



Faculty Of Science

# **Physico-Chemical Studies of Some Polymeric-based Paints**

*Submitted by*

**Haydi Bahig Kamal Aziz**

*(B.Sc. in Chemistry)*

**For The Award of The M.Sc. Degree in  
Chemistry**

**To  
Chemistry Department  
Faculty of Science  
Ain Shams University  
Cairo, Egypt  
2009**

# **Physico-Chemical Studies of Some Polymeric-based Paints**

M.Sc. Thesis  
(Chemistry)

*Supervised by*

**Prof. Dr. Mohamed Ahmed Mohamed  
Mekewi**

*Professor of Physical Chemistry, Faculty of Science,  
Ain Shams University*

**Prof. Dr. Maged Shafik Antonious**

*Professor of Physical Chemistry, Faculty of Science,  
Ain Shams University*

**Prof. Dr. Abdel-Fattah Mohsen Badawi**

*Professor of Petrochemicals, Egyptian Petroleum  
Research Institute, Nasr City, Cairo*

## **APPROVAL SHEET**

# **Physico-Chemical Studies of Some Polymeric-based Paints**

By

**Haydi Bahig Kamal Aziz**  
(B.Sc. in Chemistry)

**This thesis for Master Degree has been approved by:**

**Prof. Dr. Mohamed Ahmed Mohamed Mekewi.**

**Prof. Dr. Maged Shafik Antonious.**

**Prof. Dr. Abdel-Fattah Mohsen Badawi.**

**Head of Department**

**Prof. Dr. Fakhry Abd-El Aziz El-Basiony**

## **Acknowledgments**

Thanks first and last to **Allah** for the utmost help and support during this work.

I am greatly indebted to **Prof. Dr. Mohamed A. M. Mekewi**, professor of physical chemistry, Faculty of Science, Ain Shams University, for suggesting the point, his supervision, valuable leading comments during the progress of this work and critical reading and reviewing of this work.

The author is also grateful to **Prof. Dr. Maged S. Antonious**, professor of physical chemistry, Faculty of Science, Ain Shams University and Prof. Dr. **Abdel-Fattah M. Badawi**, professor of petrochemicals, Egyptian Petroleum Research Institute, Nasr City, Cairo, for their supervision, stimulating guidance, valuable discussion and suggestions.

The author is also grateful to **Dr. Khaled Zakaria**, lecturer of microbiology, Faculty of Science, Ain Shams University, for participating in the analysis of samples, his supervision, valuable discussion and suggestions.

The author is also grateful to **Prof. Dr. Sahar Ahmed**, professor of petrochemicals, Egyptian Petroleum

Research Institute, Nasr City, Cairo and **Dr. Trease Albert**, lecturer of inorganic chemistry, Faculty of Science, Ain Shams University, for participating in the synthesis of different compounds, their supervision, valuable discussion and suggestions.

My thanks are also passed to the staff members and colleagues of chemistry department, Egyptian Petroleum Research Institute, petroleum Pipes Company, Moustorood and Yasmo Misr Company for the various help they offered me throughout this study.

Sincere thanks are also due to **my Family** who supported me greatly during the preparation of this work.

