citation

Kruger, Martin R., "Corrosion Ability and the Chemistry of Mercuric Chloride and Related Compounds" (1986). Retrospective Theses and Dissertations. 4939.
https://stars.library.ucf.edu/rtd/4939

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
CORROSION ABILITY AND THE CHEMISTRY OF MERCURIC CHLORIDE AND RELATED COMPOUNDS

By

MARTIN ROBERT KRUGER
B.S., University of Buffalo, 1983

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the Master of Science degree in Industrial Chemistry in the Graduate Studies Program of the College of Arts and Sciences University of Central Florida Orlando, Florida

Summer Term 1986
ACKNOWLEDGEMENTS

I would like to thank the faculty and staff of the University of Central Florida Department of Chemistry for their support throughout my graduate years. I am most deeply indebted to Dr. Graeme Baker for his guidance, patience, friendship and encouragement. I would also like to thank all my co-workers at the Nuclear Power School for their ability to maintain my spirit.
ABSTRACT

This research project found that a solution of methanol and methylene chloride saturated with mercuric chloride was very effective at diffusing through a paint film and destroying an aluminum barrier below. The project also found evidence that mercuric chloride chemically reacts with dimethylformamide and dimethysulfoxide. The project concluded that corrosion of metals in an organic solvent media is best studied by thermal analysis.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS ........................................ iii

LIST OF TABLES .................................................. vi

LIST OF FIGURES ................................................ vii

STATEMENT OF PURPOSE ................................. 1

PART I - INTRODUCTION ..................................... 2
  EXPERIMENTAL .............................................. 4
  DISCUSSION .................................................. 22
  CONCLUSIONS ............................................... 53
  RECOMMENDATIONS ........................................ 54

PART II - INTRODUCTION .................................. 55
  EXPERIMENTAL .............................................. 56
  DISCUSSION .................................................. 61
  CONCLUSIONS ............................................... 76
  RECOMMENDATIONS ........................................ 78

PART III - INTRODUCTION ................................ 79
  RESULTS ..................................................... 80
  DISCUSSION .................................................. 88
  CONCLUSIONS ............................................... 91
  RECOMMENDATIONS ........................................ 92
LIST OF TABLES

I. Penetrations times for single solvents ............... 14
II. Composition of MS1 series ........................... 16
III. Summary results for MS1 formulations ............... 17
IV. Composition of MS2 series ........................... 18
V. Summary results for MS2 formulations ............... 19
VI. Composition of MS3 series ........................... 20
VII. Summary results for MS3 series ................... 21
VIII. Ranking of MS1 series constituents ................. 49
IX. Ranking of MS2 series constituents ................. 49
X. Ranking of MS3 series constituents ................. 51
XI. Effect of stress on penetration times .............. 95
LIST OF FIGURES

1. Concentration of mercuric chloride in pure solvents .......... 6
2. ATR solvent penetration test cell ............................. 6
3. Acetonitrile penetration ........................................ 8
4. Relative penetration rate through polyurethane paint film ... 9
5. Relative swell of polyurethane .................................. 10
6. Transport evaluation apparatus (TEA1) .......................... 11
7. Transport evaluation apparatus (TEA2) ......................... 11
8. Correlation of solvent penetration rate with polymer swell . 23
9. Relationship between concentration and bare barrier times . 26
10. Relationship between boiling point and bare barrier times . 27
11. Relationship between surface tension and bare barrier times 28
12. Relationship between density and bare barrier times ........ 29
13. Relationship between Hildebrand solubility parameter and bare barrier times .......................... 30
14. Relationship between concentration and barrier times ....... 31
15. Relationship between boiling point and barrier times ........ 32
16. Relationship between density and barrier times ............... 33
17. Relationship between Hildebrand solubility parameter and barrier times .......................... 34
18. Relationship between surface tension and barrier times ... 35
19. Relationship between the effect of water on barrier times and concentration .......................... 36
20. Relationship between the effect of water on barrier times and surface tension .......................... 37
21. Relationship between the effect of water on barrier times and boiling point .................. 38
22. Relationship between the effect of water on barrier times and density ...................... 39
23. Relationship between the effect of water on barrier times and Hildebrand solubility parameter ............ 40
24. Relationship between bare barrier time/concentration and density ............................ 42
25. Relationship between bare barrier/time concentration and boiling point of solvent .......................... 43
26. Relationship between bare barrier/time concentration and Hildebrand solubility parameter .............. 44
27. Relationship between bare barrier time/concentration and molecular weight of solvent ............ 45
28. Relationship between bare barrier time/concentration and surface tension of solvent .................. 46
29. Proportion variation in MS3 formulations ...................................... 52
30. Infrared spectrum of MS1-5 solution ........................................................................ 57
31. Infrared spectrum of MS1-5 with mercuric chloride ................................................. 57
32. Infrared spectrum of MS1-12 solution ........................................................................ 58
33. Infrared spectrum of MS1-12 with mercuric chloride ................................................. 58
34. Infrared spectrum of MS1-13 ................................................................................... 59
35. Infrared spectrum of MS1-13 with mercuric chloride ................................................. 59
36. Infrared spectrum of MS1-16 solution ........................................................................ 60
37. Infrared spectrum of MS1-16 with mercuric chloride ................................................. 60
38. Acetonitrile ........................................................................................................ 62
39. Infrared spectrum of acetonitrile/mercuric chloride solid residue with nujol ..................... 62
40. Dimethylsulfoxide ................................................................................................ 63
41. Infrared spectrum of dimethylsulfoxide/mercuric chloride solid with nujol ..................... 63

viii
42. Dimethylformamide

43. Infrared spectrum of dimethylformamide/mercuric chloride solid residue with nujol

44. Infrared spectrum of dimethylsulfoxide/mercuric chloride with no water added

45. Infrared spectrum of dimethylsulfoxide/mercuric chloride with water

46. Infrared spectrum of dimethylformamide/mercuric chloride solid residue

47. Infrared spectrum of dimethylformamide/mercuric chloride solid residue with and without water

48. Infrared spectrum of dimethylformamide/mercuric chloride solid residue (not dried)

49. Dimethylformamide summary

50. Infrared spectrum of MS1-5 solid residue

51. Infrared spectrum of MS1-12 solid residue

52. Infrared spectrum of MS1-13 solid residue

53. Infrared spectrum of MS1-15 solid residue

54. Infrared spectrum of MS1-16 solid residue

55. Circuit diagram

56. Galvanic cell

57. Double cylinder arrangement

58. Apparatus for measuring the temperature of corroding aluminum as a function of time

59. Results from thermal study

60. Tests on stressed aluminum

61. Infrared spectrum of mercuric acetate and nujol

62. Infrared spectrum of residue from mercuric acetate and dimethylformamide

63. Infrared spectrum of residue from mercuric acetate and dimethylsulfoxide
<table>
<thead>
<tr>
<th>Page</th>
<th>Infrared Spectrum Details</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.</td>
<td>Infrared spectrum of mercuric bromide and nujol</td>
<td>98.</td>
</tr>
<tr>
<td>65.</td>
<td>Infrared spectrum of residue from mercuric bromide and dimethylformamide</td>
<td>99.</td>
</tr>
<tr>
<td>66.</td>
<td>Infrared spectrum of residue from mercuric bromide and dimethylsulfoxide</td>
<td>99.</td>
</tr>
<tr>
<td>67.</td>
<td>Infrared spectrum of mercuric nitrate and nujol</td>
<td>100.</td>
</tr>
<tr>
<td>68.</td>
<td>Infrared spectrum of residue from mercuric nitrate and dimethylformamide</td>
<td>100.</td>
</tr>
<tr>
<td>69.</td>
<td>Infrared spectrum of residue from mercuric nitrate and dimethylsulfoxide</td>
<td>101.</td>
</tr>
<tr>
<td>70.</td>
<td>Comparison between residue from a mercuric chloride and dimethylformamide solution</td>
<td>105.</td>
</tr>
<tr>
<td>71.</td>
<td>Effect of adding water to dimethylformamide solutions saturated with either mercuric chloride or mercuric bromide</td>
<td>105.</td>
</tr>
<tr>
<td>72.</td>
<td>Comparison between residue from mercuric chloride/dimethylsulfoxide with residue from mercuric bromide/dimethylsulfoxide</td>
<td>106.</td>
</tr>
</tbody>
</table>
STATEMENT OF PURPOSE

The purpose of this project was to identify a solvent system capable of transporting an appreciable quantity of mercuric chloride through a paint film so that the mercuric chloride could corrode the underlying metal. To this end the study evolved into four major objectives.

The first major objective, to study the efficiency of the overall transport and corrosion process, formed the basis for the work done in Part I of the project. The nature of the oxide layer of aluminum was studied, the concentration of mercuric chloride in solvents was measured, and apparatus to measure the solvent transport rates was designed and tested.

Part II studied precipitates which were observed to form in some solvent systems saturated with mercuric chloride. These solutions had been prepared to test the fitness of various solvent systems in meeting the objectives named above.

Part III attempted to quantitatively measure the corrosion process via electrochemical techniques.

Part IV compares the corrosive action of mercuric chloride with a few selected mercury-containing compounds. The objective was to gain some predictive ability concerning the corrosivity of yet unstudied, mercury-containing compounds.
PART I
INTRODUCTION

The first part of this research project had several objectives. First, the nature of the oxide layer on aluminum was examined. Second, a reliable procedure for measuring the concentration of mercuric chloride in different solvents was needed. Third, the ability of different solvent/mercuric chloride systems to penetrate an organic paint film was examined. Lastly, a comparison of the effectiveness of different solvent mercuric chloride systems to penetrate a paint film and damage aluminum metal underneath was to be made.

The exact nature of the oxide layer on aluminum, though it has received considerable study, remains obscure. A summary of key findings will be presented here. Aluminum is generally covered with a corrosion-resistant oxide layer. The oxide layer is usually formed by either air oxidation or anodic oxidation of aluminum. Electron diffraction studies have shown that the natural oxide film which occurs on aluminum surfaces in the presence of air is not crystalline. On average it is about 100Å in thickness. It is of interest to note that researchers studying the nature of the aluminum oxide film have used dilute solutions of mercuric chloride in alcohol solutions to strip the oxide film from the aluminum layer.¹

The anodic oxide layer is believed to have crystalline sections which are thought to be more porous than amorphous sections of the oxide film. There are various techniques available for sealing porous oxide
These techniques were not utilized in this project because the aluminum foil used was assumed to have a non-porous, amorphous air-aged oxide film.

It was important to know what the concentration of mercuric chloride was in different solvents, because it was presumed that the total damage to aluminum would be proportional to the amount of mercuric chloride available to the surface of the aluminum.

The time it takes for various solvent systems to diffuse through a paint film was important to know, since the major objective of this part of the project was to design a solvent system saturated in mercuric chloride that was the fastest at penetrating though a painted aluminum barrier. The time of penetration through a painted aluminum barrier consists of the time required for the delivery of mercuric chloride to the aluminum surface plus the time required for mercuric chloride to corrode through an aluminum barrier. It was hoped that the time required for the diffusion of a solvent through a paint film would be proportional to the time required for the transport of mercuric chloride from the surface of a painted metal to the metal-paint interface.

In direct fulfillment of the overall project objective, various solvent systems saturated with mercuric chloride were tested for their ability to penetrate through a protective polymer film and an underlying aluminum film.
Determination of Solubility of Mercuric Chloride in Various Solvents.

The earliest approach taken to determine the solubility of mercuric chloride in solvents was by simple evaporation of solvent from known volumes of saturated solutions. The residual mass was presumed to be mercuric chloride, and the results are reported as grams of mercuric chloride per 100 milliliters of solution. The procedure proved inadequate due to the tendency of some of the solvents (e.g., dimethylsulfoxide and methanol) to absorb water from the air resulting in errors in residual masses. Attempts to remove the water by heating were hindered by the volatility of the mercuric chloride which led to low values and inconsistent data.

