

كلية العلوم / قسم الكيمياء

# Using of Polyurethane as Surface Coating Material

A Thesis Submitted for fulfillment of the requirements for the Degree of Master In Science (Chemistry)

By

Ahmed Hamed Ammar Sayed

B. Sc. (Chemistry), Ain shams University

To

Department of Chemistry Faculty of Science Ain shams University

2012



# البولى يوريثان كمادة طلاء سطحية

رساله مقدمه للحصول على درجه الماجستير في العلوم ( كيمياء )

مقدمه من

الطالبم/ أحمد حامد عمار سيد بكالوريوس العلوم (كيمياء) جامعه عين شمس

الي

کلیه العلوم — هسم الکیمیاء جامعه عین شمس

2012



### APPROVAL SHEET FOR SUBMISSION

## • Title of [M. Sc.] Thesis:

Using of polyurethane as surface coating material

### • Name of the Candidate:

### **Ahmed Hamed Ammar Sayed**

B. Sc. (Chemistry), Ain shams University (2006)

This thesis has been approved for submission by the supervision:

### 1- Dr. Gamal Abdel-Aziz Meligi

Assist Professor of organic chemistry, Faculty of Science, Ain shams University.

#### 2- Dr. Hussein Hussein Elnahas

Assist Professor of Radiation Chemistry - National Center for Radiation Research and Technology (NCRRT)-Atomic Energy Authority.

Head of Chemistry Department Prof. Dr. Maged Shafik Antonious

#### Acknowledgement

Praise is to Allah, who guided me to do this; and in no way could I have been guided, unless Allah has guided me.

Heartily, I wish to express my deep thanks and gratitude to *Dr. Gamal Abdel-Aziz Meligi*, Assist Professor of organic chemistry, Faculty of Science, Ain shams University, for his supervision, revision of the thesis and for his sincere advice.

Great thanks and gratitude to *Dr. Hussein Hussein Elnahas*, Assist Professor of Radiation Chemistry, National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority, for valuable helpful discussion, theoretical and experimental advice, and encouragement during the execution of this thesis.

I wish to express my thanks to the Department of Radiation Research of Polymer Chemistry (NCRRT), Egyptian Airports Company (EAC) –Ministry of Civil Aviation, Department of Chemistry–Faculty of science –Ain Shams university and also, Grandy Company of chemistry industrial - Egypt.

*My Parents* have a major influence along with their help in attaining my achievements. I would like to say thanks to them for the values and principles they have brought me on and in fact I dedicate this thesis to them.

Ahmed Hamed Ammar

## **ABBREVIATION**

| Symbol            | Nomenclature                                   |
|-------------------|--|
| PU                | Polyurethane                                   |
| TDI               | Toluene diisocyanate                           |
| polyol            | A substance containing several hydroxyl groups |
|                   | , A diol, triol and tetrol contain 2,3 and 4   |
|                   | hydroxyl groups respectively.                  |
| VAcVe             | vinyl acetate versatic ester copolymer         |
| Mg.silicate       | magnesium silicate                             |
| CaCO <sub>3</sub> | calcium carbonate                              |
| $TiO_2$           | titanium dioxide                               |
| rpm               | round per minute (stirring rate)               |
| Phr               | per hundred part                               |
| $T_b$             | Tensile strength at break                      |
| $E_b$             | Elongation at break                            |
| Mrad              | Mega-rad= 10 KGy                               |
| KGy               | Kilo-gray                                      |
| EB                | Electron beam                                  |
| DOP               | Dioctyl-phathalate                             |
| Shore A           | Is used with relatively soft material.         |
| Shore D           | Is used with slightly harder material.         |
| Composite         | A putting together of parts to form a whole.   |
| Solubility        | Capable of being dissolved in a liquid.        |
|                   |  |

| Crosslinking      | The establishment of chemical bonds between   |
|-------------------|---|
|                   | polymer molecule chains. It may be accomplished by heat, vulcanization, irradiation or the addition of a suitable chemical agent.   |
| Degradation       | The state of being reduced in polymer molecular chain. It may be accomplished by heat, vulcanization, irradiation or the addition of a suitable chemical agent.                           |
| PU- modeling clay | Polyurethane component mixed with either magnesium silicate or wood powder.   |
| Two-pack          | (Miscellaneous Technologies / Building) (of a paint, filler, etc.) supplied as two separate components, for example a base and a catalyst, that are mixed together immediately before use |

