การสังเคราะห์และสมบัติของอนุพันธ์ของยางสน-พอลิเอทิลีนไกลคอลเพื่อการผลิตฟลักซ์บัดกรี

นางสาวกัลยา ผ่าโผน

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย
The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)
are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
สาขาวิชาปิโตรเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2558
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS AND PROPERTIES OF ROSIN-POLYETHYLENE GLYCOL DERIVATIVES FOR PRODUCTION OF SOLDERING FLUXES

Miss Kanlaya Phaphon

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Petrochemistry
Faculty of Science
Chulalongkorn University
Academic Year 2015

Copyright of Chulalongkorn University

Thesis Title	SYNTHESIS AND PROPERTIES OF ROSIN-POLYETHYLENE GLYCOL DERIVATIVES FOR PRODUCTION OF SOLDERING FLUXES
By	Miss Kanlaya Phaphon
Field of Study	Petrochemistry
Thesis Advisor	Associate Professor Amorn Petsom, Ph.D.
Thesis Co-Advisor	Assistant Professor Sumrit Wacharasindhu, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

....Dean of the Faculty of Science
(Associate Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

....Chairman
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

....Thesis Advisor
(Associate Professor Amorn Petsom, Ph.D.)

....Thesis Co-Advisor
(Assistant Professor Sumrit Wacharasindhu, Ph.D.)

....Examiner
(Associate Professor Nuanphun Chantarasiri, Ph.D.)

....Examiner
(Associate Professor Polkit Sangvanich, Ph.D.)

....External Examiner
(Damrong Sommit, Ph.D.)

กัลยา ผ่าโผน : การสังเคราะห์และสมบัติของอนุพันธ์ของยางสน-พอลิเอทิลีนไกลคอลเพื่อการผลิตฟลักซ์บัดกรี (SYNTHESIS AND PROPERTIES OF ROSIN-POLYETHYLENE GLYCOL DERIVATIVES FOR PRODUCTION OF SOLDERING FLUXES) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.อมร เพชรสม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร.สัมฤทธิ์ วัชรสินธุ์, 80 หน้า.

ในการทำวิจัยนี้ได้สังเคราะห์อนุพันธ์ของยางสน-พอลิเอทิลีนไกลคอล (PEG) เพื่อใช้ผลิตฟลักซ์บัดกรีที่มีสมบัติละลายน้ำได้ เฮไลด์ต่ำ การกัดกร่อนต่ำและสามารถบัดกรีได้ดีจากยางสนธรรมชาติและพอลิเอทิลีนไกลคอล รวมถึงศึกษาสภาวะของปฏิกิริยาที่เหมาะสมโดยศึกษาผลกระทบของชนิดของตัวเร่งปฏิกิริยา ความเข้มข้นของตัวเร่งปฏิกริยา อุณหภูมิ ระยะเวลา และชนิดของ PEG เป็นต้น รวมถึงศึกษาสมบัติทางเคมีและกายภาพของอนุพันธ์ยางสนที่สังเคราะห์ได้ด้วยเทคนิคอินฟราเรดสเปกโทรสโกปี (FT-IR) คาร์บอน-13นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี (^{13}C-NMR) ดิฟเฟอเรนเชียลสแกนนิงแคลอริมิเตอร์ (DSC) เจลเพอร์มีเอชันโครมาโทกราฟี (GPC) ในการวิจัยครั้งนี้ได้ผลิตฟลักซ์บัดกรีและศึกษาสมบัติของฟลักซ์ตามมาตรฐาน JIS พบว่าสามารถสังเคราะห์อนุพันธ์ของยางสน-พอลิเอทิลีนไกลคอลที่สามารถละลายน้ำ (WSR) จากยางสนธรรมชาติและPEG ใช้ ZnO ความเข้มข้น 2% เป็นตัวเร่งปฏิกิริยา อัตราส่วนของยางสนต่อ PEG 2:1 โมลาร์ ที่อุณหภูมิ 250 $^{\circ}$C และใช้เวลา 9 ชม. และพบว่าอนุพันธุ์ของยางสน-PEG3000 มีจุดหลอมเหลวสูงสุดที่ 55.2 $^{\circ}$C การวิจัยครั้งนี้ต้องการผลิตฟลักซ์ชนิดแข็ง ดังนั้นอนุพันธ์ยางสน-PEG3000 จึงถูกเลือกเพื่อใช้ในการศึกษาการผลิตฟลักซ์บัดกรี จากการศึกษาพบว่า กรดซัคซินิก, กรดกลูตาริก, เอทิลแอมโมเนียมคลอไรด์และไดเอทิลแอมโมเนียมโบรไมด์ แสดงสมบัติการแผ่ได้ดีและใช้เพื่อการผลิตคอร์ฟลักซ์บัดกรีละลายน้ำได้ ฟลักซ์ WSRF09 และ WSRF04 เป็นฟลักซ์ที่แสดงสมบัติการบัดกรีดีที่สุดเมื่อใช้โลหะบัดกรีไร้สารตะกั่ว Sn-0.7Cu มีปริมาณเฮไลด์ต่ำ (น้อยกว่า 1500 ppm) ความต้านทานการนำไฟฟ้าสูง และการกัดกร่อนน้อย และสามารถฉีดเพื่อเป็นโลหะบัดกรีไร้สารตะกั่วชนิดเส้นได้และมีปริมาณฟลักซ์ที่ต่อเนื่องและคงที่

CHULALONGKORN UNIVERSITY

สาขาวิชา ปิโตรเคมี

ปีการศึกษา 2558

ลายมือชื่อนิสิต ....

ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5472806123 : MAJOR PETROCHEMISTRY

KEYWORDS: ROSIN, PEG-ROSIN, POLYETHYLENE GLYCOL, FLUX, SOLDER, SN-CU

KANLAYA PHAPHON: SYNTHESIS AND PROPERTIES OF ROSIN-POLYETHYLENE GLYCOL DERIVATIVES FOR PRODUCTION OF SOLDERING FLUXES. ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., CO-ADVISOR: ASST. PROF. SUMRIT WACHARASINDHU, Ph.D., 80 pp.

This research aims to synthesize rosin-polyethylene glycol derivatives from rosin and polyethylene glycol (PEG) for the production of solid soldering fluxes. The rosin-PEG derivatives would be water-soluble and the resulting solid soldering fluxes would have reasonable wetting ability when combined with a low halide content activator. The reaction conditions (including catalyst type, catalyst concentration, reaction temperature, and PEG type) were optimized for the synthesis of rosin-PEG derivatives. The chemical and physical properties of rosin-PEG derivatives were characterized by Fourier transform infrared (FT-IR) spectroscopy, carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrometry, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC). The production and characteristics of water-soluble rosin fluxes (WSRFs) were studied according to the standards of the Japanese Industrial Standards (JIS) Committees. It found that rosin-PEG derivatives were successfully synthesized from rosin and PEG using 2% ZnO as a catalyst, with a 2:1 molar ratio of rosin:PEG at 250 °C over 9 hours. The resulting rosin-PEG derivatives were completely soluble in water. Since the rosin-PEG3000 derivative had the highest melting point (55.2 °C), it was chosen for the preparation of the WSRFs. Activators such as succinic acid, glutaric acid, ethylamine hydrochloride, and diethylamine hydrobromide were selected for use in the production of the fluxes. It was found that WSRF 09 and WSRF 04 gave the best performance with the lead-free Sn-0.7Cu solder alloy in terms of good solderability, low halide content (less than 1500 ppm), high insulation resistance, and low corrosion. WSRFs were stable flux content and extrude-able in lead free solder wire product.

Field of Study: Petrochemistry
Academic Year: 2015

Student's Signature ....
Advisor's Signature ....
Co-Advisor's Signature ....