The second procedure examined was a colorimetric assay. A small amount of each of the solvent/mercuric chloride systems was added to a .01% solution of diphenylthiocarbazole in CC14. Mercuric chloride forms a colored complex of indeterminate structure but presumably proportional to the concentration of mercuric chloride in the solvent. This procedure proved inadequate due to variation in data, presumably the result of a solvent effect (e.g., a methanol/mercuric chloride system did not behave identically with a dimethylformamide/mercuric chloride system).

Flame emission was ultimately examined and deemed adequate for the determination of the amount of mercuric chloride in the various saturated solutions. The concentration of mercuric chloride in various
saturated solvent systems tested\(^3\) is shown in Fig. 1. Ambient conditions were used in all of these studies (e.g., 25\(^\circ\)C).

Rate of Diffusion of Pure Solvent Through a Reference Polyurethane Film.

Since it was believed that the rate of transport of mercuric chloride to the aluminum surface was proportional to the rate of diffusion of the solvent system through the paint film, an infrared technique was developed for determining the rate of diffusion of pure solvent through a paint film. A standard paint film was applied to a KRS-5 crystal suited to attenuated total reflectance measurement in the 2-15 micron region. The method for applying the standard thickness paint film was developed by Engineering Technology, Inc. The paint used was the top coat of MIL-C-46168B, the army chemical agent resistant polyurethane. A schematic of the test cell\(^4\) is shown in Fig. 2.

Internal reflections which take place in the crystal cause characteristic wave lengths to be absorbed which are a function of the materials in intimate contact with the crystal surface. If this surface contact is disrupted the attendant absorbance is lost. Therefore an absorbance that is characteristic of the paint can be monitored as a function of time, with disruption signaled by a change in absorbance. Disruption, however, could result from either true diffusion of the solvent to the crystal surface and subsequent release of the paint/crystal bond, or by simple stressing of the polymer film to the extent that the adhesion of the film to crystal is disturbed. It was therefore necessary to check as quickly as possible for the present of solvent at the crystal surface after disruption was sensed. This was done by running a pre- and post-infrared spectrum and subtracting the pre-spectrum from the post-spectrum. If the resulting spectrum
Figure 1. Concentration of mercuric chloride in pure solvents.

Figure 2. ATR solvent penetration test cell.
contained solvent peaks, then penetration of the solvent had occurred. An example of the infrared spectrum generated in this time drive study is shown in Fig. 3. The results of this study are shown graphically in Fig. 4.

A study was also performed on the ability of various solvents to cause polyurethane paint to swell. The work in this study was performed by Engineering Technology, Inc., but is included here for completeness. It was felt that a recognizable correlation would exist between the swell phenomenon and rate of penetration. Results did not provide unequivocal verification of this idea but of all correlations attempted this one remains the best. The results of this study are shown graphically in Fig. 5.

Measure of Overall Penetration and Corrosive Action

Two cells were built and evaluated to test the ability of solvent/mercuric chloride systems to penetrate through a painted aluminum barrier. Penetration through a painted barrier consisted of two events. First the solvent system had to transport mercuric chloride in a useable form to the surface of the aluminum, and secondly the mercuric chloride had to corrode through the aluminum barrier. The first design (TEA1) is shown in Fig. 6.

The basic principle of this and other apparatus tried is that the solvent/mercuric chloride system will diffuse through the paint barrier and corrode the metal aluminum foil underneath. In this trial, once the barrier had been destroyed, excess solvent/mercuric chloride would drip into a solution of diphenylcarbazide in ethanol. The solution changed from green to orange upon addition of only a drop or two of a solvent containing mercuric chloride. The time interval between application of
Figure 3. Acetonitrile penetration.
Figure 4. Relative penetration rate through polyurethane paint film.
Figure 5. Relative swell of polyurethane.

Relative penetration rate

Solvents

Methylene Chloride
Methylene Bromide
Methanol
Acetonitrile
Tetrahydrofuran
Dimethylformamide
2-Butanone
n-Propyl Acetate
2,4-Pentandione
2,5-Hexandione
4-Methyl-2-Pentanone-4-ol
1-Butanol
Triethanolamine
Figure 6. Transport evaluation apparatus (TEA1).

Figure 7. Transport evaluation apparatus (TEA2).
the solvent system to the barrier and visually noted change of color of the indicator was recorded as the time of penetration.

This apparatus suffered from many difficulties. The O-rings which were used to effect a seal suffered many complications. One problem noted was that repeated use of the same O-ring led to increased times required for penetration. If new O-rings were used, times returned to normal. When the O-rings that had been used were removed, rinsed and allowed to stand for a period of time before re-use, typical penetration times were once again obtained. During some runs, problems were encountered with teflon O-rings not remaining properly seated. Neoprene O-rings provided a better seal but several solvents interacted with them to a considerable degree. Another problem with the apparatus was that during some runs it appeared that a hole had formed, but nothing was eluted from the apparatus. The precise cause for this has not been determined but some possibilities are that surface tension of the solvent systems might be great enough to prevent flow through a small hole, or there might be an immediate reseal of any small holes formed by the corrosive action of the insoluble salts. In an effort to overcome this problem two design changes were attempted. However, neither increasing the height of the column of solvent/mercuric chloride nor vibrating the entire apparatus succeeded in developing suitable reliability. Stress around the O-rings was another drawback of this apparatus. During many runs damage to the aluminum was more severe around the O-rings than in the center of the aluminum barrier. These known problems and probably others led to irreproducibility that forced the abandonment of this apparatus.
The second transport evaluation apparatus (TEA2), is shown in Fig. 7. Penetration time (time required for transport of mercuric chloride to the aluminum surface by the solvent, plus time required for the mercuric chloride to corrode through the barrier) is based on the first visual appearance of barrier disruption on the backside of the barrier. In this apparatus epoxy cement was reasonably resistant to all solvents except methylene chloride. This apparatus was superior to the O-ring setup because it minimized stress on the surface and allowed for superior visual observation of the penetration process. The results of this test, although still plagued by response variations, were nonetheless suited to statistical treatment.

Single solvent tests were performed on both bare barriers and painted barriers. Penetration time through a bare barrier is the time required for the mercuric chloride to corrode through the aluminum surface. Penetration through a painted barrier \( T_{cb} \) is the time required for the transport of mercuric chloride to the aluminum surface by the solvent system plus the time required for the mercuric chloride to corrode through the aluminum barrier \( T_{bb} \). The eight solvents used were chosen to satisfy one or more of the criteria below:

1. a saturated solution of the solvent should have a high concentration of mercuric chloride.
2. the solvent should be highly disruptive to paint.
3. the solvent should have a low molecular weight or a small molecular size.
4. the solvent should have the potential to complex with mercuric chloride.

Runs were also performed with and without adding water to the solvent. The results are shown in Table I.

Tests were performed on multi-solvent mixtures with the ambition of
### TABLE I

Penetration times for single solvents through the coated barrier

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time to penetrate in seconds</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>9067</td>
<td>3254</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>10097</td>
<td>16562</td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>27699</td>
<td>37282</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>&gt;24000</td>
<td>9654</td>
</tr>
<tr>
<td>methanol</td>
<td>5860</td>
<td>3910</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>4789</td>
<td>4710</td>
</tr>
<tr>
<td>methylene chloride</td>
<td>26898</td>
<td>15401</td>
</tr>
<tr>
<td>2,4-pentanedione</td>
<td>1561</td>
<td>3594</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>13954</td>
<td>2799</td>
</tr>
<tr>
<td>water</td>
<td>-</td>
<td>6950</td>
</tr>
</tbody>
</table>

Penetration times for single solvents through the bare barrier

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time to penetrate in seconds</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>387</td>
<td>870</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>539</td>
<td>342</td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>50K</td>
<td>2159</td>
</tr>
<tr>
<td>methanol</td>
<td>149</td>
<td>221</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>362</td>
<td>342</td>
</tr>
<tr>
<td>methylene chloride</td>
<td>17075</td>
<td>6504</td>
</tr>
<tr>
<td>2,4-pentanedione</td>
<td>541</td>
<td>128</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>422</td>
<td>347</td>
</tr>
<tr>
<td>water</td>
<td>-</td>
<td>146</td>
</tr>
</tbody>
</table>
reducing overall penetration times. The MS1 series tested solvent systems containing random amounts of eight solvents, with a small amount of water added. Water had been shown to affect the results, and since keeping the solutions water-free was considered unnecessarily difficult, standardization of results was achieved by adding water to all solutions tested. The compositions of MS1 formulations\textsuperscript{11} are shown in Table II. The bare barrier penetration times and the coated barrier penetration times of MS1 formulations\textsuperscript{12} are shown in Table III.

The MS2 series also used solvent systems of varying compositions. MS2 formulations contained amounts of only the five best performing solvents based on MS1 results. The compositions of MS2 formulations\textsuperscript{13} are shown in Table IV. Bare barrier (bb) and coated barrier (cb) penetration times for MS2 formulations\textsuperscript{14} are shown in Table V.

The top three performing solvents, based on MS2 results, were studied in MS3 formulations. The compositions of MS3 formulations\textsuperscript{15} are shown in Table VI. Bare barrier and coated barrier penetration times\textsuperscript{16} are shown in Table VII.
Table II
Composition of initial multi-solvent formulations (MS1 series)