# List of Contents

| Content.                                                        | page |
|-----------------------------------------------------------------|------|
| <b><u>List of Figures</u></b> .....                             | V    |
| <b><u>List of Tables</u></b> .....                              | IX   |
| <b><u>Abstract</u></b> .....                                    | XI   |
| <b><u>Chapter 1- Introduction</u></b> .....                     | 1    |
| 1. History and Overview.....                                    | 1    |
| • Earliest Record of Painting.....                              | 1    |
| • Lost in the Dark Ages.....                                    | 2    |
| • Renaissance Revival.....                                      | 2    |
| Importance of Paints.....                                       | 3    |
| 1. Composition of Paints and Coatings.....                      | 5    |
| 1.1. Binder.....                                                | 6    |
| 1.2. Pigments.....                                              | 21   |
| 1.3. Solvents and Thinners.....                                 | 24   |
| 1.4. Additives.....                                             | 30   |
| 2. Types of Paints.....                                         | 32   |
| 2.1. Emulsion Paint System (Water-based Paint).....             | 32   |
| 2.2. Solvent Free Solid System (Powder Coating).....            | 36   |
| 2.3. Solvent-based System.....                                  | 37   |
| 2. Literatures Survey.....                                      | 39   |
| 1. Epoxy Resins.....                                            | 39   |
| 2. Curing of Epoxy Resin by using Cycloaliphatic Polyamine..... | 48   |
| 3. Coating Application of Cured Epoxy Resins.....               | 50   |
| 4. Additives and Response to Epoxy Resins.....                  | 53   |
| <b><u>Aim of the Present Work</u></b> .....                     | 71   |

|                                                                    |           |
|--------------------------------------------------------------------|-----------|
| <b><u>Chapter 2- Experimental and Techniques.....</u></b>          | <b>72</b> |
| <b>2.1. Materials.....</b>                                         | <b>72</b> |
| <b>2.2. Preparation and Synthesis.....</b>                         | <b>72</b> |
| <b>2.2.1. Surface Preparation of Test Specimens.....</b>           | <b>72</b> |
| <b>2.2.2. Synthesis of Epoxy Paint Additives.....</b>              | <b>73</b> |
| <b>2.2.2.1. Synthesis of Amine Silicates.....</b>                  | <b>73</b> |
| <b>2.2.2.2. Synthesis of Bis-(diphenylthiocarbazono)</b>           |           |
| <b>mercury (II) Complex .....</b>                                  | <b>75</b> |
| <b>2.2.2.3. Synthesis of Salen Complexes .....</b>                 | <b>76</b> |
| <b>2.3. Methodology.....</b>                                       | <b>79</b> |
| <b>2.3.1. Preparation of Native Epoxy Paint .....</b>              | <b>79</b> |
| <b>2.3.2. Preparation of Modified Epoxy Paints.....</b>            | <b>79</b> |
| <b>2.3.2.1. Preparation of Epoxy Paint Modified by Amine</b>       |           |
| <b>Silicates.....</b>                                              | <b>79</b> |
| <b>2.3.2.2. Preparation of Epoxy Paint Modified by Hg</b>          |           |
| <b>(HDz)<sub>2</sub> Complex.....</b>                              | <b>83</b> |
| <b>2.3.2.3. Preparation of Epoxy Paint Modified by Salen</b>       |           |
| <b>Complexes .....</b>                                             | <b>83</b> |
| <b>2.3.3. Structural Conformation of Epoxy Paint Samples using</b> |           |
| <b>FT-IR Spectroscopy.....</b>                                     | <b>84</b> |
| <b>2.3.4. Preparation and Testing of Coating.....</b>              | <b>84</b> |
| <b>2.3.5. Physico-mechanical Properties.....</b>                   | <b>85</b> |
| <b>2.3.6. Thermo-gravimetric Analysis (TGA).....</b>               | <b>85</b> |
| <b>2.3.7. Chemical Resistance.....</b>                             | <b>85</b> |
| <b>2.3.8. Kinetics Study.....</b>                                  | <b>86</b> |
| <b>2.3.9. Photo Stability .....</b>                                | <b>86</b> |
| <b>2.3.10. Anti-microbial Activity.....</b>                        | <b>87</b> |