ACKNOWLEDGEMENTS

I would like to thank my thesis adviser Assoc. Prof. Dr. Amorn Petsom, Ph.D. and my co-thesis adviser Asst. Prof. Sumrit Wacharasindhu, Ph.D. for being the best advisers anyone could ever ask for. There are no words that can express and depth of gratitude that I have towards them. They have supported me whole heartedly in everything that I set out to improve the synthesis skills that I have right now, believe in me even at the moment of my life when I was down and helped me to get back on my feet.

I am also grateful to Asst. Prof. Warinthorn Chavasiri, Ph.D. for serving as the chairman, and Assoc. Prof. Nuanphun Chantarasiri, Ph.D., Assoc. Prof. Polkit Sangvanich, Ph.D. and Damrong Sommit, Ph.D. for serving as the members of my thesis committee, respectively, for all their valuable suggestion and comments.

I sincerely thank Mr. Varut Thavivaradilok Managing Director of ULTRACORE CO., LTD. for financial and laboratory facilities support to conduct this research. In addition, I would like to thank my colleague in ULTRACORE CO., LTD. for all supports to my entire education. I also thank Center of Petrochemical and graduated School of Chulalongkorn University for partial support to conduct this research.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Finally, I am grateful to my family for their love, understanding, and great encouragement throughout the entire course of my study.

CONTENTS

Page

THAI ABSTRACT iv

ENGLISH ABSTRACT v

ACKNOWLEDGEMENTS vi

CONTENTS vii

LIST OF TABLES xii

LIST OF FIGURES xiv

LIST OF ABBREVIATIONS xvi

CHAPTER I INTRODUCTION 18

  1.1 Background and statement of problem 18

  1.2 Objective and scope of this research 19

    1.2.1 Objective of research 19

    1.2.2 Scope of research 20

CHAPTER II THEORY AND LITERATURE REVIEW 22

  2.1 Rosin 22

    2.1.1 Resin acids chemical reactivity 24

      2.1.1.1 Reactions of the olefin system 24

        2.1.1.1.1 Oxidation, hydrogenation and dehydrogenation 24

        2.1.1.1.2 Functionalization of dehydroabietic acid aromatic ring 25

        2.1.1.1.3 Isomerization 25

        2.1.1.1.4 Diels–Alder reactions 26

        2.1.1.1.5 Reactions with formaldehyde and phenol 27

      2.1.1.2 Reactions of the carboxylic group 28

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Page

2.1.1.3 Miscellaneous reactions.. 28

2.2 Introduction of soldering and soldering process 29

2.2.1 The nature of soldering and of the soldered joint....................................... 29

2.2.2 The roles of solder, flux and heat 29

2.2.3 The flux.. 29

2.2.3.1 Tasks and action of the soldering flux... 29

2.2.3.1.1 Removing oxide skins 29

2.2.3.1.2 The oxide skin on molten solder 30

2.2.3.1.3 Wetting and interfacial tension 31

2.2.3.2 Rosin fluxes.. 32

2.2.3.3 Problems with rosin fluxes 32

2.2.3.4 Water soluble fluxes.. 33

2.2.3.5 Solvents used in fluxes 33

2.2.4 Cleaning after soldering.. 33

2.2.4.1 Basic considerations... 33

2.2.4.2 Reasons for cleaning.. 34

2.2.4.2.1 Electrical problems.. 34

2.2.4.2.2 Chemical problems 34

2.2.4.2.2.1 Corrosion 34

2.2.4.2.2.2 Formation of dendrites 35

2.2.4.2.2.3 Problems arising with follow-on processes ... 36

2.2.4.2.3 Environmental acceptability.. 36

2.4 Literature review.. 36

Page

CHAPTER III EXPERIMENTAL 39

3.1 Chemicals and Material 39

3.2 Instruments and apparatus 39

3.3 Experimental procedure 40

3.3.1 Part 1: Optimized conditions for the synthesis of rosin-polyethylene glycol derivatives (rosin-PEG) 40

3.3.1.1 The procedure of synthesis reaction of rosin-PEG derivatives 40

3.3.1.2 Study on influence of catalyst type on the esterification reaction 41

3.3.1.3 Study on influence of catalyst concentration on the esterification reaction 41

3.3.1.4 Study on influence of the rosin:PEG ratio on the esterification reaction 42

3.3.1.5 Study on Influence of temperature on the esterification reaction 43

3.3.1.6 Study on influence of the reaction time on the esterification reaction 43

3.3.1.7 Study on influence of PEG type on the esterification reaction 44

3.3.1.8 Study on influence of resin type on the esterification reaction 44

3.3.2 Part 2: Preparation of water-soluble solid soldering flux 45

3.3.2.1 Selection of activators for water-soluble rosin soldering fluxes 45

3.3.2.2 Preparation of water-soluble solid soldering flux 47

3.3.2.3 Characterization of water-soluble rosin soldering fluxes 48

3.3.2.3.1 Acid value of reaction and WSRFs 48

Page

3.3.2.3.2 Solubility of rosin-PEG and water soluble rosin soldering fluxes 48

3.3.2.3.3 Halide content test of water soluble rosin soldering fluxes 49

3.3.2.3.4 Spreading ratio test of water soluble rosin soldering fluxes 50

3.3.2.3.5 Copper plate corrosion test of water soluble rosin soldering fluxes 50

3.3.2.3.6 Insulation Resistance test of water soluble rosin soldering fluxes 51

3.3.2.3.7 Resistivity test of aqueous solution of water soluble rosin soldering fluxes 51

3.3.2.3.8 Ionic Residue Test of water soluble rosin soldering fluxes 51

3.3.2.3.9 Flux Induced Corrosion (Copper Mirror Method) test of water soluble rosin soldering fluxes 52

3.3.3 Production of water soluble cored flux solder wire 53

CHAPTER IV RESULTS AND DISSCUSSION 55

4.1 Optimized conditions for synthetic reaction of rosin-PEG derivatives 55

4.1.1 Influence of catalyst type on the esterification reaction 55

4.1.2 Influence of catalyst concentration on the esterification reaction 56

4.1.3 Influence of the rosin:PEG ratio on the esterification reaction 57

4.1.4 Influence of temperature on the esterification reaction 58

4.1.5 Influence of the reaction time on the esterification reaction 59

4.1.6 Influence of the resin type on the resin type 60

Page

4.2 Characterization of rosin-PEG derivatives 61
    4.2.1 FT-IR and ^{13}C NMR spectroscopy measurement 61
    4.2.2 DSC measurement 64
    4.2.3 XRF measurement 66
4.3 Investigations of water-soluble rosin soldering fluxes produced from rosin-PEG derivatives 68
    4.3.1 Selection of activator for production of WSRFs 68
    4.3.2 Characteristics of water-soluble rosin soldering fluxes 69
    4.3.2 Water-soluble cored flux solder wire production 73
CHAPTER V CONCLUSION AND SUGESTION 75
5.1 Conclusion 75
5.2 Suggestion for further work 75
REFERENCES 76
VITA 80

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

LIST OF TABLES

Table Page

Table 2. 1 The rosin grades and relative properties 24

Table 3. 1 The amount of reactant used for studying influence of catalyst type on rosin-PEG derivatives synthesis reaction. 41

Table 3. 2 The amount of reactant used for studying influence of catalyst concentration on rosin-PEG derivatives synthesis reaction. 42

Table 3. 3 The amount of reactant used for studying influence of rosin: polyethylene glycol ratio on rosin-PEG derivatives synthesis reaction. 42

Table 3. 4 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction. 43

Table 3. 5 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction. 44

Table 3. 6 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction. 44

Table 3. 7 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction. 45

Table 3. 8 The formula of sample for spreading factor test by various the concentration of acid and amine halide. 46