## **Contents**

| List of figures and tables                            | i   |
|---|-----|
| Aim of work   | vi  |
| Summary   | vii |
| CHAPTER (I): Introduction & Literature Review         |     |
| 1. Introduction                                       | 1   |
| 1.1. Polyurethane synthesis                           | 2   |
| 1.1.1. Flexible polyurethane foam                     | 4   |
| 1.1.2. Catalyst for polyurethane                      | 8   |
| 1.1.3. Cure rate                                      | 10  |
| 1.1.4. Raw materials                                  | 11  |
| 1.1.4.a. Isocyanates                                  | 11  |
| 1.1.4.b. Polyols                                      | 22  |
| 1.1.4.c. Alkyds                                       | 26  |
| 1.1.4.d. Castor oil                                   | 29  |
| 1.1.5. Vinyl acetate versatic ester copolymer         | 31  |
| 1.1.6. Additives                                      | 32  |
| 1.1.7. Extenders, fillers, and supplementary pigments | 37  |
| 1.2. Manufacturing                                    | 39  |
| 1.2.a. Dispensing equipment                           | 41  |
| 1.2.b. Tooling  | 42  |
| 1.3. Effect of Radiation                              | 42  |
| 1.3.1. Radiation-curing polymers                      | 44  |

| 1.4. Coating with polyurethane                          | 47 |
|---|----|
| 1.4.1. Polyurethane putties for wood repairing and      |    |
| cracks injection  | 54 |
| 1.4.2. Modeling of polyurethane composites mixing       | 55 |
| cycles  |    |
| 1.4.3. Polyurethane paint for outdoor application       | 56 |
| CHAPTER (II): Materials & Experimental                  |    |
| <b>Techniques</b>                                       |    |
| 2. Materials & Techniques                               | 63 |
| 2.1. Materials  | 63 |
| 2.2. Experimental Techniques                            | 64 |
| 2.2.1. Preparation of self hardening-modeling polyuret- |    |
| -hane for wood repairing and cracks injection           | 64 |
| 2.2.2. Preparation of polyurethane paint for outdoor    |    |
| application   | 66 |
| 2.2.3. Irradiation instruments                          | 66 |
| 2.2.3. a. Gamma cell                                    | 66 |
| 2.2.3. b. Electron Beam accelerator                     | 68 |
| 2.2.3. c. Direct sun light exposure                     | 70 |
| 2.2.4. Tensile strength and elongation at break         | 70 |
| 2.2.5. Compressive strength                             | 71 |
| 2.2.6. Film recovery                                    | 72 |
| 2.2.7. Tear strength                                    | 72 |

| 2.2.8. Surface hardness                                 | 73       |
|---|----------|
| 2.2.9. Water absorption                                 | 73       |
| 2.2.10. Solubility in solvent                           | 73       |
| 2.2.11. Thermal Ageing                                  | 74       |
| 2.2.12. Scanning Electron Microscope (SEM) Analysis     | 74       |
| <b>CHAPTER (III): Results &amp; Discussion</b>          |          |
| 3. Results and Discussion                               | 75       |
| 3.1.1. Polyurethane modeling –clay processing time      | 75       |
| 3.1.2. Morphology of polyurethane modeling-clay         | 77       |
| 3.1.3. Factors affecting polyurethane modeling-clay     |          |
| properties  | 79       |
| 3.1.3.a. Effect of toluene diisocyanate                 | 79       |
| 3.1.3.b. Effect of radiation hardness and               | 0.6      |
| compressive strength                                    | 82       |
| 3.1.3.c. Effect of radiation on water absorption of     | o =      |
| PU-modeling clay  | 85       |
| 3.1.4. Application of polyurethane modeling-clay        | 87       |
| 3.1.4.a. Wood repairing                                 | 87       |
| 3.1.4.b. Cracks injection                               | 88       |
| 3.1.4. c. Architectural views                           | 89       |
| 3.2. Preparation of polyurethane paint for outdoor      | 0.0      |
| application   | 90       |
| 3.2.1. Factors affecting the properties of polyurethane | <b>.</b> |
| paint   | 91       |

| 3.2.1.a. Effect of different types of polyols          | 91  |
|--|-----|
| 3.2.1.b. Effect of different types of fillers          | 97  |
| 3.2.1.c. Effect of solvent and plasticizer             | 102 |
| 3.2.2. Effect of high energy radiation                 | 105 |
| 3.2.3. Environmental and Aging properties              | 109 |
| 3.2.3.a. Effect of Temperature                         | 109 |
| -Strength properties at elevated temperature           | 113 |
| -Continued crystal growth                              | 114 |
| 3.2.4. Application of the prepared polyurethane paints | 115 |
| 3.2.4.a. Flooring hard                                 | 115 |
| 3.2.4.b. Semi-hard for wood and metals                 | 116 |
| 3.2.4.c. Elastic for sporting and athletic track       | 116 |
|  |     |
| References   | 117 |
|  |     |
| Summary in Arabic                                      |     |