|                                                                                                                      |           |
|----------------------------------------------------------------------------------------------------------------------|-----------|
| 2.3.10.1. Bacterial Clinical Isolates.....                                                                           | 87        |
| 2.3.10.2. Growth and Maintenance of Bacterial Clinical Isolates.....                                                 | 88        |
| 2.3.10.3. Preparation of Bacterial Inoculum.....                                                                     | 88        |
| 2.3.10.4. Identification of Clinical Isolates.....                                                                   | 88        |
| 2.3.10.5. Preparation of Paint Discs.....                                                                            | 89        |
| 2.3.10.6. Bacterial Sensitivity Test.....                                                                            | 89        |
| <b>Chapter 3- Results and Discussion.....</b>                                                                        | <b>91</b> |
| 3.1. Structural Conformation (FT-IR) Studies.....                                                                    | 91        |
| 3.1.1. Native Epoxy Paint and its Components Profiles.....                                                           | 92        |
| 3.1.2. Epoxy paint in Presence of n-Decylamine Silicate:CoCl <sub>2</sub> (DAS:CoCl <sub>2</sub> )Profile.....       | 92        |
| 3.1.3. Epoxy Paint in Presence of Bis-(diphenylthiocarbazono) mercury(II) complex (Hg (HDz) <sub>2</sub> ).....      | 97        |
| 3.1.4. Epoxy Paint in Presence of (2-Amino-1-(4-nitrophenyl)-1, 3-propandiol Silicate (APDS:CoCl <sub>2</sub> )..... | 100       |
| 3.1.5. Epoxy Paint in Presence of (3-Amino-1, 2, 4-triazole Silicate (ATS: CoCl <sub>2</sub> ).....                  | 101       |
| 3.1.6. Epoxy Paint in Presence of Different Complexes.....                                                           | 103       |
| 3.2. Physico-mechanical Properties.....                                                                              | 108       |
| 3.3. Thermo-gravimetric Analysis (TGA).....                                                                          | 112       |
| 3.4. Chemical Resistance.....                                                                                        | 120       |
| 3.4.1. Resistance to Acids Attack.....                                                                               | 120       |
| 3.4.2. Resistance to Alkali Attack.....                                                                              | 123       |
| 3.4.3. Resistance to Artificial Sea Water.....                                                                       | 127       |
| 3.5. The Kinetics Study.....                                                                                         | 130       |
| 3.6. Photo Stability .....                                                                                           | 134       |
| 3.7. Anti-microbial Activity.....                                                                                    | 136       |



|                                 |     |
|---------------------------------|-----|
| <b><u>Conclusions</u></b> ..... | 147 |
| <b><u>References</u></b> .....  | 149 |
| <b><u>Arabic Summary</u></b>    |     |

## List of Figures

| Figure.                                                                               | Page |
|---------------------------------------------------------------------------------------|------|
| Fig. (1a) FT-IR spectra of epoxy resin.....                                           | 91   |
| Fig. (1b) FT-IR spectra of hardener.....                                              | 91   |
| Fig. (1c) FT-IR spectra of native epoxy paint.....                                    | 91   |
| Fig. (2a) FT-IR spectra of DAS .....                                                  | 93   |
| Fig. (2b) FT-IR spectra of epoxy paint in presence of DAS:CoCl <sub>2</sub> .....     | 93   |
| Fig. (3a) FT-IR spectra of Hg (HDZ) <sub>2</sub> .....                                | 97   |
| Fig. (3b) FT-IR spectra of epoxy paint in presence of Hg (HDZ) <sub>2</sub> .....     | 97   |
| Fig. (4a) FT-IR spectra of APDS.....                                                  | 101  |
| Fig. (4b) FT-IR spectra of epoxy paint in presence of APDS: CoCl <sub>2</sub> .....   | 101  |
| Fig. (5a) FT-IR spectra of AT silicate.....                                           | 102  |
| Fig. (5b) FT-IR spectra of epoxy paint in presence of ATS: CoCl <sub>2</sub> .....    | 102  |
| Fig. (6a) FT-IR spectra of Cobalt Salen (1:1) complex.....                            | 104  |
| Fig. (6b) FT-IR spectra of epoxy paint in presence of Cobalt Salen (1:1) complex..... | 104  |
| Fig. (7a) FT-IR spectra of Cobalt Salen (1:2) complex.....                            | 105  |
| Fig. (7b) FT-IR spectra of epoxy paint in presence of Cobalt Salen (1:2) complex..... | 105  |
| Fig. (8a) FT-IR spectra of ferric Salen (1:1) complex.....                            | 106  |
| Fig. (8b) FT-IR spectra of epoxy paint in presence of ferric Salen                    |      |