Table 3. 9 The amount of activator for water soluble rosin soldering fluxes (WSRFs). 47

Table 3. 10 Test methods and residual ion value 52

Table 4. 1 Acid value, conversion percentage, and water solubility of reaction product at temperatures of 100°C, 150°C, 200°C, 225°C, and 250°C. 59

Table 4. 2 Physical and chemical properties of rosin-PEG derivatives. 65

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 4. 3 Physical and chemical properties of rosin-PEG derivatives using difference resin type. 66

Table 4. 4 Spreading ratio of various amine hydrohalides and various dicarboxylic acids using Sn-0.7Cu at 270°C. 68

Table 4. 5 Characteristics of WSRFs. 70

Table 4. 6 Ionic contamination test results of WSRF04 and 09. 72

Table 4. 7 Water solution resistivity test results of WSRF04 and 09. 72

Table 4. 8 Summary of test result of water-soluble flux cored lead free solder wire. 73

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

LIST OF FIGURES

Figure Page

Figure 2. 1 Diterpene carbon skeletons found in the most common resin acids 22

Figure 2. 2 Structures of the most common abietane-type resin acids 23

Figure 2. 3 Structures of the most common pimarane-type resin acids 23

Figure 2. 4 Oxidation of levopimaric acid with formation of an endoperoxide 25

Figure 2. 5 Nitration of dehydroabietic acid 25

Figure 2. 6 Diels–Alder reaction of levopimaric acid with maleic anhydride. 26

Figure 2. 7 Formation of dimeric ketones of maleopimaric-type adducts 26

Figure 2. 8 Addition of formaldehyde to abietic acid 27

Figure 2. 9 Formation of rosin-modified phenol–formaldehyde resins 28

Figure 2. 10 The function of the flux in soldering 30

Figure 2. 11 The solder wire/flux experiment 30

Figure 2. 12 Surface tension and the molten solder wire 31

Figure 2. 13 Icicles, bridges, and surface tension 31

Figure 2. 14 Electrolytic corrosion 35

Figure 2. 15 Formation of dendrites 35

Figure 3. 1 Copper plate for testing 50

Figure 3. 2 Relation between ionic residue and resistivity by NaCl conversion 52

Figure 3. 3 Flux type classification by copper mirror test 53

Figure 3. 4 Extrusion machine used for production of water soluble rosin flux cored solder wire. 54

Figure 3. 5 Solderability test equipment for water soluble rosin soldering fluxes cored solder wire. 54

Figure 4. 1 Conversion percentage of reaction versus time for the esterification reaction between rosin and PEG1500 using Zn dust, ZnO, and Tin Chloride as catalysts. 55

Figure 4. 2 Conversion percentage of reaction and acid value (mg.KOH/g of sample) versus catalyst concentration (%) for the esterification reaction between rosin and PEG1500 using ZnO catalyst. 56

Figure 4. 3 Rate of reaction of rosin-PEG derivatives using different molar ratios of rosin:PEG1500. 57

Figure 4. 4 Conversion percentage of rosin-PEG derivatives using ZnO 2%, rosin 2 mol : PEG 1 mol at 250°C for 10 hr. 60

Figure 4. 5 Infrared spectra of China rosin, PEG and the rosin-PEG1500 derivative at 0 hour, 5 hours, 10 hours. 61

Figure 4. 6 Infrared spectra of rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000. 62

Figure 4. 7 ^{13}C-NMR spectra of rosin-PEG derivatives (rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000). 63

Figure 4. 8 Reaction scheme of rosin-PEG derivatives synthesis. 64

Figure 4. 9 DSC spectrum of rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000. 64

Figure 4. 10 XRF spectra of Zn in rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000. 67

Figure 4. 11 Cross section of water-soluble fluxed core lead free solder wire 11 mm storage at room temp. for 30 days. 74

Figure 4. 12 Picture of soldering time of water-soluble flux cored lead free solder wire U5204-WRSF04 and U5204-WRSF09 @ 380 ^{O}C. 74

LIST OF ABBREVIATIONS

cm^{-1}	A reciprocal wavelength
mil	a unit of length equal to 0.001 of an inch (0.0254 mm)
BS	British Standard
C-NMR	Carbon Nuclear magnetic resonance
CFCs	Chlorofluorocarbons
cm.	Centimeter
Cat.	Catalyst
Conc.	Concentration
DSC	Differential scanning calorimeter
^{O}C	Degree Celsius
^{O}F	Degree Fahrenheit
e.g.	Exampli gatia
etc.	et cetera
Fig.	Figure
FT-IR	Fourier transform infrared spectroscopy
g.	gram
Δ	Heat
Hr	Hour
ICs	Integrated Circuits
i.e.	in the other word
IPC	Interconnecting and Packaging Electronic Circuits
JIS	Japanese Industrial Standards
m	Meter
mil	Military Specifications and Standards
min.	Minimum
max.	Maximum
μS	micro Siemen
MΩ	Mega Ohm

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

mm.	millimeter
Mw	Molecular weight
Mn	Molecular number
Min	minute
mg.	Milligram
ml.	Milliliter
KOH	Potassium Hydroxide
Ω	Ohm
ppm	part per million
PCB	Printed Circuit Board
PEG	Polyethylene Glycol
RA	Rosin Activated
RMA	Rosin Mindy activated
cm^2	square centimeter
SIR	Surface insulation resistance
ISO	The International Organization for Standardization
USA	United Stated Of America
V	Volt
VOC	Volatile Organic compounds
WSRF	Water Soluble Rosin Flux
WSR	Water Soluble Rosin
XRF	X-ray fluorescence

CHAPTER I

INTRODUCTION

1.1 Background and statement of problem

Soldering is an importance technique in the assembly of electronics products. In electronics mass production hundreds of millions of solder joint is being formed daily. A standard radio receiver contains about 500 joints, a black and white television set about 1000 and color television set about 2000. Large computers and telephone systems have over 10^5 solder joints (1).

Solder alloy and flux are used in soldering process for joint the electronics part and PCB board together. Compositions of solder alloy are tin, silver, copper etc. Soldering flux is a compound with the objective facilitating strong electrical connection of electronics parts and solder alloy. The flux compositions are rosin solvents, organic acids, inorganic acids, etc..

In soldering process it is important to form a good solder joint with this enhanced by the quality of and characteristics of the soldering flux employed. It is advantageous in many applications for soldering flux to remove surface oxide, decrease surface tension of molten solder, and inhibit formation of surface oxides at elevated temperatures to insure formation of stronger, more secure solder bonds in a reliably predictable uniform fashion. It is necessary that residues of solder flux be completely removed, advantageously, with either a water based or solvent based cleaning fluid, particularly where soldering is used on a circuit board that is to be conformal coated or dipped into any type of protective lacquer since flux residues prevent adhesion of lacquers and other polymer films used to the surface of the circuit card (2).

Most fluxes and cleaning chemicals used by industry to manufacture electronic circuits, such as military hardware, are either contributing to ozone depletion of the atmosphere or are considered by local environmental agencies, as environmental pollutants or health hazards. For example, it has been reported that if CFCs (chlorofluorohydrocarbons), which are used in vapor degreasing to clean soldered parts where a rosin flux is employed, are released to the atmosphere, they will remain there as an ozone depleting for nearly 100 years. Other chemicals such as rosin fluxes, alcohols, and the like pose health risks and disposal problems for industry (3).

The production of electronics products using the soldering process has shifted to more environmentally friendly processes, for example, using lead-free solder, solder paste, and “no-clean” or solvent-free cleaning processes. In the solvent-free cleaning process, water-soluble fluxes (WSFs) have become a new choice for the soldering process. The residues of these fluxes are designed to be washed away from the circuit board and its components with plain or deionized water (4).