<table>
<thead>
<tr>
<th>MS1 No.</th>
<th>CH$_3$CN</th>
<th>DMF</th>
<th>DMSO</th>
<th>MeOH</th>
<th>MEK</th>
<th>CH$<em>2$C$</em>{12}$</th>
<th>Dione</th>
<th>THF</th>
<th>TOTAL</th>
<th>% Water Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.40</td>
<td>12.20</td>
<td>7.40</td>
<td>2.00</td>
<td>32.60</td>
<td>26.50</td>
<td>9.50</td>
<td>6.10</td>
<td>99.70</td>
<td>5.00</td>
</tr>
<tr>
<td>2</td>
<td>22.10</td>
<td>11.90</td>
<td>5.10</td>
<td>23.20</td>
<td>18.10</td>
<td>14.70</td>
<td>1.10</td>
<td>3.40</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>3</td>
<td>20.30</td>
<td>5.60</td>
<td>15.40</td>
<td>13.00</td>
<td>14.60</td>
<td>4.80</td>
<td>10.10</td>
<td>15.80</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>4</td>
<td>22.40</td>
<td>13.60</td>
<td>2.90</td>
<td>3.90</td>
<td>16.00</td>
<td>21.40</td>
<td>0.40</td>
<td>19.00</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>5</td>
<td>23.80</td>
<td>22.30</td>
<td>3.80</td>
<td>8.50</td>
<td>15.20</td>
<td>10.00</td>
<td>12.80</td>
<td>3.30</td>
<td>99.70</td>
<td>5.00</td>
</tr>
<tr>
<td>6</td>
<td>16.30</td>
<td>4.20</td>
<td>22.40</td>
<td>15.70</td>
<td>1.80</td>
<td>1.20</td>
<td>9.60</td>
<td>28.40</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>13.50</td>
<td>15.50</td>
<td>20.80</td>
<td>6.30</td>
<td>16.00</td>
<td>7.70</td>
<td>17.40</td>
<td>3.30</td>
<td>99.50</td>
<td>5.00</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>1.00</td>
<td>18.30</td>
<td>3.50</td>
<td>23.40</td>
<td>22.90</td>
<td>25.50</td>
<td>3.50</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>9</td>
<td>5.80</td>
<td>8.10</td>
<td>21.50</td>
<td>17.40</td>
<td>0.50</td>
<td>12.70</td>
<td>9.30</td>
<td>24.40</td>
<td>99.70</td>
<td>5.00</td>
</tr>
<tr>
<td>10</td>
<td>6.30</td>
<td>17.80</td>
<td>13.10</td>
<td>25.70</td>
<td>11.00</td>
<td>12.10</td>
<td>4.70</td>
<td>8.90</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>11</td>
<td>17.20</td>
<td>13.70</td>
<td>9.80</td>
<td>16.90</td>
<td>15.80</td>
<td>9.80</td>
<td>5.90</td>
<td>10.50</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>12</td>
<td>7.40</td>
<td>5.70</td>
<td>2.20</td>
<td>20.00</td>
<td>2.20</td>
<td>26.80</td>
<td>17.10</td>
<td>18.20</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>13</td>
<td>14.70</td>
<td>11.20</td>
<td>4.30</td>
<td>3.80</td>
<td>16.00</td>
<td>13.40</td>
<td>19.40</td>
<td>16.80</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>14</td>
<td>16.10</td>
<td>0.70</td>
<td>13.30</td>
<td>6.30</td>
<td>28.80</td>
<td>15.40</td>
<td>16.90</td>
<td>2.10</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>15</td>
<td>2.70</td>
<td>4.90</td>
<td>22.60</td>
<td>13.20</td>
<td>10.40</td>
<td>8.80</td>
<td>23.20</td>
<td>13.80</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>16</td>
<td>19.70</td>
<td>8.00</td>
<td>6.10</td>
<td>20.90</td>
<td>9.80</td>
<td>20.90</td>
<td>1.80</td>
<td>12.30</td>
<td>99.50</td>
<td>5.00</td>
</tr>
<tr>
<td>17</td>
<td>17.40</td>
<td>10.00</td>
<td>18.90</td>
<td>7.70</td>
<td>10.40</td>
<td>8.50</td>
<td>15.50</td>
<td>11.20</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>18</td>
<td>12.80</td>
<td>0.50</td>
<td>22.30</td>
<td>14.50</td>
<td>17.30</td>
<td>3.90</td>
<td>20.10</td>
<td>8.30</td>
<td>99.70</td>
<td>5.00</td>
</tr>
<tr>
<td>19</td>
<td>22.30</td>
<td>8.60</td>
<td>7.00</td>
<td>5.90</td>
<td>13.00</td>
<td>24.40</td>
<td>1.00</td>
<td>16.30</td>
<td>98.50</td>
<td>5.00</td>
</tr>
<tr>
<td>20</td>
<td>0.70</td>
<td>12.70</td>
<td>15.10</td>
<td>17.60</td>
<td>13.40</td>
<td>15.10</td>
<td>8.10</td>
<td>16.90</td>
<td>99.60</td>
<td>5.00</td>
</tr>
</tbody>
</table>
# Table III

Summary results for MS1 formulations

<table>
<thead>
<tr>
<th>Order</th>
<th>MS1 No.</th>
<th>Compound A Conc.</th>
<th>Penetration Time</th>
<th>Time Ctd-Bare</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc. (gm/100 ml)</td>
<td>Bare sec.</td>
<td>Coated sec.</td>
</tr>
<tr>
<td>1</td>
<td>12</td>
<td>35.86</td>
<td>551</td>
<td>486</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>33.97</td>
<td>140</td>
<td>509</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>37.55</td>
<td>169</td>
<td>575</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>36.82</td>
<td>948</td>
<td>671</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>42.91</td>
<td>254</td>
<td>672</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>38.21</td>
<td>132</td>
<td>688</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>38.41</td>
<td>188</td>
<td>1060</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>23.11</td>
<td>545</td>
<td>1477</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>39.61</td>
<td>157</td>
<td>1512</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>35.46</td>
<td>140</td>
<td>1531</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>38.51</td>
<td>442</td>
<td>1755</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>26.40</td>
<td>774</td>
<td>1767</td>
</tr>
<tr>
<td>13</td>
<td>17</td>
<td>34.53</td>
<td>322</td>
<td>1968</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>48.47</td>
<td>184</td>
<td>1969</td>
</tr>
<tr>
<td>15</td>
<td>18</td>
<td>29.84</td>
<td>331</td>
<td>2777</td>
</tr>
<tr>
<td>16</td>
<td>19</td>
<td>37.05</td>
<td>734</td>
<td>3055</td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td>42.05</td>
<td>611</td>
<td>3437</td>
</tr>
<tr>
<td>18</td>
<td>7</td>
<td>29.38</td>
<td>294</td>
<td>4196</td>
</tr>
<tr>
<td>19</td>
<td>15</td>
<td>32.18</td>
<td>458</td>
<td>4420</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>18.41</td>
<td>268</td>
<td>6018</td>
</tr>
</tbody>
</table>

\(^a\)Concentration by flame spectrophotometry
### Table IV
Composition of multi-solvent formulations (MS2 series)

<table>
<thead>
<tr>
<th>MS2 No.</th>
<th>CH$_3$CN</th>
<th>DMF</th>
<th>MeOH</th>
<th>CH$_2$Cl$_2$</th>
<th>THF</th>
<th>Total</th>
<th>Water Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>2</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>3</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>4</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>5</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>6</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>30.00</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>8</td>
<td>17.50</td>
<td>30.00</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>9</td>
<td>17.50</td>
<td>17.50</td>
<td>30.00</td>
<td>17.50</td>
<td>17.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>10</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>30.00</td>
<td>17.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>11</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>17.50</td>
<td>30.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>12</td>
<td>10.00</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>13</td>
<td>22.50</td>
<td>10.00</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>14</td>
<td>22.50</td>
<td>22.50</td>
<td>10.00</td>
<td>22.50</td>
<td>22.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>15</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>10.00</td>
<td>22.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>16</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>22.50</td>
<td>10.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>17$^a$</td>
<td>17.44</td>
<td>14.38</td>
<td>25.46</td>
<td>24.22</td>
<td>18.50</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>18$^b$</td>
<td>31.25</td>
<td>31.25</td>
<td>3.13</td>
<td>31.25</td>
<td>3.13</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>19$^c$</td>
<td>3.13</td>
<td>31.25</td>
<td>31.25</td>
<td>31.25</td>
<td>3.13</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>20$^d$</td>
<td>5.00</td>
<td>15.00</td>
<td>35.00</td>
<td>40.00</td>
<td>5.00</td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>21$^e$</td>
<td>45.45</td>
<td>4.55</td>
<td>4.55</td>
<td>4.55</td>
<td>45.45</td>
<td>100.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>

$^a$17-average composition from five best MS1 formulations.

$^b$18-predicted minimum penetration time through coated barrier from SAS analysis of MS1 results.

$^c$19-predicted minimum penetration time through coated barrier from SAS analysis of MS1 results.

$^d$20-predicted minimum penetration time through coated barrier from SAS analysis of MS1 results.

$^e$21-predicted minimum penetration time through coated barrier from SAS analysis of MS1 most effective use of a given amount of compound A.
**Table V**

Summary results for MS2 formulations

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc. (gm/100 ml)</td>
<td>Bare sec.</td>
<td>Coated sec.</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>41.80</td>
<td>121</td>
<td>189</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>41.16</td>
<td>89</td>
<td>254</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>46.74</td>
<td>134</td>
<td>269</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>48.79</td>
<td>137</td>
<td>269</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>48.66</td>
<td>90</td>
<td>272</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>47.70</td>
<td>118</td>
<td>278</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>49.87</td>
<td>255</td>
<td>291</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>46.61</td>
<td>105</td>
<td>302</td>
</tr>
<tr>
<td>9</td>
<td>11</td>
<td>54.24</td>
<td>135</td>
<td>346</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>46.29</td>
<td>601</td>
<td>351</td>
</tr>
<tr>
<td>11</td>
<td>8</td>
<td>49.11</td>
<td>114</td>
<td>380</td>
</tr>
<tr>
<td>12</td>
<td>15</td>
<td>53.60</td>
<td>90</td>
<td>496</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>44.87</td>
<td>925</td>
<td>605</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>59.50</td>
<td>138</td>
<td>1051</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>34.62</td>
<td>90</td>
<td>1058</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>49.62</td>
<td>126</td>
<td>2814</td>
</tr>
</tbody>
</table>

---

1 20 30.00 42.00 157 78 -79.00
2 17 44.09 59.00 153 212 68.00
3 19 35.44 36.00 176 291 115.00
4 18 35.16 34.00 117 305 188.00
5 21 74.11 68.00 881 7134 6253.00

aConcentration by flame spectrophotometry.
<table>
<thead>
<tr>
<th>MS3 No.</th>
<th>CH$_3$CN</th>
<th>DMF</th>
<th>DMSO</th>
<th>MeOH</th>
<th>MEK</th>
<th>CH$_2$Cl$_2$</th>
<th>Dione</th>
<th>THF</th>
<th>Total</th>
<th>Water Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.33</td>
<td>33.33</td>
<td>33.33</td>
<td>33.33</td>
<td>99.99</td>
<td></td>
<td></td>
<td></td>
<td>99.99</td>
<td>5.00</td>
</tr>
<tr>
<td>1a</td>
<td>33.33</td>
<td>33.33</td>
<td>33.33</td>
<td>99.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99.99</td>
<td>0.00</td>
</tr>
<tr>
<td>1b</td>
<td>30.00</td>
<td>30.00</td>
<td>30.00</td>
<td>30.00</td>
<td>10.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>2</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>10.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>3</td>
<td>50.00</td>
<td>50.00</td>
<td>50.00</td>
<td>10.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>4</td>
<td>50.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>5</td>
<td>25.00</td>
<td>50.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>6</td>
<td>25.00</td>
<td>50.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>25.00</td>
<td>50.00</td>
<td>25.00</td>
<td>25.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>8</td>
<td>20.00</td>
<td>40.00</td>
<td>40.00</td>
<td>40.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>9</td>
<td>40.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>10</td>
<td>40.00</td>
<td>40.00</td>
<td>40.00</td>
<td>40.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>11</td>
<td>10.00</td>
<td>15.00</td>
<td>40.00</td>
<td>35.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>11a</td>
<td>10.00</td>
<td>15.00</td>
<td>40.00</td>
<td>35.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>12</td>
<td>5.00</td>
<td>15.00</td>
<td>35.00</td>
<td>40.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>13</td>
<td>7.40</td>
<td>5.70</td>
<td>2.20</td>
<td>20.00</td>
<td>2.20</td>
<td>26.80</td>
<td>17.10</td>
<td>18.20</td>
<td>99.60</td>
<td>5.00</td>
</tr>
<tr>
<td>14</td>
<td>19.70</td>
<td>8.00</td>
<td>6.10</td>
<td>20.90</td>
<td>9.80</td>
<td>20.90</td>
<td>1.80</td>
<td>12.30</td>
<td>99.50</td>
<td>5.00</td>
</tr>
<tr>
<td>15</td>
<td>4.35</td>
<td>43.48</td>
<td>4.35</td>
<td>4.35</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>16</td>
<td>12.50</td>
<td>18.75</td>
<td>6.25</td>
<td>62.50</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
<tr>
<td>17</td>
<td>20.00</td>
<td>10.00</td>
<td>70.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00</td>
<td>5.00</td>
</tr>
</tbody>
</table>

**NOTES:**
- No. 11 postulated formulation for good paint disruption and barrier disruption.
- No. 11a MS3-11 without water.
- No. 12 repeat of Ms2-20.
- No. 13 repeat of MS1-12. (Best MS1).
- No. 14 repeat of MS1-16. (Biggest Coated-Bare negative).
- No. 15 predicted maximum concentration Compound A from SAS analysis of MS1 results.
- No. 16 predicted minimum penetration time through bare barrier from SAS analysis of MS1 results.
- No. 17 postulated formulation for good paint disrupter and high Compound A concentration.
Table VII