|                                                                                                                                   |            |
|-----------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>(1:1) complex.....</b>                                                                                                         | <b>106</b> |
| <b>Fig. (9a) FT-IR spectra of ferric Salen ABZ (1:1:1) complex.....</b>                                                           | <b>107</b> |
| <b>Fig. (9b) FT-IR spectra of epoxy paint in presence of ferric Salen ABZ (1:1:1) complex.....</b>                                | <b>107</b> |
| <b>Fig. (10a) Thermo-gravimetric analysis of native epoxy paint.....</b>                                                          | <b>112</b> |
| <b>Fig. (10b) Thermo-gravimetric analysis of epoxy paint in presence of DAS:CoCl<sub>2</sub> .....</b>                            | <b>112</b> |
| <b>Fig. (10c) Thermo-gravimetric analysis of epoxy paint in presence of (Hg (HDz)<sub>2</sub>).....</b>                           | <b>112</b> |
| <b>Fig. (11d) Thermo-gravimetric analysis of epoxy paint in presence of ADPS:CoCl<sub>2</sub>.....</b>                            | <b>118</b> |
| <b>Fig. (11e) Thermo-gravimetric analysis of epoxy paint in presence of ATS:CoCl<sub>2</sub>.....</b>                             | <b>118</b> |
| <b>Fig. (11f) Thermo-gravimetric analysis of epoxy paint in presence of Fe Sal ABZ.....</b>                                       | <b>118</b> |
| <b>Fig. (12g) Thermo-gravimetric analysis of epoxy paint in presence of Co Sal1.....</b>                                          | <b>119</b> |
| <b>Fig. (12h) Thermo-gravimetric analysis of epoxy paint in presence of Co Sal2.....</b>                                          | <b>119</b> |
| <b>Fig. (12i) Thermo-gravimetric analysis of epoxy paint in presence of Fe Sal.....</b>                                           | <b>119</b> |
| <b>Fig. (13) Relationship between the weight loss % of immersed paint samples and immersion time in 10% HCl acid solution ...</b> | <b>123</b> |
| <b>Fig. (14) Relationship between the weight loss % of immersed</b>                                                               |            |

|                                                                                                                                                                                                                                                                                                                                                                          |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| paint samples and immersion time in 5% NaOH solution .....                                                                                                                                                                                                                                                                                                               | 126 |
| Fig. (15) Relationship between the weight loss% of immersed paint samples and immersion time for artificial sea water resistance.....                                                                                                                                                                                                                                    | 129 |
| Fig. (16) The visible absorption spectra of $(1.7 \times 10^{-5})$ M Hg (HDz) <sub>2</sub> in benzene at 30 °C.....                                                                                                                                                                                                                                                      | 130 |
| Fig. (17) Plot of $\ln (A_t - A_\infty)$ at $\lambda=620$ nm vs. time in dry benzene at 30 °C.....                                                                                                                                                                                                                                                                       | 133 |
| Fig. (18) Plot of $\ln (A_\infty - A_t)$ at $\lambda=480$ nm vs. time in dry benzene at 30 °C.....                                                                                                                                                                                                                                                                       | 134 |
| Fig. (19) The photo stability of Hg (HDz) <sub>2</sub> complex solution.....                                                                                                                                                                                                                                                                                             | 135 |
| Fig. (20) The photo stability of epoxy paint modified by Hg (HDz) <sub>2</sub> .....                                                                                                                                                                                                                                                                                     | 136 |
| Fig. (21) Antimicrobial activities of paints against 10 clinical isolates. V <sub>b</sub> , paint discs impregnated with Hg (HDz) <sub>2</sub> , II <sub>c</sub> , paint discs impregnated with DAS: CoCl <sub>2</sub> .....                                                                                                                                             | 139 |
| Fig. (22) Antimicrobial activities of paints against (A) <i>Staphylococcus aureus</i> Sa1, (B) <i>Staphylococcus aureus</i> Sa2. V <sub>b</sub> , paint disc impregnated with Hg (HDz) <sub>2</sub> , II <sub>c</sub> , paint disc impregnated with DAS: CoCl <sub>2</sub> . 1: DAS, 2: DAS: CoCl <sub>2</sub> , 3: CoCl <sub>2</sub> and 4: Hg (HDz) <sub>2</sub> ..... | 140 |
| Fig. (23) Antimicrobial activities of paints against A) <i>Staphylococcus aureus</i> Sa3, B) <i>Staphylococcus aureus</i> Sa4. V <sub>b</sub> , paint disc impregnated with Hg (HDz) <sub>2</sub> , II <sub>c</sub> , paint disc impregnated with DAS: CoCl <sub>2</sub> . 1: DAS, 2: DAS: CoCl <sub>2</sub> , 3: CoCl <sub>2</sub> and 4: Hg (HDz) <sub>2</sub> .....   | 141 |