# List of Figures, Tables and Schemes

| No. of<br>Figures | Title of figure   | No. of<br>Page |
|-------------------|---|----------------|
| (1)               | Effect of time on surface hardness of PU modeling clay (Modeling-curing time)                   | 76             |
| (2)               | Scanning electron microscope of PU modeling clay  | 77             |
| (3)               | Effect of TDI percent in TDI / polyol ratio on surface hardness of PU-modeling clay             | 80             |
| (4)               | Effect of TDI percent in TDI / polyol ratio on compressive strength of PU-modeling clay         | 81             |
| (5)               | Effect of different sources of radiation on surface hardness of PU-modeling clay full cure.     | 83             |
| (6)               | Effect of different sources of radiation on compressive strength of PU-modeling clay full cure. | 84             |
| (7)               | Effect of irradiation dose of gamma ray on water absorption of PU-modeling clay.                | 86             |
| (8)               | Photographic views show the application of PU- modeling clay                                    | 87,88,89       |
| (9)               | Effect of different types of polyol on surface hardness of polyurethane                         | 93             |

| (10) | Effect of different types of polyol on tensile strength (T <sub>b</sub> ) of polyurethane           | 94  |
|------|---|-----|
| (11) | Effect of different types of polyol on elongationat break (E <sub>b</sub> ) of polyurethane         | 95  |
| (12) | Effect of polyol percent on tear strength of polyurethane   | 96  |
| (13) | Effect of different types of filler on surface hardness of polyurethane                             | 98  |
| (14) | Effect of different types of filler on tensile strength (T <sub>b</sub> ) of polyurethane           | 99  |
| (15) | Effect of concentration of different types of filler on elongation at break $(E_b)$ of polyurethane | 100 |
| (16) | Effect of different filler concentration (phr) on tear strength of polyurethane                     | 101 |
| (17) | Effect of solvent on film recovery of polyurethane  | 103 |
| (18) | Effect of plasticizer on film recovery of polyurethane  | 104 |
| (19) | Effect of gamma irradiation dose on surface hardness of polyurethane                                | 106 |
| (20) | Effect of gamma irradiation dose on film recovery of polyurethane                                   | 107 |
| (21) | Effect of gamma irradiation dose on tear strength of polyurethane                                   | 108 |

List of Figure &Tables

| (22)          | Effect of aging time on surface hardness of polyurethane                   | 110            |
|---------------|--|----------------|
| (23)          | Effect of aging time on tensile strength (T <sub>b</sub> ) of polyurethane | 111            |
| (24)          | Effect of aging time on elongation at break ( $E_b$ ) of polyurethane      | 112            |
| (25)          | Photographic views show the application of polyurethane paints             | 115,116        |
| No. of tables | Title of tables  | No. of<br>Page |
| (1)           | Typical reactions and reaction conditions for isocyanates                  | 14             |
| (2)           | Composition of major oils used in surface coatings                         | 30             |
| (3)           | Some typical extenders   | 39             |
| (4)           | Blocked Isocyanates for One Component<br>System                            | 51             |
| (5)           | Typical Formulation of Polyurethane-<br>Modeling Clay                      | 65             |
| (6)           | Typical formulation of polyurethane paint based on polyether polyol        | 90             |

| No. of<br>Scheme | Title of Scheme  | No. of<br>Page |
|------------------|--|----------------|
| (1)              | Equations for preparation, chain extension, and curing of polyurethanes.   | 8              |
| (2)              | Reactions used in the manufacture of commercial isocyanates.(a) TDI. (b) PMDI and MDI. (c) Aliphatic triisocyanate | 14             |
| (3)              | Addition of alcohols to isocyanates.   | 15             |
| (4)              | Addition of primary amines to isocyanates.   | 15             |
| (5)              | Reaction of water with isocyanates.  | 16             |
| (6)              | Reaction of urethanes with isocyanates leading to allophanates.  | 16             |
| (7)              | Reaction of ureas with isocyanates leading to biurets.   | 17             |
| (8)              | Formation of isocyanurates.  | 17             |
| (9)              | Formation of uretdiones.   | 18             |
| (10)             | HDI biuret HDI isocyanurate HDI uretdione.   | 20             |
| (11)             | Reactions used in the manufacture of macroglycols.   | 23             |

#### List of Figure & Tables

| (12) | Schematic representation of glycerol alkyd polymer formation.   | 28 |
|------|---|----|
| (13) | The reaction pathway for the preparation of urethane derivative of polypropylene glycol.                                      | 35 |
| (14) | A possible reaction between the free isocyanate groups in urethane derivative of PPG and cellulosic sisal fiber.              | 36 |
| (15) | (I) The reaction pathway for the formation of HTPB-TDI urethane (II)The reaction for formation of Lignin-HTPB Copolyurethane. | 37 |
| (16) | Typical diisocyanates used in coatings resins.  | 48 |
| (17) | Reactions of macrocyclic ureas used as masked diisocyanates.  | 52 |