Summary results for MS3 formulations

<table>
<thead>
<tr>
<th>Order</th>
<th>No.</th>
<th>Compound A Conc. Calc. (gm/100 ml)</th>
<th>Meas.*</th>
<th>Penetration Time</th>
<th>Time Ctd-Bare sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bare sec</td>
<td>Coated sec</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>20.25</td>
<td>41.00</td>
<td>144</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>28.00</td>
<td>41.00</td>
<td>143</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>25.00</td>
<td>33.00</td>
<td>144</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>33.16</td>
<td>39.00</td>
<td>136</td>
<td>130</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>31.80</td>
<td>40.50</td>
<td>162</td>
<td>156</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>39.85</td>
<td>43.00</td>
<td>166</td>
<td>158</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>29.75</td>
<td>37.00</td>
<td>137</td>
<td>164</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>33.16</td>
<td>43.00</td>
<td>194</td>
<td>188</td>
</tr>
<tr>
<td>9</td>
<td>6</td>
<td>34.87</td>
<td>38.00</td>
<td>152</td>
<td>209</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>39.70</td>
<td>43.50</td>
<td>180</td>
<td>423</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>39.62</td>
<td>44.00</td>
<td>221</td>
<td>454</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>49.50</td>
<td>46.00</td>
<td>384</td>
<td>3011</td>
</tr>
</tbody>
</table>

|       |     |                                   |        |                  |                   |
| 1     | 12  | 30.00                             | 47.00  | 151              | 59                | -92.00            |
| 2     | 11a | 28.93                             | 48.00  | 169              | 68                | -101.00           |
| 3     | 11  | 28.93                             | 49.00  | 132              | 70                | -62.00            |
| 4     | 13  | 35.86                             | 78.00  | 489              | 342               | -147.00           |
| 5     | 14  | 36.82                             | 86.00  | 854              | 396               | -458.00           |
| 6     | 17  | 41.70                             | 68.50  | 546              | 1990              | 1444.00           |
| 7     | 15  | 72.59                             | 75.00  | 523              | 5195              | 4672.00           |
| 8     | 16  | 80.94                             | 62.00  | 765              | 6254              | 7489.00           |

*concentration by flame spectrophotometry
DISCUSSION

It was hypothesized that diffusion times of solvents through paint films obtained using infrared spectroscopy techniques would correlate with solvent solubility parameters. It was found however, that no useful correlation existed between diffusion times and the generalized Hildebrand solubility parameter or with the more specialized values (Hanson criterion) based on dispersion forces, dipole forces, and hydrogen bonding. A solubility parameter is proportional to the energy of vaporization per unit volume. There was also no useful correlation found between the amount of swell produced in the polyurethane by various solvents and the generalized Hildebrand solubility parameter or with the more specialized values. A possible useful correlation seems to exist between the diffusion time and percent swell produced in polyurethane by the solvent.\(^{17}\) This is shown in Fig. 8.

As illustrated in this section, the top three solvents for diffusing through a paint film were methylene chloride, methanol, and acetonitrile. An attempt was made to correlate this with penetration times through painted barriers generated with the TEA2 penetration test apparatus. If the solvents are ranked according to the magnitude of coated barrier penetration times minus bare barrier penetration times, the following order is generated:
Figure 8. Correlation of solvent penetration rate with polymer swell.
## Dried saturated solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-pentanediione</td>
<td>fastest</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td></td>
</tr>
<tr>
<td>acetonitrile</td>
<td></td>
</tr>
<tr>
<td>dimethylformamide</td>
<td></td>
</tr>
<tr>
<td>methylene chloride</td>
<td></td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>slowest</td>
</tr>
</tbody>
</table>

## Saturated solvent with water

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>fastest</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>2,4-pentanediione</td>
<td></td>
</tr>
<tr>
<td>methanol</td>
<td></td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td></td>
</tr>
<tr>
<td>methylene chloride</td>
<td></td>
</tr>
<tr>
<td>dimethylformamide</td>
<td></td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>slowest</td>
</tr>
</tbody>
</table>

As can be seen by comparing these lists with the best performing solvents in the infrared studies, the two tests do not correlate well. This was not entirely unexpected because while the infrared technique measures diffusion of solvents through paint barriers, the coated barrier time minus the bare barrier penetration time, as determined by the TEA2 apparatus, measures the time necessary for mercuric chloride to be transported to the barrier surface.

When comparing results of dried solvent penetration times through bare barriers and through coated barriers with times by solvents with small amounts of water added, again no clear relationship is seen. In bare barrier times, 5% water addition accelerated the penetration of solvents through the barrier for all solvents except dimethylsulfoxide, dimethylformamide, and 2,4-pentanediione. The addition of water improved the penetration times through the coated barrier for acetonitrile and methanol. There is no explanation for these results at this time.

Statistical analysis, using the "curfit" software package and an IBM Personal Computer, was performed to see if bare barrier times were a
function of the concentration of mercuric chloride in the solvent, surface tension of the solvent, boiling point of the solvent, or the generalized Hildebrand solubility parameter. The best correlation was found between the penetration time through the bare barrier and the density of the solvent. The correlation suggests that lower density solvents resulted in shorter bare barrier penetration times. Little faith was put in this correlation, however, due to data scatter. Graphs and statistics of the computer-generated correlations are shown in Figs. 9 through 13.

Statistical analysis, using IBM's curfit software package, was performed to see if the time of penetration through a painted barrier was a function of concentration of mercuric chloride in solvent, surface tension of solvent, boiling point of solvent, density of solvent, or the generalized Hildebrand solubility parameter. The best correlation was found between the density of the solvent and coated barrier penetration times. The correlation found that lower densities are better for lower penetration times. Again, this correlation may be questionable due to date scatter. Graphs and statistics showing proposed correlations are depicted in Figs. 14 through 18.

Statistical analysis, using IBM's curfit software package was performed to see if the quantity:

\[ \frac{\text{Bare Barrier time (solvent + H}_2\text{O)} - \text{Bare Barrier time (solvent only)}}{\text{Bare Barrier time (solvent + H}_2\text{O)}} \]

was a function of the concentration of mercuric chloride in solvent, surface tension of solvent, boiling point of solvent, density of solvent or the generalized Hildebrand solubility parameter. Graphs and statistics of the correlations are shown in Figs. 19 through 23.
Fitted equation is \( Y = A + B \times X \)

Coefficient of determination = 0.200614
Coefficient of correlation = 0.4478995
Standard error of estimate = 5693.66

Fitted equation is \( Y = A + B \times X + C \times (X^2) \)

Coefficient of determination = 0.5163302
Coefficient of correlation = 0.7185612
Standard error of estimate = 4851.526

Figure 9. Relationship between concentration and bare barrier times.
Fitted equation is $Y = A + B \cdot X + C \cdot (X^2)$

Coefficient of determination = .6487825  
Coefficient of correlation = .5436306  
Standard error of estimate = 5344.95

Fitted equation is $Y = A + B \cdot X$

Coefficient of determination = .295534  
Coefficient of correlation = .5436306  
Standard error of estimate = 5344.95

Figure 10. Relationship between boiling point and bare barrier times.
Figure 11. Relationship between surface tension and bare barrier times.
FITTED EQUATION IS Y + A + B*X

COEFFICIENT OF DETERMINATION = .4671051
COEFFICIENT OF CORRELATION = .6834508
STANDARD ERROR OF ESTIMATE = 4648.727

FITTED EQUATION IS Y + A + B*X + C*(X^2)

COEFFICIENT OF DETERMINATION = .8419022
COEFFICIENT OF CORRELATION = .9175524
STANDARD ERROR OF ESTIMATE = 2773.627

Figure 12. Relationship between density and bare barrier times.
Fitted equation is $Y = A + B \times X$

Coefficient of determination = .1178239
Coefficient of correlation = .3432549
Standard error of estimate = 6486.047

Fitted equation is $Y + A + B \times X + C \times (X^2)$

Coefficient of determination = .1281316
Coefficient of correlation = .3579547
Standard error of estimate = 7209.137

Figure 13. Relationship between Hildebrand solubility parameter and bare barrier times.
Fitted equation is $Y = A + B \times X$

Coefficient of determination = 5.453267E-02
Coefficient of correlation = 0.2335223
Standard error of estimate = 10360.57

Fitted equation is $Y = A + B \times X + C \times (X^2)$

Coefficient of determination = 0.3683734
Coefficient of correlation = 0.6069378
Standard error of estimate = 9276.439

Figure 14. Relationship between concentration and barrier times (Tcb).
Fitted equation is \( Y + A + B \times X \)

Coefficient of determination = 1.503117E-02
Coefficient of correlation = .1226017
Standard error of estimate = 10574.79

Fitted equation is \( Y + A + B \times X + C(X^2) \)

Coefficient of determination = .7604388
Coefficient of correlation = .8720314
Standard error of estimate = 5712.915

Figure 15. Relationship between boiling point and barrier times (Tcb).
Fitted equation is $Y = A + B \times X$

Coefficient of determination = 0.5775953
Coefficient of correlation = 0.7599969
Standard error of estimate = 6925.081

Fitted equation is $Y = A + B \times X + C(X^2)$

Coefficient of determination = 0.5941296
Coefficient of correlation = 0.770793
Standard error of estimate = 7436.088

Figure 16. Relationship between density and barrier times (Tcb).
Fitted equation is $Y = A + B \times X$

Coefficient of Determination = 0.1228792
Coefficient of Correlation = 0.3505413
Standard Error of Estimate = 8551.446

Fitted equation is $Y = A + B \times X + C(X^2)$

Coefficient of Determination = 0.1353838
Coefficient of Correlation = 0.3679454
Standard Error of Estimate = 9492.418

Figure 17. Relationship between Hildebrand solubility parameter and barrier times ($T_{cb}$).
Figure 18. Relationship between surface tension and barrier times (Tcb).
Fitted equation is $Y = A + B \cdot X$

Coefficient of determination = .2027637
Coefficient of correlation = .4502929
Standard error of estimate = 3605.449

Fitted equation is $Y = A + B \cdot X + C \cdot (X^2)$

Coefficient of determination = .5363067
Coefficient of correlation = .7323296
Standard error of estimate = 3012.117

Figure 19. Relationship between the effect of water on barrier times and concentration.
Fitted equation is \( Y = A + B \times X \)

Coefficient of determination = \(2.056426 \times 10^{-2}\)
Coefficient of correlation = 0.1434024
Standard error of estimate = 3996.26

Fitted equation is \( Y = A + B \times X + C(X^2) \)

Coefficient of determination = 0.0949741
Coefficient of correlation = 0.3081787
Standard error of estimate = 4208.11

Figure 20. Relationship between the effect of water on barrier times and surface tension.
Fitted equation is \( Y = A + B \times X \)

Coefficient of determination = 0.2771858  
Coefficient of correlation = 0.5264844  
Standard error of estimate = 3433.042

Fitted equation is \( Y = A + B \times X + C \times (X^2) \)

Coefficient of determination = 0.6257616  
Coefficient of correlation = 0.791051  
Standard error of estimate = 2706.015

Figure 21. Relationship between the effect of water on barrier times and boiling point.
Fitted equation is \( Y = A + B \times X \)

Coefficient of determination = .4857672
Coefficient of correlation = .696967
Standard error of estimate = 2895.648

Fitted equation is \( Y = A + B \times X + C(X^2) \)

Coefficient of determination = .8264288
Coefficient of correlation = .9090813
Standard error of estimate = 1842.807

Figure 22. Relationship between the effect of water on barrier times and density.
Fitted equation is $Y = A + B \times X$

Coefficient of determination = 0.122469
Coefficient of correlation = 0.3499384
Standard error of estimate = 4100.025

Fitted equation is $Y = A + B \times X + C(X^2)$

Coefficient of determination = 0.1360544
Coefficient of correlation = 0.3688556
Standard error of estimate = 4548.319

Figure 23. Relationship between the effect of water on barrier times and Hildebrand solubility parameter.
The next set of figures tested to see if the quantity:

\[(\text{Bare barrier/time concentration of mercuric chloride})\]

was a function of the density of solvent, the boiling point of solvent, the generalized Hildebrand solubility parameter, the molecular weight of solvent, or the surface tension of solvent. The bare barrier penetration times were divided by the concentration because it was believed that bare barrier times should be a direct function of concentration of mercuric chloride in the solvent. Again, no useful correlations were found, and the reason(s) for these unexpected results is not clear. The graphs of these correlations are shown in Figs. 24 through 28.