**Fig. (24) Antimicrobial activities of paints against A) *Pseudomonas aeruginosa* Pa1, B) *Pseudomonas aeruginosa* Pa2. V<sub>b</sub>, paint disc impregnated with Hg (HDz)<sub>2</sub>, II<sub>c</sub>, paint disc impregnated with DAS: CoCl<sub>2</sub>.....** 142

## List of Tables

| Table                                                                                                                                                        | Page |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Table (1) The Composition of Different Additives .....                                                                                                       | 74   |
| Table (2) Native and Modified Epoxy Paint Samples at Varied Concentration for Effectiveness Optimization .....                                               | 80   |
| Table (3) The Active Groups of (a) Epoxy Resin, (b) Polyamine Hardener and (c) Native Epoxy Paint and their Position in FT-IR Spectra.....                   | 92   |
| Table (4) The Active Groups of (a) DAS Compound and (b) Epoxy Paint in presence of DAS:CoCl <sub>2</sub> and their Position in FT-IR Spectra.....            | 94   |
| Table (5) The Active Groups of (a) Hg (HDz) <sub>2</sub> and (b) Epoxy Paint in presence of Hg (HDz) <sub>2</sub> and their Position in FT-IR Spectra.....   | 98   |
| Table (6) Mechanical Properties of Epoxy Painted Samples.....                                                                                                | 108  |
| Table (7) Thermo-gravimetric Studies (TGA) of Epoxy Paint Samples.....                                                                                       | 113  |
| Table (8) Effect of 10% HCl acid on Epoxy Paint by Weight Loss (W L).....                                                                                    | 121  |
| Table (9) Effect of 5 % Sodium hydroxide on Epoxy paint by weight Loss (W L).....                                                                            | 124  |
| Table (10) Effect of Corrosion by Artificial Sea Water on Epoxy Paint Samples.....                                                                           | 127  |
| Table (11) Kinetics of The Return Rate of (1.7x10 <sup>-5</sup> )M Hg (HD <sub>z</sub> ) <sub>2</sub> in Pure Dry Benzene at 30 °c at Wavelength 620 nm..... | 132  |

|                                                                                                                                                                             |            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b>Table (12) Kinetics of The Return Rate of <math>(1.7 \times 10^{-5})</math> M Hg <math>(\text{HD}_2)_2</math> in Pure Dry Benzene at 30 °c at Wavelength 480 nm.....</b> | <b>133</b> |
| <b>Table (13) Diameter of Inhibition Zones of Paint Discs (cm) against 10 Clinical Isolates.....</b>                                                                        | <b>138</b> |
| <b>Table (14) Diameter of Inhibition Zones of Different Antibiotics (cm) against 30 Clinical Isolates.....</b>                                                              | <b>143</b> |