Even though polyethylene glycols (PEGs) are used as flux vehicles in water soluble rosin fluxes (WRSFs) for some industrial electronic applications (5, 6), their applications are limited. There are no reports on the use of a rosin-PEG derivative as a flux vehicle. For this reason, this study aims to synthesize Rosin-PEG derivatives for the preparation of water-soluble soldering fluxes. Catalyst types, catalyst concentrations, reaction temperatures, reaction times, and catalyst ratios are investigated. Low halide, low corrosion, water-soluble solid fluxes are prepared from rosin-PEG derivatives and characterized. These fluxes are intended to be used as core solder flux to make lead-free solder wire, which is still essential in the application of retouching after a wave soldering process using lead-free solder.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

1.2 Objective and scope of this research

1.2.1 Objective of research

This study aims to synthesize rosin-PEG derivatives for the production of water-soluble soldering fluxes. Catalyst types, catalyst concentrations, reaction temperatures, reaction times, and catalyst ratios are investigated. Low halide, low corrosion, water-soluble solid fluxes are prepared from rosin-PEG derivatives and characterized. These fluxes are intended to be used as core solder flux to make lead-free solder wire, which is still essential in the application of retouching after a wave soldering process using lead-free solder.

1.2.2 Scope of research

1. Review of related literature
2. Study on optimized conditions for synthesis reaction of rosin-polyethylene glycol
    2.1. Effect of catalyst type such as zinc dust, zinc oxide and tin chloride on rosin-PEG derivatives synthesis reaction
    2.2. Effect of catalyst concentration at 0%, 0.5 %, 1.0%, 1.5%, 2.0% of rosin concentration on rosin-PEG derivatives synthesis reaction
    2.3. Concentration ratio of rosin and polyethylene glycol at 1:1, 1.5:1, 2:1 on rosin-PEG derivatives synthesis reaction
    2.4. Reaction temperature at 100, 150, 200, 250 ^{O}C on solubility and acid value of rosin-polyethylene glycol derivatives.
3. Synthesis and study on chemical and physical properties of rosin-maleic anhydride-PEG derivatives and tetrahydroabietic acid-PEG derivatives.
4. Study on chemical and physical properties of rosin-polyethylene glycol derivatives.
    4.1. Study on functional group of derivatives using Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance spectroscopy etc.
    4.2. Acid value using titration method with potassium hydroxide solution 0.1 M
    4.3. Water solubility of rosin-polyethylene glycol derivatives.(7)
    4.4. Molecular weight and polydispersity index using gel permeation chromatography.
    4.5. Measurement of melting point using differential scanning calorimetry techniques.
    4.6. Study and compare of water solubility of rosin-PEG1000, rosin-PE1500, rosin-PEG2000 and rosin-PEG 3000
5. Study on preparation condition of water soluble fluxes
    5.1. Concentration and type of activators such as succinic acid, maleic acid, adipic acid, amine hydrochloride etc.
6. Study on properties of water soluble fluxes
    6.1. Acid value using titration method with potassium hydroxide solution 0.1 M
    6.2. Water solubility of rosin-polyethylene glycol derivatives.(7)

    - 6.3. Halide content using automatic potentiometric titrator (KEM-510)
    - 6.4. Expansion ratio conforming to JIS Z 3197-1999
    - 6.5. Copper corrosion conforming to JIS Z 3197-1999
    - 6.6. Copper mirror corrosion test conforming to JIS Z 3197-1999
    - 6.7. Lead free solder wire extrusion
7. Discussion, conclusion and thesis writing

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Rosin

Regardless of its origin (gum, wood or tall oil), rosin is mainly composed (90–95 per cent) of diterpenic monocarboxylic acids, commonly known as resin acids whose generic formula is $C_{19}H_{29}COOH$. The remaining components are essentially made up of neutral compounds, the nature of which depends on the specific origin of the rosin. The most common resin acids found in pine rosin are derived from the three basic tricyclic carbon skeletons abietane, pimarane and isopimarane and the less common bicyclic labdane skeleton (Fig. 2.1). The abietane skeleton is shared by four resin acids (Fig. 2.2), namely abietic, neoabietic, palustric and levopimaric acids and pimarane-type (Fig. 2.3)

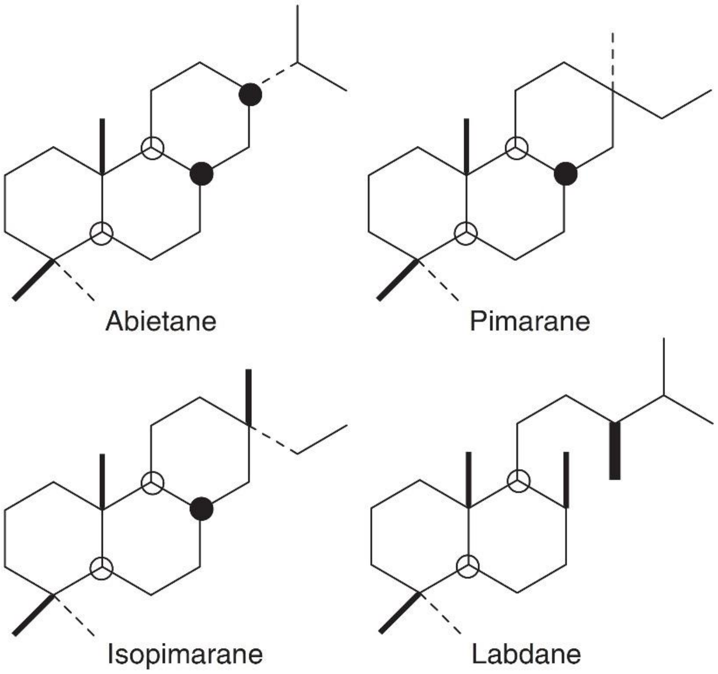
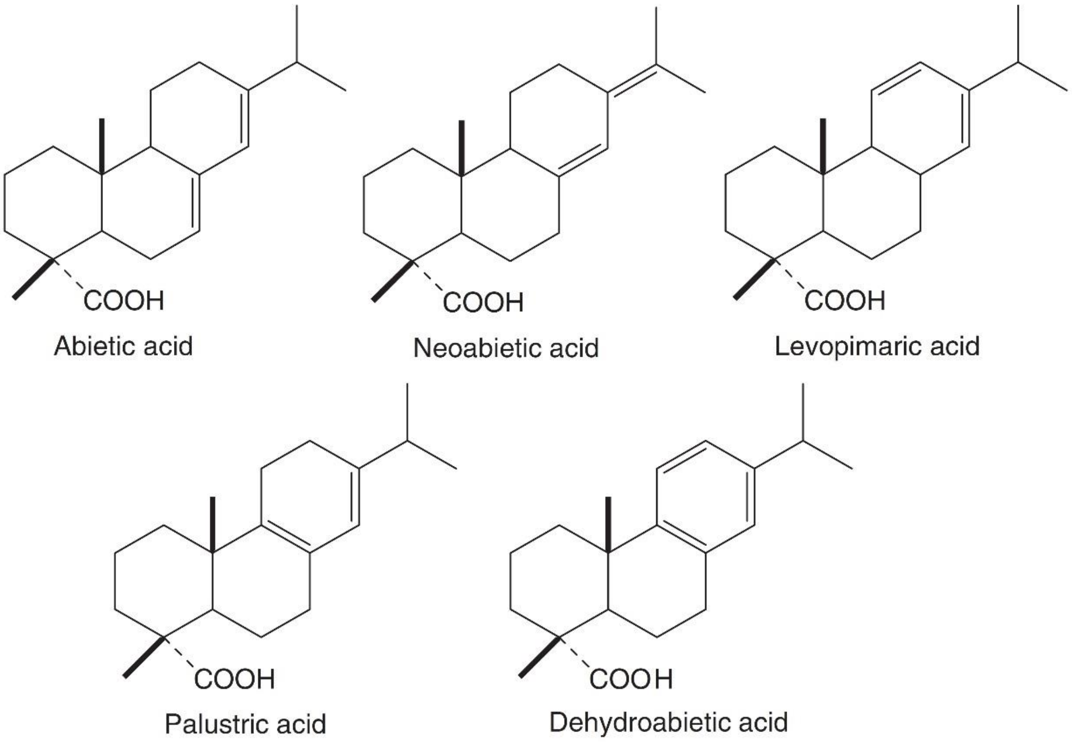
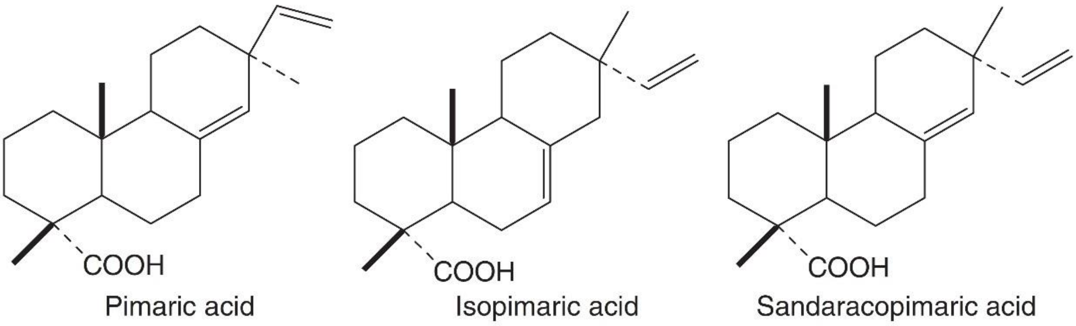