It is of interest to note that in the figures just discussed, the methylene chloride point consistently deviated the most from suggested fits. It is not clear why this was observed.

MS1 results were computer analyzed using software available from the SAS Institute Inc. Statistical correlations were performed evaluating each of the solvents' effectiveness in MS1 bare barrier penetration time results, MS1 coated barrier time results and in promoting a high concentration of mercuric chloride in the MS1 solvent mixtures. From the computer results the solvents were grouped in terms of their contribution to low penetration times for the coated barrier as follows:
Fitted equation is \( Y = A + B \times X \)

Coefficient of determination = 0.458559
Coefficient of correlation = 0.6771698
Standard error of estimate = 0.1598671

Fitted equation is \( Y = A + B \times X + C(X^2) \)

Coefficient of determination = 0.4873629
Coefficient of correlation = 0.6981138
Standard error of estimate = 0.1704137

Figure 24. Relationship between bare barrier time/concentration and density.
Figure 25. Relationship between bare barrier time/concentration and boiling point of solvent.
Figure 26. Relationship between bare barrier time/concentration and Hildebrand solubility parameter.

Fitted equation is $Y = A + B \cdot X$

Coefficient of determination = .1114899
Coefficient of correlation = .333901
Standard error of estimate = 1.986956

Fitted equation is $Y = A + B \cdot X + C(X^2)$

Coefficient of determination = .1810449
Coefficient of correlation = .4254938
Standard error of estimate = 2.132992
FITTED EQUATION IS $Y = A + B \times X$

COEFFICIENT OF DETERMINATION = 8.313648E-02
COEFFICIENT OF CORRELATION = .288334
STANDARD ERROR OF ESTIMATE = 23.07607

FITTED EQUATION IS $Y = A + B \times X + C(X \cdot 2)$

COEFFICIENT OF DETERMINATION = .5851517
COEFFICIENT OF CORRELATION = .7649521
STANDARD ERROR OF ESTIMATE = 17.02397

Figure 27. Relationship between bare barrier time/concentration and molecular weight of solvent.
Fitted equation is $Y = A + B \times X$

Coefficient of determination = $2.240951 \times 10^{-2}$
Coefficient of correlation = 0.1496981
Standard error of estimate = 7.679597

Fitted equation is $Y = A + B \times X + C \times (X^2)$

Coefficient of determination = 0.1241074
Coefficient of correlation = 0.3522888
Standard error of estimate = 7.963884

Figure 28. Relationship between bare barrier time/concentration and surface tension of solvent.
The solvents which, according to the statistical analysis, had the greatest effect in minimizing bare barrier penetration times were dimethylsulfoxide, 2,4-pentanediione, dimethyl sulfoxide, methanol, and acetonitrile.

As shown in the results section for MS1, the concentration of mercuric chloride in the solvent mixture was both measured and predicted from the amount of mercuric chloride each constituent solvent was expected to be able to hold, based upon its maximum solubility. Computer analysis of MS1 data was performed to determine which solvents were best in promoting a high actual concentration of mercuric chloride in solvent mixtures and which were best in causing the actual concentration to exceed that expected from individual contributions. Methanol, tetrahydrofuran, acetonitrile, methylene chloride, and dimethylformamide were found to be good solvents in promoting a high measured concentration of mercuric chloride in solvent mixtures. Methylene chloride, methanol, acetonitrile, tetrahydrofuran, and dimethylformamide were found to promote the dissolution of mercuric
chloride in the mixture beyond that expected from individual solvent contributions. A summary of MS1 computer results\textsuperscript{18} appears in Table VIII.

Due to the fact that methyl ethyl ketone, dimethylsulfoxide, and 2,3-pentanediol were not effective in promoting fast coated barrier times and high concentrations of mercuric chloride in solvent mixtures, these solvents were eliminated from consideration in MS2 solvent mixtures.

MS2 results were also analyzed using the SAS computer software package. The results of the computer analysis\textsuperscript{19} are shown in Table IX. As can be seen, methanol and methylene chloride, which were the best performers in the infrared studies, were statistically shown to be the best solvents, among the five solvents considered in MS2 tests, at promoting low penetration times through a painted barrier. The fact that this MS2 computer generated conclusion is in closer agreement with infrared studies rather than with single solvent studies suggests that diffusion of the solvent system through a paint barrier is generally more rate-limiting than the destruction of the barrier. At this point, it might have been guessed that a methylene chloride/methanol solvent system would be best at minimizing coated barrier times. This is based on the solvent's ability to go through a paint film quickly, and on methanol's ability to dissolve a large amount of mercuric chloride.

Only three solvents were considered in MS3 solvent mixtures. Methanol and methylene chloride were considered because computer analysis showed these solvents were effective in promoting low penetration times through coated barriers. Dimethylformamide was considered based on computer interpretation of MS2 results, indicating
### Table VIII

**Ranking of MS1 Series Constituents**

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Minimum Penetration Time</th>
<th>Concentration Synergism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best</td>
<td>MeOH Coated: DMSO</td>
<td>MeOH</td>
</tr>
<tr>
<td></td>
<td>DMF Bare: DMF</td>
<td>THF</td>
</tr>
<tr>
<td></td>
<td>CH₃CN: DMF</td>
<td>CH₃CN</td>
</tr>
<tr>
<td></td>
<td>THF*: CH₂Cl₂</td>
<td>CH₂Cl₂</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂: CH₃CN*</td>
<td>DMF*</td>
</tr>
<tr>
<td></td>
<td>MEK: THF</td>
<td>DIONE</td>
</tr>
<tr>
<td>Worst</td>
<td>DIONE: CH₂Cl₂</td>
<td>DIONE</td>
</tr>
</tbody>
</table>

* = correlation coefficient changes sign

### Table IX

**Ranking of MS2 Series Constituents**

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Minimum Penetration Time</th>
<th>Concentration Synergism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best</td>
<td>MeOH Coated: DMF*</td>
<td>MeOH</td>
</tr>
<tr>
<td></td>
<td>CH₂Cl₂: CH₃CN</td>
<td>CH₂Cl₂*</td>
</tr>
<tr>
<td></td>
<td>THF: CH₂Cl₂</td>
<td>THF</td>
</tr>
<tr>
<td></td>
<td>DMF: MeOH</td>
<td>CH₂Cl₂*</td>
</tr>
<tr>
<td>Worst</td>
<td>CH₃CN: THF</td>
<td>DMF</td>
</tr>
</tbody>
</table>

* = correlation coefficient changes sign
that dimethylformamide was effective in promoting low penetration times through bare barriers. Exceptions to this were MS3-11 through MS3-17 solvent mixtures which are described in Table VI. Computer analysis\textsuperscript{20} of data shown in Table X indicated methylene chloride contributed the most to low penetration times. Fig. 29 shows that penetration times decreased as the concentration of methylene chloride approaches 50 volume percent. The minimum time through the painted barrier was achieved by using an equal amount of methanol and methylene chloride as the solvent system.
Table X

Ranking of MS3 series constituents

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Minimum Penetration Time</th>
<th>Difference</th>
<th>Concentration Synergism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coated</td>
<td>Bare</td>
<td></td>
</tr>
<tr>
<td>Best</td>
<td>CH₂Cl₂*</td>
<td>CH₂Cl₂*</td>
<td>CH₂Cl₂*</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>MeOH</td>
<td>MeOH</td>
</tr>
<tr>
<td>Worst</td>
<td>DMF</td>
<td>DMF</td>
<td>DMF</td>
</tr>
</tbody>
</table>

* = correlation coefficient changes sign
Figure 29. Proportion variation in MS3 formulations.
CONCLUSIONS

The literature study concerning the aluminum oxide layer concluded that the air-grown oxide layer is amorphous and non-porous. The infrared studies showed that methylene chloride and methanol were the most effective solvents in diffusing through a paint film. The pure solvent studies of penetration times through bare barriers and coated barriers using the TEA2 apparatus were not very successful, since results did not correlate very well to any solvent properties.

MS1 results enabled the elimination of three solvents from a field of eight being considered in design of a solvent system which would minimize coated barrier penetration times.

MS2 results enabled the elimination of two solvents from a field of five solvents being considered in the design of a solvent system which would minimize coated barrier times.

MS3 results were successful in finding a solvent system which could rapidly penetrate through a coated barrier.
RECOMMENDATIONS

Work leading either to a better understanding of the diffusion of solvents through paint or to a better understanding of reactions which occur between mercuric chloride and aluminum might be useful in explaining the results obtained in this part.

Future work using techniques utilized in this part is not recommended. This part did not suffer from a lack of data, only from a lack of good correlations to explain the data.
PART II
INTRODUCTION

This part of the study examined the chemistry of mercuric chloride in various solvent systems. This interest developed because MS1 solutions, when aged, were observed to form a large amount of precipitate. The bulk volume of the precipitate seemed to be far in excess of the amount of mercuric chloride that had been added to the solution.

There were three objectives:

1. To compare infrared spectra of several pure solvents with the infrared spectra of comparable solvent/mercuric chloride solutions. The infrared spectra of some of the pure solvent MS1 systems and some selected binary solvent systems were also compared with the infrared spectra of comparable mixtures containing mercuric chloride.

2. To compare the NMR spectra of several pure solvents with the NMR spectra of comparable systems with mercuric chloride added.

3. To compare the infrared spectra of residual solids (obtained by evaporation of solvent from solutions saturated with mercuric chloride) with the spectrum of pure mercuric chloride. The MS1 systems were examined in a similar fashion.
EXPERIMENTAL

In pursuit of the first objective the infrared spectra of the following solvent systems were compared to the infrared spectra of the same solvent systems after saturation with mercuric chloride. All solutions were prepared at room temperature and only liquid phases were used. These spectra of MS1 solvent systems are shown in Figs. 30-37.

<table>
<thead>
<tr>
<th>Pure solvents</th>
<th>Binary mixtures/equal volumes</th>
<th>Selected MS1 Solvent systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrile</td>
<td>acetonitrile/2,4-pentanedione</td>
<td>MS1-5</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>acetonitrile/dimethylformamide</td>
<td>MS1-12</td>
</tr>
<tr>
<td>methanol</td>
<td>acetonitrile/methanol</td>
<td>MS1-13</td>
</tr>
<tr>
<td>methylene chloride</td>
<td>acetonitrile/methylene chloride</td>
<td>MS1-16</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>2,4-pentanedione/dimethylformamide</td>
<td></td>
</tr>
<tr>
<td>2,4-pentanedione</td>
<td>2,4-pentanedione/methanol</td>
<td></td>
</tr>
<tr>
<td>dimethylsulfoxide</td>
<td>2,4-pentanedione/methylene chloride</td>
<td></td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>dimethylformamide/methanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dimethylformamide/methylene chloride</td>
<td></td>
</tr>
</tbody>
</table>

The second objective was accomplished in a similar way by comparing the NMR spectra of the solvent systems shown below before and after the addition of mercuric chloride:

- acetonitrile
- dimethylformamide
- methanol
- methylene chloride
- methyl ethyl ketone
- 2,4-pentanedione
- dimethylsulfoxide
- tetrahydrofuran

To accomplish the third objective, solvents were removed from various solvent systems saturated with mercuric chloride and infrared spectra were run on the resulting residues. The solvent was removed by placing the solvent system in a vacuum dessicator maintained at a temperature of approximately 100°C for the time required to evaporate the solvent. These spectra were compared with those of mercuric chloride and corresponding solvents.
Figure 30. Infrared spectrum of MS1-5 solution.

Figure 31. Infrared spectrum of MS1-5 with mercuric chloride.
Figure 32. Infrared spectrum of MS1-12 solution.

Figure 33. Infrared spectrum of MS1-12 with mercuric chloride.
Figure 34. Infrared spectrum of MS1-13.

Figure 35. Infrared spectrum of MS1-13 with mercuric chloride.
Figure 36. Infrared spectrum of MS1-16 solution.

Figure 37. Infrared spectrum of MS1-16 solution with mercuric chloride.
DISCUSSION

Comparisons of the infrared spectra of the various solvent systems, both pure and mixed, when saturated with mercuric chloride suggests either that no organic mercury compounds have been formed or that if formed, their solubility is very low. This conclusion is based on the fact that there was no observed change in spectra pre- and post-saturation with mercuric chloride.

More interesting results were obtained in the pursuit of the third objective. The infrared spectra of the solid residues that remained after solvent removal from saturated solutions of methanol, methylene chloride, methyl ethyl ketone, 2,4-pentanedione and tetrahydrofuran did not differ from the infrared spectrum of pure mercuric chloride. The infrared spectra of similarly obtained residues from saturated solutions of acetonitrile, dimethylsulfoxide, and dimethylformamide did differ from that of mercuric chloride. These results can be seen in Figs. 38 through 43.

With regard to the saturated solution of mercuric chloride in acetonitrile, the spectrum of the residue exhibited extra peaks at 1695, 1260, 1049, and 986. This suggests the presence of an insoluble acetonitrile-mercuric chloride species. This suggestion must be tempered, however, due to a problem in reproducing the results. Nonetheless the existence of an acetonitrile-mercuric chloride species must be considered a possibility since a small amount of material will gradually precipitate out of a filtered saturated acetonitrile-mercuric
Figure 38. Acetonitrile.

Figure 39. Infrared spectrum of acetonitrile/mercuric chloride solid residue with nujol.
Figure 40. Dimethylsulfoxide.

Figure 41. Infrared spectrum of dimethylsulfoxide/mercuric chloride solid with nujol.
Figure 42. Dimethylformamide.

Figure 43. Infrared spectrum of dimethylformamide/mercuric chloride solid residue with nujol.
chloride solution that is left standing in a sealed container for several weeks. The problem with reproducibility could stem from a reaction (or a series of reactions) that occur slowly over a several week period.

Similar evidence and arguments prevail for DMSO and DMF systems. For example, the spectrum of the solid residue from dimethylsulfoxide contains peaks at 1021, 993, 942, and 711 which cannot be attributed to mercuric chloride or nujol. This is shown in Fig. 41. In this case, the spectrum of the solid residue is reproducible. The solid residue formed from a dried (water-free) DMSO-mercuric chloride saturated solution has the same infrared spectrum as the solid residue obtained from a DMSO-mercuric chloride solution to which water had been added. This is shown in Figs. 44 and 45. Part I of this project has shown that the addition of water affected penetration times through coated barriers by mercuric chloride containing solvent systems. This was an attempt to explain this result. Again, support for the gradual production of an insoluble DMSO-mercuric chloride species comes from the large amount of solid precipitate that will form in a sealed solution that has been filtered and is allowed to age in a sealed bottle for several months. Compounding the enigma is that the solids will precipitate suddenly at some point in time, usually weeks or months after the saturated solution was prepared. The spectrum of this solid does not differ from the spectrum of the solid residue obtained from heating to dryness a newly prepared DMSO-mercuric chloride solution. This is shown in Fig. 44. Another interesting property of saturated DMSO-mercuric chloride solutions is that addition of water causes the formation of a large volume of solid precipitate. The infrared spectrum of this solid is the
Figure 44. Infrared spectrum of dimethylsulfoxide/mercuric chloride with no water added.

Figure 45. Infrared spectrum of dimethylsulfoxide/mercuric chloride with water.
same as the infrared spectrum of the solid residue obtained by heating to dryness either a new or aged saturated DMSO-mercuric chloride solution. This is interpreted as a possible indication that if a DMSO-mercuric chloride species exists, water may act as a catalyst or intermediate in its formation. It should also be borne in mind that a series of reactions involving differing kinetics could be involved, which would seriously complicate any and all spectral interpretations.

In the case of dimethylformamide, the infrared spectrum of the solid residue obtained from the saturated solution once again differs from that of mercuric chloride alone. This is shown in Fig. 46. The peaks in the spectrum at 1628, 1101, and 811 cannot be attributed to either mercuric chloride or nujol. Once again when a dimethylformamide solution saturated with mercuric chloride is filtered and allowed to age in a sealed bottle a small amount of solid precipitates over a several week time frame. Saturated DMF-mercuric chloride solutions, not unlike saturated DMSO-mercuric chloride solutions, exhibit the same unusual behavior when water is added. When water is added to a saturated DMF-mercuric chloride solution a large amount of white precipitate forms. Unlike saturated DMSO-mercuric chloride solutions however, the infrared spectrum of this solid differs from the infrared spectrum of the solid residue obtained by heating to dryness a saturated DMF-mercuric chloride solution. As can be seen in Fig. 47 the major difference between the two spectra is that there is a peak at 1628 in the spectrum of the solid residue obtained from the dry system whereas we find an absorbance of 1561 in the spectrum of the solid obtained from a saturated DMF-mercuric chloride solution to which water has been added. The infrared spectrum of the solid residue from a DMF-mercuric chloride solution to which
Figure 46. Infrared spectrum of dimethylsulfoxide/mercuric chloride solid residue.

Figure 47. Infrared spectrum of dimethylformamide/mercuric chloride solid residue with and without water.
water was added or if the solution is not dried using a molecular sieve is shown in Figs. 43, 47 and 48. Note the peaks at 1561, 1008, and 810 in Fig. 48 that cannot be explained by DMF, mercuric chloride, or by nujol. This is interpreted as possible indication of the existence of a DMF-mercuric chloride-water species. Fig. 49 summarizes the results discussed above. Spectrum A in Fig. 49 is the infrared spectrum of the solid residue obtained from an aged, non-dried DMF-mercuric chloride solution. Spectrum B is the spectrum of the solid residue obtained from a dried DMF-mercuric chloride solution. Spectrum C is the spectrum of the solid residue in a newly prepared saturated DMF-mercuric chloride solution.

A possible structure for the suggested DMF-mercuric chloride species is shown below:

```
\[ \text{H-C}=N \]
\[ \text{OHgCl} \quad \text{CH}_3 \]
```

This secondary amide would be expected to have a peak at about 1560. Such a structure should also have a peak at 810 due to the out-of-plane deformation of a carbon-hydrogen bond, and a peak at about 1000 due to the carbon-oxygen bond.

These results appear consistent with NMR work presently being done by Dr. W.D. Perry at the University of Auburn. Dr. Perry has shown that mercuric nitrate in aqueous nitric acid will react slowly over time with acetone. The reaction involves the replacement of the hydrogens with mercury. The reaction proceeds slowly with multiple substitutions possible. A slow reaction, having several products, would go far in
Figure 48. Infrared spectrum of dimethylformamide/mercuric solid residue (not dried).

Figure 49. Dimethylformamide summary.
explaining the problems encountered in Part I of this project in obtaining reproducible results.

All of the solid dried residues from saturated pure solvents were tested for activity on an aluminum surface, and all were shown to be able to corrode aluminum foil.

Various MS1 solvent mixtures were prepared and saturated with mercuric chloride. Infrared spectrum of the solid residue that remained when they were heated to dryness were prepared. Fig. 50 shows the infrared spectrum of the solid residue from the MS1-5 solvent mixture. Some of the peaks can now be identified based on the previous work with single solvents. The peak at 3472 is believed to be due to water. The peaks at 1618, 1568, 1008, and 811 are believed to be due to a DMF-mercuric chloride complex. The peaks at 948 and 811 are believed to be due to a DMSO-mercuric chloride complex. In Fig. 51 the infrared spectrum of the solid residue from the MS1-12 solvent mixture saturated with mercuric chloride is shown. The peaks at 1561, 1008, and 811 are believed to be due to a DMF-mercuric chloride species. The peak at 711 might be due to a DMSO-mercuric chloride species. Fig. 52 shows the infrared spectrum of the solid residue from the MS1-13 solvent mixture saturated with mercuric chloride. The peaks at 1625, 1561, 1008, and 811 are believed to be due to the DMF-mercuric chloride complex. Peaks at 1021, 991, 942, and 711 are believed to be due to a DMSO-mercuric chloride complex. Fig. 53 shows the infrared spectrum of the MS1-15 solvent mixture saturated with mercuric chloride. The peaks at 1558, 1008, and 808 are believed to be due to a DMF-mercuric chloride species. The peak at 717 is believed to be due to a DMSO-mercuric chloride complex. Fig. 54 shows the spectrum of the solid residue from
Figure 50. Infrared spectrum of MS1-4 solid residue.

Figure 51. Infrared spectrum of MS1-12 solid residue.
Figure 52. Infrared spectrum of MS1-13 solid residue.

Figure 53. Infrared spectrum of MS1-15 solid residue.
Figure 54. Infrared spectrum of MS1-16 solid residue.
the MS1-16 solvent mixture saturated with mercuric chloride. Peaks at 1628 and 1008 are believed to be due to the DMF-mercuric chloride complex. Peaks at 1018, 985, 931, and 711 are believed to be due to a DMSO-mercuric chloride complex.
CONCLUSIONS

It appears that no soluble solvent-mercuric chloride species existed for the solvents considered in the MS1 test results. This was shown by comparing the infrared spectra of pure solvents and mixtures of solvents with the infrared spectrum of pure solvent and mixtures of solvents saturated with mercuric chloride. These results were corroborated by comparing the NMR spectrum of pure solvents with the NMR spectrum of pure solvents saturated with mercuric chloride.

These findings, however, do not preclude the existence of insoluble solvent-mercuric chloride species. The comparison of infrared spectra of the dried residues from pure solvents saturated with mercuric chloride with the infrared spectrums of pure mercuric chloride suggest the existence of insoluble compounds. Insoluble compounds may have been formed in reactions involving mercuric chloride, water, and respectively, acetonitrile, dimethylformamide, and dimethylsulfoxide. Further evidence of the existence of insoluble compound formation was the formation of precipitates in bottles containing filtered, saturated solutions of mercuric chloride in acetonitrile, dimethylformamide, and dimethylsulfoxide, and formation of large amounts of precipitates in bottles containing MS1 solvent mixtures saturated with mercuric chloride. Additionally, the existence of insoluble compounds formed between solvents and mercuric chloride is suggested by the fact that some peaks in the infrared spectra of solids formed in MS1 solvent mixtures saturated with mercuric chloride were also seen in the infrared...
spectrums of the solid residues obtained from pure solvents saturated with mercuric chloride.
RECOMMENDATIONS

Having an elemental analysis performed on dried residues from solvents saturated with mercuric chloride would be helpful in identifying them. This could also prove their existence, which was only strongly suggested by the evidence uncovered in this part of the research project.

A potentially useful offshoot of the first part of this research project might be to determine penetration times as a function of the age of the saturated solvent. The possible formation of insoluble solvent-mercuric chloride species might effect penetration times of a solvent system.
PART III
INTRODUCTION

The major objective of this part was to develop a quantitative technique for the measurement of the rate and extent of corrosion of aluminum by a solvent saturated with mercuric chloride. Two electrochemical techniques were attempted. In the first, an aluminum wire was immersed in the solvent/mercuric chloride system and its conductance was monitored as a function of time. Conceptually, as the aluminum corroded, the reduction in the cross-sectional area of the aluminum would increase its electrode resistance. In the second procedure the half-cell potential of an aluminum electrode immersed in a solvent saturated with mercuric chloride was measured against a reference as a function of time, with the presumption that the potential of the reference would remain constant.