Figure 2. 1 Diterpene carbon skeletons found in the most common resin acids (8).



Abietic acid
Neoabietic acid
Levopimaric acid
Palustric acid
Dehydroabietic acid

Figure 2. 2 Structures of the most common abietane-type resin acids (8).

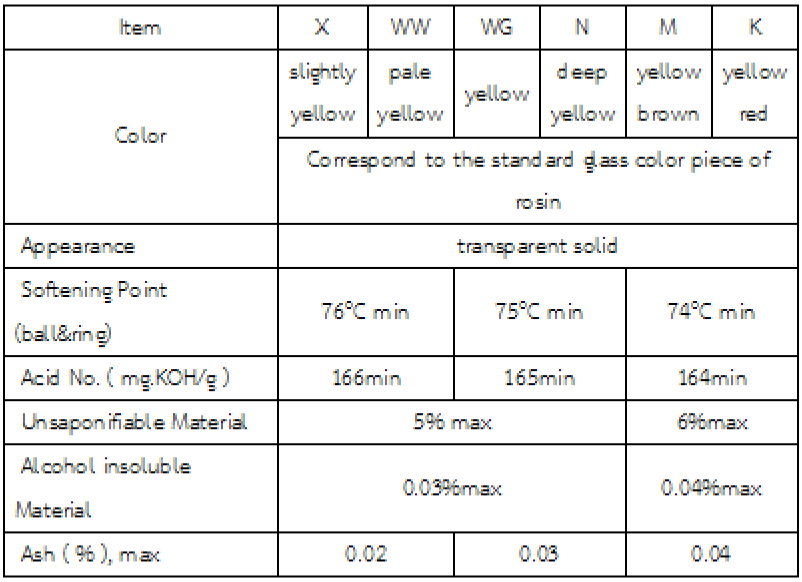


Pimaric acid
Isopimaric acid
Sandaracopimaric acid

Figure 2. 3 Structures of the most common pimarane-type resin acids (8).

Gum rosin is classified to different grades based on the color and the softening point of the rosin. The table 2.1 shows some of the rosin grades and relative properties (9).

Table 2. 1 The rosin grades and relative properties (9).



Item	X	WW	WG	N	M	K
Color	slightly yellow	pale yellow	yellow	deep yellow	yellow brown	yellow red
	Correspond to the standard glass color piece of rosin					
Appearance	transparent solid					
Softening Point (ball&ring)	76°C min		75°C min		74°C min	
Acid No. (mg.KOH/g)	166min		165min		164min	
Unsaponifiable Material	5% max				6%max	
Alcohol insoluble Material	0.03%max				0.04%max	
Ash (%), max	0.02		0.03		0.04	

2.1.1 Resin acids chemical reactivity

The chemical reactivity of resin acids is determined by the presence of both the double- bond system and the COOH group.

2.1.1.1 Reactions of the olefin system

The conjugated double bond system of abietadienoic acids is simultaneously a source of instability, detrimental for many rosin applications and, conversely, an interesting reactive center for further modifications.

2.1.1.1.1 Oxidation, hydrogenation and dehydrogenation

The conjugated double bond is responsible for rosin yellowing arising from oxygen addition, isomerization and other reactions. In many applications, this colouring is associated with a loss of product quality. Oxygen addition is normally photochemically induced, leading to the formation of epoxides, hydroxylated derivatives and endoperoxides (Fig. 2.4). These unwanted reactions can be suppressed by dehydrogenation or hydrogenation processes.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

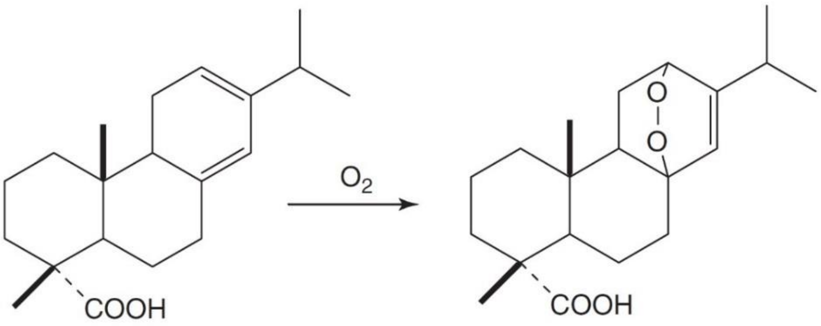


Figure 2. 4 Oxidation of levopimaric acid with formation of an endoperoxide (8).

2.1.1.1.2 Functionalization of dehydroabietic acid aromatic ring

Dehydroabietic acid can undergo typical aromatic substitution reactions (e.g.acylation, chlorosulphonation, sulphonation and nitration) with preferential functionalization of the more reactive 12 position, followed in some cases by the 14 position. These reactions were first exploited in the 1930s–1940s. The nitration of dehydroabietic acid was one of the first reactions studied because of the synthetic versatility of the nitro group, namely as precursor of amino groups. More recently, this reaction has been optimized using less harsh condition (Fig. 2.5).

2.1.1.1.3 Isomerization

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

The chemical modifications of abietic-type acids through the conjugated double bond system must take into account a fundamental feature of these moieties, viz. their proneness to isomerization under heat and/or acidic condition.

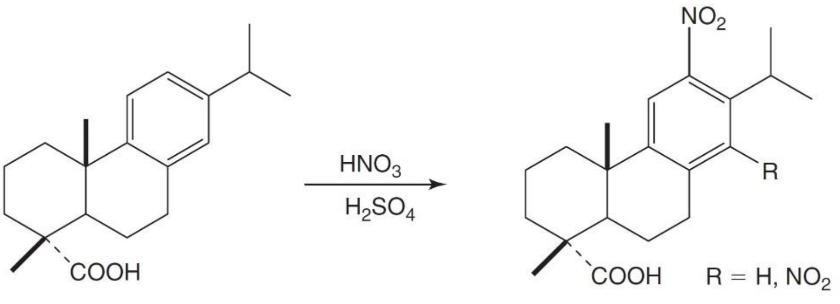


Figure 2. 5 Nitration of dehydroabietic acid (8).