The feasibility of a thermal process in measuring the rate of a corrosion process was also studied. The presumption behind this approach was that the corrosion of aluminum by mercuric chloride is an exothermic process. Measuring the temperature of aluminum under mercuric chloride attack as a function of time would therefore reveal information about the corrosion reaction rate and the extent of the corrosive attack.
RESULTS

Based upon the assumption that there would be measurable change in the resistance of an aluminum wire immersed in solvents saturated with mercuric chloride as a function of time, initial conductance measurements were made using the circuit shown in Fig. 55.

This circuit and several variants however, did not provide a suitable correlation between measured conductance and degree of corrosion. Conductance was nearly constant throughout the test up to the point of physical breakage of the wire. Even the time of physical breakage was not reproducible.

With the failure of the conductance measurement, a study of electrode potential was conducted. The apparatus was a simple galvanic cell, constructed in accord with the apparatus shown in Fig. 56. It was hoped that the slope of an aluminum electrode potential versus time curve would provide information concerning corrosion rates. It was also hoped that the time necessary for the formation of a stable, protective corrosion film, if one formed, could be deduced if the aluminum electrode potential came to a steady state value. Results of this procedure, however, were inconsistent. The potential of aluminum electrode in methanol solutions saturated mercuric chloride solutions increased with time. The opposite effect was seen with mercuric chloride saturated solutions of 2,4-pentanedione, methylene chloride, dimethylformamide, and methyl ethyl ketone. The electrode potential of the aluminum wire in a saturated solution of mercuric chloride in
Figure 55. Circuit diagram.

Figure 56. Galvanic cell.
dimethylsulfoxide remained constant with time, and the electrode potential of aluminum wire in an acetonitrile solution saturated with mercuric chloride was erratic.

The same cell apparatus was used to measure the electrode potential of an aluminum wire in pure solvents. In the cell shown in Fig. 55, the potential of the aluminum wire electrode in pure solvents was compared to the potential of a reference electrode. The potential of aluminum electrodes in pure methanol, and methylene chloride increased with time. The potential of the aluminum wire electrode in dimethylformamide, acetonitrile, dimethylsulfoxide, methyl ethyl ketone, and 2,4-pentanederone decreased as a function of time. The potential of aluminum in tetrahydrofuran remained constant with time. These results were disappointing, as it was expected that the potential of aluminum electrodes would be constant with time. Conclusions based on these results are not possible, since it was not determined if the potential variation with time was due to the reference or the test electrode. Solvent effects on the reference or test electrode could be influencing results.

A procedure was performed to test the effect the oxide layer on aluminum was having on the test results. Aluminum wire was immersed in concentrated hydrochloric acid for two minutes and then rinsed in water followed by pure solvent. The pretreated aluminum wire was then immersed in pure solvent saturated with mercuric chloride and its electrode potential compared to a reference electrode was recorded as a function of time. This procedure was performed first using methanol as the pure solvent, and then repeated using 2,4-pentanederone as the pure solvent. Results obtained using aluminum wire pretreated as described
above in methanol were not significantly different from results obtained using untreated aluminum. Results obtained using 2,4-pentanedione solution saturated with mercuric chloride were more greatly affected by the pretreating process. In this case pretreating caused the potential of the aluminum electrode to increase with time rather than decrease with time as was the case with untreated aluminum. This might indicate that the electrode potential of aluminum in methanol is relatively independent of the oxide layer whereas the electrode potential of aluminum in 2,4-pentanedione is not. This contention would be consistent with the fact that mercuric chloride/methanol solutions can go through the oxide layer quickly. It could also only indicate that the oxide layer of aluminum forms very quickly.

Interpretation of cell potential measurement rests, of course, upon the presumed stability of the reference electrode and attempts were made to verify this. The reference electrode was soaked in the solvent for 30 minutes prior to the aluminum electrode being immersed in the corrosive solution. The purpose of this change in the procedure was to improve the stability of the reference electrode. The potential of test aluminum electrodes in pure solvents still varied widely compared to the reference electrode.

A cell which did not use a reference electrode was examined. When using the apparatus shown in Fig. 57, it was no longer necessary to worry about whether the reference electrode was maintaining a constant cell potential. The results obtained from this apparatus were consistent with results obtained by measuring the electrode potential of aluminum in solvents containing mercuric chloride against a reference electrode. When the same apparatus shown in Fig. 57 was used with pure
Figure 57. Double cylinder arrangement.

Figure 58. Apparatus for measuring the temperature of corroding aluminum as a function of time.
solvent in both the inner and outer cylinder, the potential varied widely with time. This caused doubt regarding previously obtained results. At this point, attempts to measure the electrochemical potentials of these straight organic systems were abandoned.

A different approach was undertaken involving water as an electrolyte. Eighteen gauge aluminum wire was soaked in selected pure solvents and in selected solvents saturated with mercuric chloride for varying lengths of time. The electrode potential of the aluminum wire was then measured in water and referenced to an Ag/AgCl reference electrode. When the aluminum wire was soaked in pure solvents, the electrode potential of the aluminum measured against the reference electrode was about \(-1000\) mV. This result was relatively independent of solvent identity. When the aluminum wire was soaked in solvents saturated with mercuric chloride, the electrode potential of the aluminum wire measured against a reference electrode was about \(-1500\) mV. This result was also relatively independent of solvent identity.

The apparatus for measuring the temperature of a thimble-shaped aluminum sample under attack by mercuric chloride is shown in Fig. 58. Fig. 59 shows the results of the thermal study in a graphical form. Three trials were executed. In the first trial, a methanol solution saturated with mercuric chloride was added to the aluminum test thimble. Cellophane tape was used to cover the top of the thimble to minimize solvent evaporation. The temperature of the thimble was measured as a function of time using a thermister. The temperature-time relationship is shown in Fig. 59. The second and third trials tested solutions of 2,4-pentanedione and dimethylformamide saturated with mercuric chloride respectively. Fig. 59 also shows how the temperature
Figure 59. Results from thermal study.
of the aluminum thimble being exposed to these corrosive solutions varied with time.
DISCUSSION

Electrochemical measurements have been utilized by many researchers interested in determining corrosion rates of metals in aqueous environments. Attempts to utilize electrochemical measurements in this project when non-aqueous systems were involved were unsuccessful.

The first technique, which involved measuring the resistance of a corroding aluminum wire with time, failed to provide useful results. The resistance of the aluminum remained constant with time until the aluminum wire broke. This is believed to have occurred because the reaction of aluminum with mercuric chloride deposits metallic mercury on the surface of the aluminum. The loss of conductivity of the aluminum due to corrosion was possibly being compensated for by the formation of metallic mercury on the aluminum surface.

Attempts to monitor variations in the potential of aluminum electrodes in a solvent saturated with mercuric chloride were also unsuccessful and probably ill-conceived. Our system was simply inappropriate for measuring the potential change at the surface of the aluminum in high resistance, non-aqueous systems.

The last approach was undertaken in an effort to avoid the problem caused by organic solvents having a low conductivity. The aluminum wire was allowed to corrode in organic solvents saturated with mercuric chloride for varying amounts of time. At the conclusion of the soak time the potential of the aluminum electrode was measured in an aqueous solution. The results of this procedure, though it failed to provide a measurable potential/time response, still proved interesting. When the
aluminum was soaked in pure solvent for any amount of time, its electrode potential was always around -1000 mV. When the aluminum was exposed to mercuric chloride for any length of time the potential of the aluminum electrode changed to approximately -1500 mV. This suggests that at least the surface corrosion of aluminum by mercuric chloride occurs quickly, and that the corrosion product specie(s) is/are independent of solvent type.

Due to time constraints, only the feasibility of using a temperature measuring device in studying the corrosion of a metal in an organic solution was intended to be demonstrated. Lessons learned in this cursory study are that ambient heat losses and heat losses due to solvent evaporation are important variables.

When comparing the results of the three solvents tested, the magnitude of the temperature change is not significant, because sample concentration was not standardized. The initial slope of the temperature-time plots is believed to be proportional to the reaction rate. As graphed, a small slope represents a large temperature change in a small time interval. If was not surprising that the methanol test graph had the smallest initial slope in the light of how well methanol performed in previous tests. In comparing 2,4-pentanedione and dimethylformamide, the 2,4-pentanedione solution had the larger initial rate of attack, but after reaching a maximum temperature, the temperature of the aluminum returned to an ambient value rapidly. The dimethylformamide solution, although not as effective in corroding the aluminum initially, seems to be able to continue corroding the aluminum for a longer period of time. This is based on the fact that the aluminum in the dimethylformamide test remained at an elevated
temperature for the longest period of time. The extent of corrosion
damage is proportional to the total heat flux produced which should be
proportional to the area under the temperature-time graph.
CONCLUSIONS

We can only conclude from this effort that electrochemical techniques are unlikely candidates for measuring corrosion rates in organic systems.

Of some significance, though, is the suggestion that products of mercuric chloride corrosion of aluminum are relatively independent of solvent type. This is an important find because if it prevails, it simplifies the problem of how to maximize the total corrosive damage done to an aluminum surface. The damage to an aluminum barrier should be only a function of the amount of mercuric chloride getting to the aluminum surface, and independent of the nature of the solvent. This does not suggest, however, that the rates of corrosion are independent. We have no evidence to date to either support or counter this suggestion.

The thermal study showed that studying the corrosion of a metal in an organic media by measuring the temperature of the metal as a function of time is feasible. The corrosion of aluminum by methanol, 2,4-pentanedirole, and dimethylformamide, each saturated with mercuric chloride, was studied by this technique. The methanol solution produced the greatest initial temperature change per unit time of the solvents studied. The dimethylformamide solution produced damage for the longest period of time of the solvents examined.
RECOMMENDATIONS

Clearly, electrochemical techniques seem to hold little promise for future study.

Due to the added complication caused by the production of metallic mercury on the surface of the aluminum by mercuric chloride, weight loss studies, or studies based on measuring a change in the resistance of a corroding aluminum wire, are also not recommended for future study.

Thermal measurements using the apparatus shown in Fig. 58 appear best suited for a continued study of the corrosion of metals in an organic solvent. An extension of the work done here would be to paint the inside of the aluminum thimbles, in hope of gaining the ability to determine the rate of diffusion of inorganic compounds in organic solvents through polymers.
PART IV
INTRODUCTION

The corrosivity of mercuric chloride was compared to mercuric acetate, mercuric nitrate, and mercuric bromide. Mercuric nitrate was chosen to compare to mercuric chloride to see what affect the increased ionic character of mercuric nitrate would have on test results. Mercuric acetate was chosen to see if its increased organic character and size would affect test results. Mercuric bromide was chosen to compare to mercuric chloride to see if it would perform similarly to mercuric chloride.

A second consideration was the interaction of dimethylsulfoxide and dimethylformamide with various other mercury salts. This was of interest based upon the evidence demonstrated in Part II suggesting that mercuric chloride might react to form organic mercury compounds with dimethylformamide and dimethylsulfoxide.
RESULTS

Activity of mercuric compounds on aluminum

The corrosive action of "dry" mercuric chloride, mercuric bromide, mercuric nitrate, and mercuric acetate was tested by applying the salts directly to the aluminum surface at ambient conditions of temperature and humidity. The activity of mercuric chloride and mercuric bromide was evidenced by the formation of greyish spores on the aluminum surface. In the case of mercuric nitrate or mercuric acetate there was very little damage done to the surface of the aluminum.

Effect of stress on the corrosive attack of aluminum by mercury-containing compounds.