2.1.1.1.4 Diels–Alder reactions

The Diels–Alder reaction with dienophiles is used to convert these acids into novel materials, its occurrence is optimized by the concomitant isomerization process giving levopimaric acid, which is the only homologue capable of producing an adduct. The functionalities of several Diels–Alder adducts, or their derivatives, have been thoroughly exploited in the synthesis of polymeric materials (Fig. 2.6, 2.7).

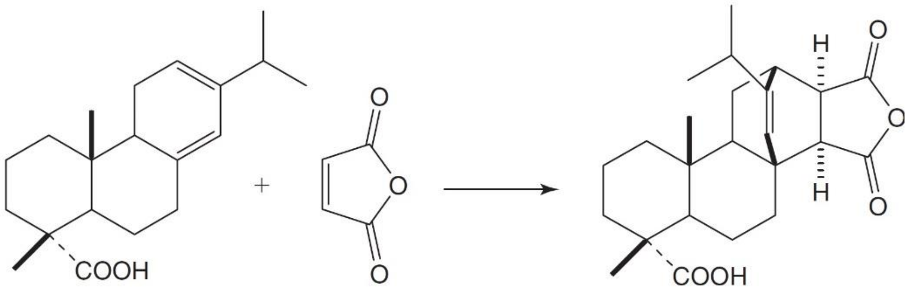


Figure 2. 6 Diels–Alder reaction of levopimaric acid with maleic anhydride(8).

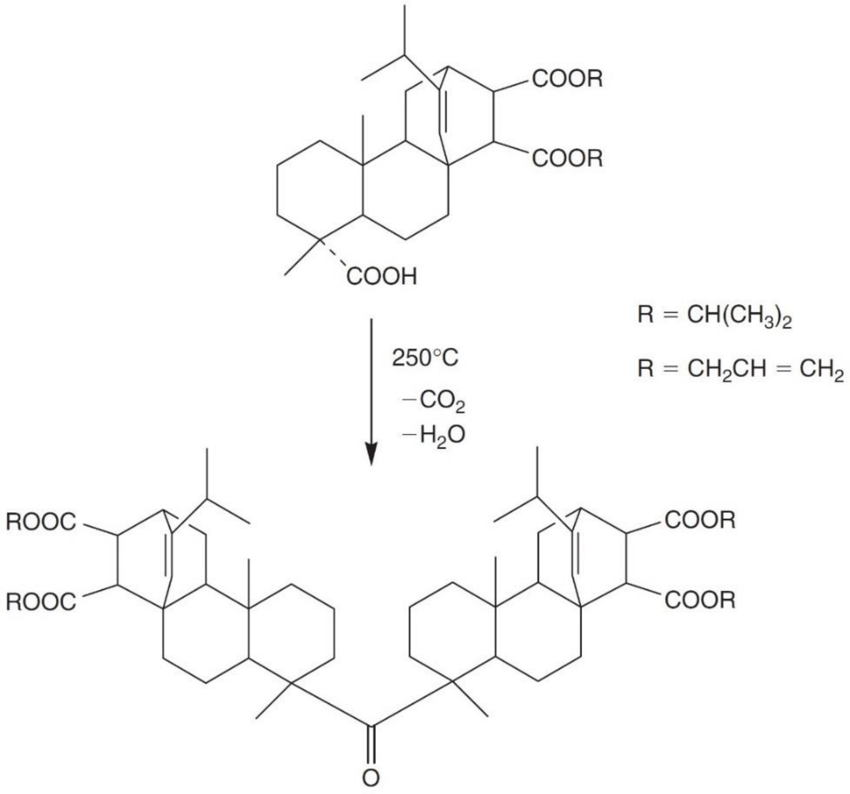


Figure 2. 7 Formation of dimeric ketones of maleopimaric-type adducts (8).

2.1.1.1.5 Reactions with formaldehyde and phenol

Other relevant reactions of resin acids are those involving their addition to formaldehyde and/or phenols. Formaldehyde adds to abietic acid to form complex mixtures containing mono and dihydroxymethyl derivatives. Under alkaline conditions, the formation of the mono derivative is favoured, whereas in acetic acid, the dihomologue (isolated as acetate) is the major product (Fig. 2.8).

Since rosin can react with formaldehyde in a similar way as phenol, rosin components have also been used in the preparation of the corresponding rosin–phenol–formaldehyde resins with molecular weights and solubility that are adequate for their incorporation into printing inks (Fig. 2.9).

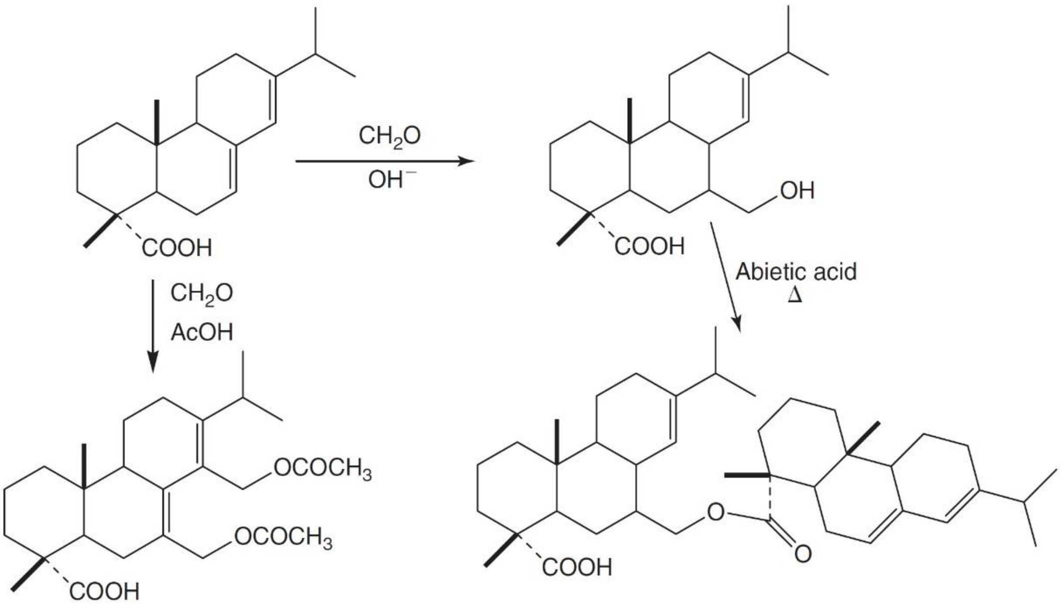


Figure 2. 8 Addition of formaldehyde to abietic acid (8).