Saturated solutions of mercuric acetate, mercuric nitrate, mercuric chloride, and mercuric bromide in methanol were prepared. These solutions were applied to an aluminum surface, and the time required for the solution to penetrate through the aluminum was recorded. The time required for penetration was defined as the time necessary for the mercuric chloride to visually corrode through the aluminum surface. This procedure was then altered by the addition of a tensile stress to the aluminum surface being tested. The stress was applied by hanging a loose weight from the aluminum foil during the penetration test. Fig. 60 shows the apparatus used in this procedure. Stress did not alter the penetration times for mercuric chloride/methanol and mercuric bromide/methanol systems, but the relative times for both mercuric acetate/methanol and mercuric nitrate/methanol systems were decreased. Data is shown in Table XI.
Table XI

Effect of stress on penetration times

<table>
<thead>
<tr>
<th></th>
<th>Without Stress</th>
<th>With Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>mercuric chloride</td>
<td>228 sec</td>
<td>243 sec</td>
</tr>
<tr>
<td>mercuric bromide</td>
<td>180 sec</td>
<td>190 sec</td>
</tr>
<tr>
<td>mercuric nitrate</td>
<td>170 sec</td>
<td>630 sec</td>
</tr>
<tr>
<td>mercuric acetate</td>
<td>180 sec</td>
<td>430 sec</td>
</tr>
</tbody>
</table>

Figure 60. Tests on stressed aluminum.
Effect of abrasion

Tests were performed to determine what effect scratching the surface of the aluminum foil would have on the ability of methanol solutions saturated with mercury-containing compounds to penetrate through an aluminum barrier. The aluminum foil was abraded by manually rubbing a stainless steel spatula over the aluminum surface for about one minute. This mechanical abrasion, presumably of the oxide layer, had little effect on the penetration time of mercuric chloride/methanol systems, but in the case of mercuric nitrate/methanol the time was reduced.

Chemistry of mercury-containing compounds in dimethylsulfoxide and dimethylformamide

Saturated solutions of mercuric acetate, mercuric bromide, and mercuric nitrate in dimethylsulfoxide and dimethylformamide were prepared. These solutions were heated to dryness, and infrared spectra of the remaining residues were taken as nujol mulls.

Comparative spectra of mercuric acetate and the dried residue from a dimethylformamide solution saturated with mercuric acetate, as well as the dried residue from a dimethylsulfoxide solution saturated with mercuric acetate are shown in Figs. 61, 62, and 63. Figs. 64 through 66 are similar to the last three figures, except mercuric bromide was substituted for mercuric acetate. Figs. 67 through 69 show the spectrum of mercuric nitrate, the solid residue from a dimethylformamide solution saturated with mercuric nitrate, and the infrared spectrum of the dried residue from a saturated solution of mercuric nitrate in dimethylsulfoxide, respectively.
Figure 61. Infrared spectrum of mercuric acetate and nujol.

Figure 62. Infrared spectrum of residue from mercuric acetate and dimethylformamide.
Figure 63. Infrared spectrum of residue from mercuric acetate and dimethylsulfoxide.

Figure 64. Infrared spectrum of mercuric bromide and nujol.
Figure 65. Infrared spectrum of residue from mercuric bromide and dimethylformamide.

Figure 66. Infrared spectrum of residue from mercuric bromide and dimethylsulfoxide.
Figure 67. Infrared spectrum of mercuric nitrate and nujol.

Figure 68. Infrared spectrum of residue from mercuric nitrate and dimethylformamide.
Figure 69. Infrared spectrum of residue from mercuric nitrate and dimethylsulfoxide.
DISCUSSION

Activity of mercury-containing compounds on aluminum

Based upon the fact that mercuric chloride and mercuric bromide were corrosive to aluminum when applied directly on the aluminum surface, it was concluded that mercuric chloride and mercuric bromide had similar corrosive properties. Both mercuric chloride and mercuric bromide had the ability to get through the oxide layer quickly and damage the metal underneath. Mercuric nitrate and mercuric acetate did not have the ability to get through an oxide layer. The ability of mercuric bromide and mercuric chloride to get through an oxide layer might be due to their molecular nature. It is likely that a molecular species would have a higher solubility in an oxide layer than would an ionic compound. The more ionic mercuric nitrate and mercuric acetate would therefore have greater difficulty penetrating through an oxide layer.

Effect of stress on the corrosive attack of aluminum by mercury-containing compounds

From the results of the procedure, which tested the effect of stress on the corrosive attack by mercury-containing compounds of aluminum, it was concluded that stress only significantly affected the penetration times of methanol solutions saturated with mercuric acetate or mercuric nitrate. Stress did not significantly affect the penetration times of methanol solutions saturated with mercuric bromide or mercuric chloride. It is not believed that stress is an actual
variable of importance in the corrosive attack of aluminum by mercury-containing compounds. The importance of stress as a variable is believed to be due to an interplay between stress and the integrity of the oxide layer. It is hypothesized that stress could cause cracks in the oxide layer, which would allow for easier attack of the aluminum by mercuric acetate or mercuric nitrate. For saturated solutions of mercuric chloride and mercuric bromide in methanol, stress would not be as important due to the apparent ability of these solutes to disrupt oxide layers. It is of interest to note that in these tests it was observed that the aluminum was most severely attacked by the methanol solution of mercuric nitrate. This can be interpreted as indication that the mercuric ion is the active corrosive agent, and therefore ionic mercury-containing compounds are more capable of attacking aluminum than mercury-containing compounds which are more covalent in nature.

Effect of scratching the surface of the aluminum

The results of this test indicated that scratching the surface of the aluminum altered penetration times of mercuric nitrate/methanol systems more than mercuric chloride/methanol systems. This is consistent with the thought that mercuric chloride is more inclined to disrupt the oxide than is mercuric nitrate.

Chemistry of mercury-containing compounds in dimethyl sulfoxide and dimethylformamide

The infrared spectrum of the dried residue from a saturated solution of mercuric acetate in dimethylformamide showed slight variations from the infrared spectrum of mercuric acetate. It is difficult to draw conclusions from this however, because the spectrum of mercuric acetate already has peaks in the 1500-1600, and 900-1050
frequency regions. It is in these wavelength regions that possible evidence of a dimethylformamide-mercuric chloride species exists. There is a variation in the spectrum between mercuric acetate and the residue in the 1500-1600 region, but due to the mercuric acetate peaks, it is hard to draw conclusions about peaks in this frequency region.

The infrared spectrum of the dried residue from a saturated solution of mercuric acetate in dimethylsulfoxide varied from the infrared spectrum of mercuric acetate. The frequency region between 950 and 1050, the region of most interest in studying possible dimethylsulfoxide-mercuric chloride compounds, is crowded with mercuric acetate peaks. This makes any conclusions concerning dimethylsulfoxide-mercuric acetate compounds difficult.

The infrared spectrum of the dried residue from a saturated solution of mercuric bromide in dimethylformamide varied from the infrared spectrum of mercuric bromide. There were unexplained peaks at 1652 and at about 1000. Fig. 70 shows the similarity between the residue from a dimethylformamide solution containing mercuric chloride and a dimethylformamide solution containing mercuric bromide. Fig. 71 shows that the effect of adding water to a saturated solution of mercuric chloride in dimethylformamide is similar to the effect of adding water to a saturated solution of mercuric bromide in dimethylformamide. Key unexplained peaks at 1558, 1008, and 811 are common to both spectra.

The infrared spectrum of the solid residue from a saturated solution of mercuric bromide in dimethylsulfoxide differs from the infrared spectrum of mercuric bromide. This is shown in Fig. 66. Fig. 72 shows the similarity between the infrared spectrum of the solid
Figure 70. Comparison between residue from a mercuric chloride and dimethylformamide solution and residue from a mercuric bromide and dimethylformamide solution.

Figure 71. Effect of adding water to dimethylformamide solutions saturated with either mercuric chloride or mercuric bromide.
Figure 72. Comparison between residue from mercuric chloride/dimethylsulfoxide with residue from mercuric bromide/dimethylsulfoxide.
residue obtained from a solution of dimethylsulfoxide saturated with mercuric bromide and the infrared spectrum of the solid residue obtained from a solution of dimethylsulfoxide saturated with mercuric chloride. In both spectra there are key unexplained peaks at 1018 and 941.

There were no key differences between the infrared spectrum of the solid residue obtained from a saturated solution of mercuric nitrate in dimethylformamide and the infrared spectrum of mercuric nitrate. The mercuric nitrate spectrum has additional peaks that the residue does not, because the mercuric nitrate used was hydrated. The additional peaks in the spectrum of mercuric nitrate are due to water.

There were significant differences between the infrared spectrum of the solid residue obtained from a saturated solution of mercuric nitrate in dimethylsulfoxide and the infrared spectrum of mercuric nitrate. There is an unexplained peak at 942 in the infrared spectrum of the residue that is common to the infrared spectrum of the residue from a saturated solution of mercuric chloride in dimethylsulfoxide.
CONCLUSIONS

Both mercuric chloride and mercuric bromide are active on an aluminum surface when applied directly to the surface. Mercuric nitrate and mercuric acetate are not able to effectively corrode an aluminum surface when they are applied directly to the surface. This is believed to be due to the covalent nature of mercuric chloride and mercuric bromide somehow aiding these molecules' ability to lift oxide layers.

Addition of tensile stress was found to assist saturated methanol solutions of mercuric acetate and mercuric nitrate penetrate through the aluminum barrier. Tensile stress was not found to be a significant factor in penetration times through aluminum by saturated methanol solutions of mercuric chloride and mercuric bromide. It is believed that the addition of stress helped to create defects in the oxide layer of aluminum, which would help mercuric acetate and mercuric nitrate to corrode aluminum.

Likewise, mechanically scratching off the oxide layer only greatly affected the penetration times of methanol solutions saturated with mercuric nitrate or mercuric acetate. The ability of mercuric nitrate and mercuric acetate to corrode an oxide-free aluminum surface, suggests that the mercuric ion is probably the active species on free aluminum.

Solid residues obtained from solutions of mercuric bromide in dimethylformamide or dimethylsulfoxide were shown to have infrared spectra similar to solid residues obtained from solutions of mercuric chloride in dimethylsulfoxide or dimethylformamide.
The infrared spectra of residues obtained from saturated solutions of mercuric acetate in dimethylformamide or dimethylsulfoxide, did not produce results from which conclusions could be drawn.

The infrared spectrum of the solid residue obtained from a saturated solution of mercuric nitrate in dimethylformamide did not differ from the infrared spectrum of mercuric nitrate. This indicates that mercuric nitrate and dimethylformamide do not form an organic mercuric compound.

The infrared spectrum of the solid residue obtained from a saturated solution of mercuric nitrate in dimethylsulfoxide was similar to the infrared spectrum of the solid residue obtained from a saturated solution of mercuric chloride in dimethylsulfoxide.
RECOMMENDATIONS

It is recommended that penetration tests using the apparatus described in Part I, namely TEA2, be performed using solvent systems containing both mercuric chloride and mercuric nitrate. The mercuric chloride would be a good component to have in a solvent system designed to minimize the time of penetration through a painted barrier due to its established ability to penetrate through an oxide layer. Mercuric nitrate would be a good component to include in a solvent system designed to minimize the time of penetration through a painted barrier due to its ability to corrode an exposed aluminum surface. Including a reducing agent, or perhaps an acid capable of attacking the oxide layer in the solvent system are also schemes that might be worth examining. Results of this part of the research project suggested that the mercuric ion is active in corroding aluminum, and thus the fairly ionic mercuric nitrate might be a desirable contributor to the ability of a solvent system to penetrate a coated barrier.

It might also prove useful to study more mercury-containing compounds, to test whether any evidence could be found for the existence of more mercury-dimethylformamide compounds or additional mercury-dimethylsulfoxide compounds. The potential gain would be a better understanding of the chemistry of mercury-containing compounds.
REFERENCES


10. Ibid, 2, 3.

11. Ibid, 23.


15. Ibid, 35.


20. Ibid. 37.