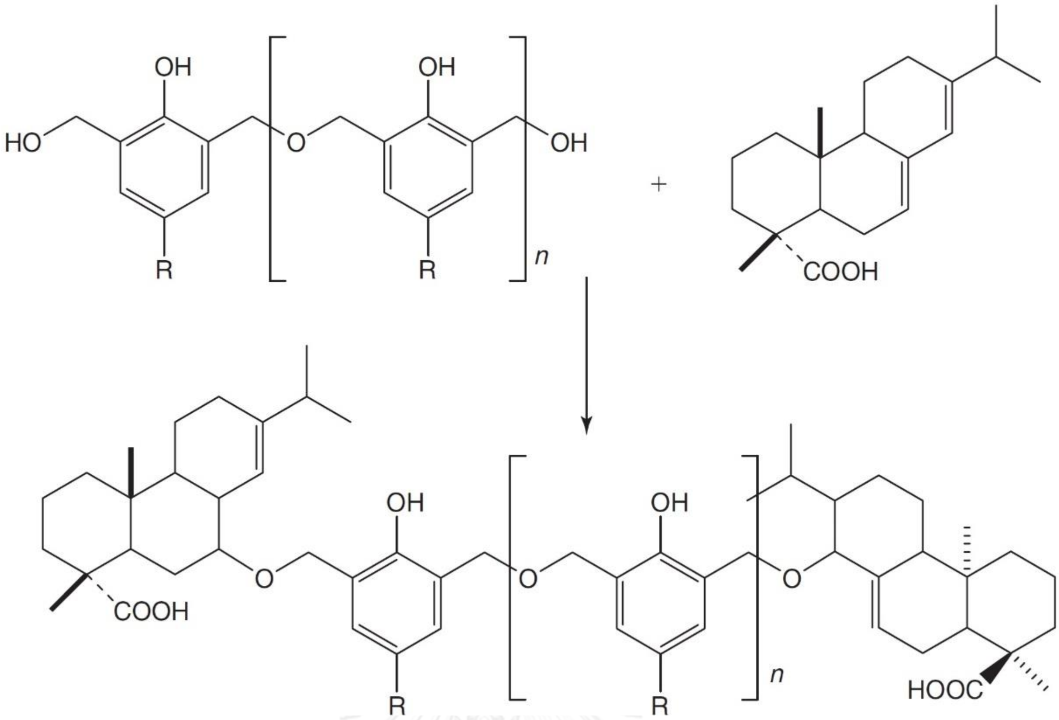


Figure 2. 9 Formation of rosin-modified phenol–formaldehyde resins (8).

2.1.1.2 Reactions of the carboxylic group

Na, Mg, Ca, Zn, Al and ammonium resin acid salts are produced industrially, albeit their relative importance has been shifting with time because of changes in their relevant applications. Na, K and ammonium salts are partially water soluble and were used as soaps in the past. Presently, resin acids sodium salts are mainly used as intermediates in paper sizing. The esterification of resin acids is carried out industrially at high temperatures (260–300°C) using metal oxides as catalysts (8).

2.1.1.3 Miscellaneous reactions

Other chemical transformations involving the carboxylic group have been explored, although their practical interest remains marginal. Anhydrides can be prepared by refluxing the corresponding acid in acetic anhydride. These derivatives have found modest applications as such (e.g.in paper sizing), but they are also useful as precursors to nitrogen derivatives (8).

2.2 Introduction of soldering and soldering process

2.2.1 The nature of soldering and of the soldered joint

Soldering, together with welding, is one of the oldest techniques of joining two pieces of metal together. Today, we distinguish between three 'metallurgical' joining methods: welding, hard soldering (or brazing) and soft soldering. The term 'metallurgical' implies that at and near to the joint interface, the microstructure has been altered by the joining process: what has happened has made one single piece of metal out of the two joint members, so that electric current can flow and mechanical forces can be transmitted from one to the other. With both hard and soft soldering, the joint gap is filled with a molten alloy (an alloy is a mixture of two or more pure metals) which has a lower melting point than the joint members themselves, but which is capable of wetting them and, on solidifying, of forming a firm and permanent bond between them (10).

2.2.2 The roles of solder, flux and heat

Soft soldering (from here on to be simply called 'soldering') is based on a surface reaction between the metal which is to be soldered (the substrate) and the molten solder. This reaction is of fundamental importance; unless it can take place, solder and substrate cannot unite, and no joint can be formed. The reaction itself is 'exothermic', which means that it requires no energy input to proceed, once it has started. Soldering heat is needed to melt the solder, because solid solder can neither react with the substrate (or only very slowly), nor flow into a joint (10).

2.2.3 The flux

2.2.3.1 Tasks and action of the soldering flux

2.2.3.1.1 Removing oxide skins

The success of any soldering operation depends critically on the condition and behavior of two surfaces: that of the substrate and that of the molten solder. The flux has to deal with both of them. By the time the molten solder encounters the substrate, the flux should have completely removed all surface oxides from both the molten solder and the substrate, so that nothing prevents or interferes with the reaction between the two: this is the precondition for the formation of a soldered joint (Figure 2.10).

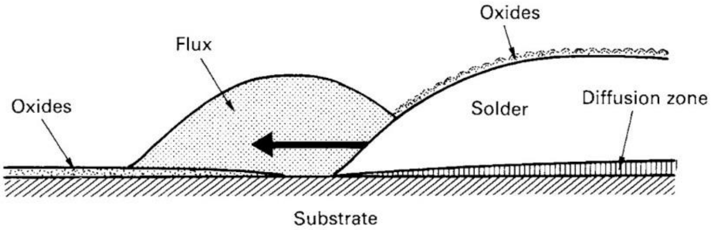


Figure 2. 10 The function of the flux in soldering (10).

2.2.3.1.2 The oxide skin on molten solder

In a normal atmosphere, a thin skin of oxide forms almost immediately on the surface of molten solder as soon as it is exposed to atmospheric oxygen. This skin acts like a tough, somewhat rigid envelope on the liquid solder and restricts its free movement. Now let one drop of soldering flux (e.g. an RMA or RA flux) fall on that sausage: the skin will disappear in an instant and the sausage turns into a shiny, perfectly spherical ball of liquid solder (Figure 2.11).

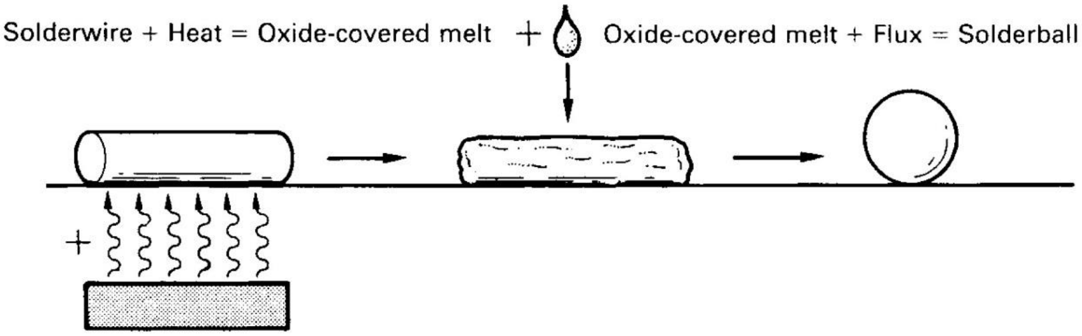


Figure 2. 11 The solder wire/flux experiment (10).

2.2.3.1.3 Wetting and interfacial tension

It is sometimes asserted that the flux lowers the surface tension of molten solder, thus helping it to spread over a substrate or penetrate into a joint. This is not correct. All the flux does to the molten solder is to let it move freely, so that it can follow the forces which act upon it. These forces are not only its own surface tension, but also the so called 'interfacial tension' or wetting force, which pulls the solder across the surface of the substrate.

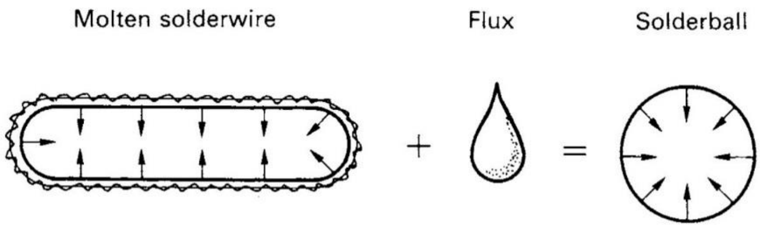


Figure 2. 12 Surface tension and the molten solder wire (10).

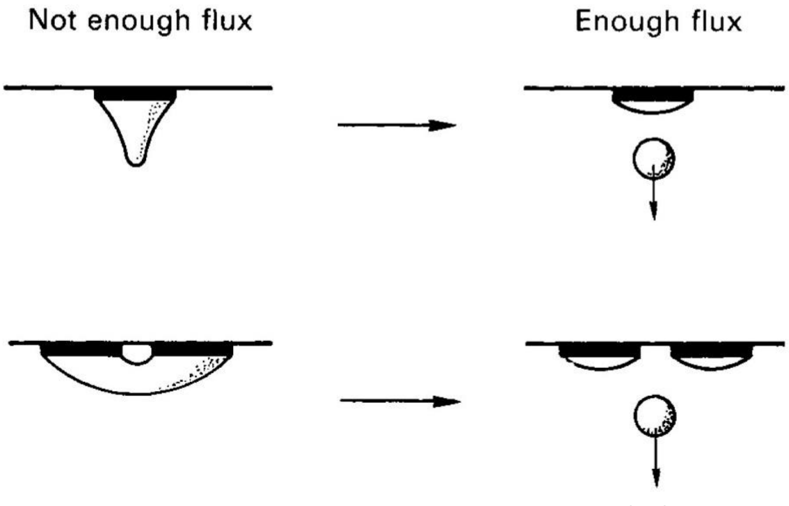


Figure 2. 13 Icicles, bridges, and surface tension (10).

The chemical affinity between the substrate and the tin in the solder is the driving force behind the formation of the intermetallic crystals. The energy set free, as the solder reacts with the copper (or nickel or silver) substrate, pulls it sideways into a flat coating or into a joint gap. This wetting force overcomes the inwards pull of the surface tension of the solder globule, forcing it to give up its spherical shape and to flow where it is needed. The wetting force is the same as the interfacial tension. What matters is that the interfacial tension is higher than the surface tension of the solder (Figure 2.12, 2.13).

2.2.3.2 Rosin fluxes

Until the seventies, only rosin-based fluxes were considered suitable for electronic soldering. In their liquid form, rosin fluxes are, or were, solutions of rosin in alcohol, with solids contents of up to 25% or more. Their residue could safely be left on the finished board, where it formed a hard, protective coating. Indeed, up to 60 ^{O}C/140 ^{O}F, pure rosin has a bulk resistivity of the same order of, if not better than, FR4. Therefore, in the early days of wave soldering, one liked to see the soldered boards coated with a hard, shiny and continuous varnish-like coating of solidified rosin. If considered necessary, this residue could easily be removed with an azeotropic mixture of CFC113 and an alcohol. Since the existing or impending banishment of the CFCs, this situation has changed (10).

2.2.3.3 Problems with rosin fluxes

1. Rosin softens and becomes chemically active above about 70 ^{O}C/160^{O}F. In a warm and humid environment, rosin, left as residue on a board, can hydrolyze and lose its insulating character.

2. Rosin flux residue, being hard and highly insulating, obstructs the contact between ATE test probes and the test pads on the board, and it also tends to gum up the tips of the probes. This problem is more serious with wave soldered boards.

3. The residue compromises the adhesion of protective conformal coatings.

4. The interaction between the rosin flux and the substrate during soldering produces complex metallic reaction products, which are not fully soluble in many of the solvent systems employed in cleaning. They form the so called ‘white residue’ (10).

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

2.2.3.4 Water soluble fluxes

If cleaning after soldering is obligatory, however non-corrosive the flux residue may be, it is sensible to choose a flux which can be removed as simply as possible. The water soluble fluxes fall in that class. Water, and the recently introduced polar solvents like the modified alcohols, offers the possibility of a greatly simplified and environmentally acceptable cleaning technology. Any completely rosin- or resin-free flux would consist of polar substances only, and is consequently soluble in polar solvents like water or any of the alcohols (10).

2.2.3.5 Solvents used in fluxes

Generally, and until recently, isopropyl alcohol (isopropanol) was used almost universally as the solvent in every soldering flux. With some formulations, a portion of a higher-boiling alcohol was added; with others, water of up to 10% or more was added to improve their performance in a foam fluxer and reduce the ‘climb through’ of the flux from the underside of the circuit board through the holes to the top, where it might interfere with the function of relays or contacts. Those latter fluxes would of course have to be free from rosin (10).

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

2.2.4 Cleaning after soldering

2.2.4.1 Basic considerations

If cleaning must be considered, its problems can be reduced. The first question has a simple answer: principally the residue from soldering fluxes, and sometimes from wave soldering oils. This is why cleaning is often called ‘defluxing’. Sometimes, contaminants from manufacturing steps which precede soldering can also be present in amounts which affect the need for cleaning and the choice of cleaning strategy, as well as the result of subsequent tests for cleanliness.

The halogenated solvents, principally the CFCs and CHCs, which were until very recently the principal and most convenient cleaning solvents for the electronic industry, have now been recognized as posing severe environmental threats, and they have been phased out almost world-wide. Therefore, the whole technology of cleaning has been forced into different cleaning media and strategies. Some of them, like cleaning with water, are already well established; others are opening up new approaches. At the time when the original CFCs and CHCs were facing extinction, several similar, but environmentally less objectionable alternative solvents like CHC 111 were introduced to the market. They showed much reduced levels of ‘ozone depletion potential’ and ‘global warming potential’, while being efficient cleaning media (see Table 2.1) (10).

2.2.4.2 Reasons for cleaning

Cleaning can become necessary for one or several of the following reasons:

2.2.4.2.1 Electrical problems

Flux residues left on a soldered assembly can cause leakage currents, ionic migration between neighboring conductors (formation of dendrites), or insulating deposits on contact surfaces such as pin-connectors, relays, or trimmer-tracks, but above all on the contact pads for test bed pins. Here, the insulating effect of the flux residue falsifies the test results. If it is sticky it contaminates the contact points of the test needles, which then need expensive and time-consuming maintenance. This problem was the initial driving force behind the development of modern low-solids fluxes (10).

2.2.4.2.2 Chemical problems

2.2.4.2.2.1 Corrosion

In hostile operating environments, flux residues can cause corrosion or promote fungus growth. Electronic assemblies which have to operate in humid tropical climates are especially at risk from the latter. Polar, water soluble components of residual flux (e.g. activator residues, or indeed residues from any water soluble flux) can, in the

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

presence of moisture, cause electrolytic corrosion between adjacent surfaces of dissimilar metals (10).

2.2.4.2.2.2 Formation of dendrites

All organic films, including protective lacquers and conformal coatings, are permeable to water vapor. Residual activator, trapped under a coating of lacquer between two adjacent metallic conductors with an electric potential between them, causes not only leakage currents, but can initiate the growth of dendrites between the conductors, which may lead to short circuits (Fig 2.15, 2.16) (10).

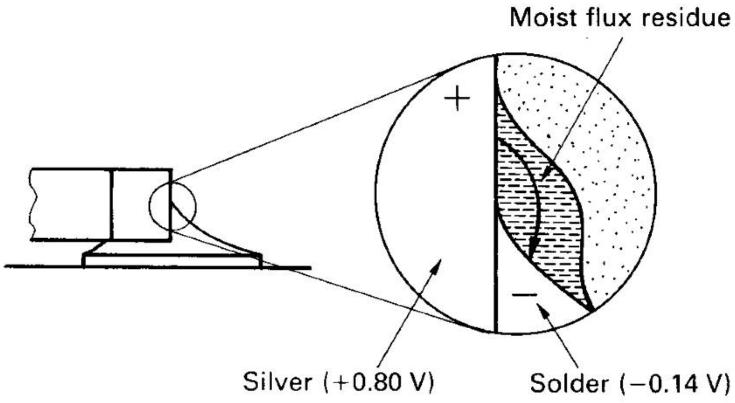


Figure 2. 14 Electrolytic corrosion (10).

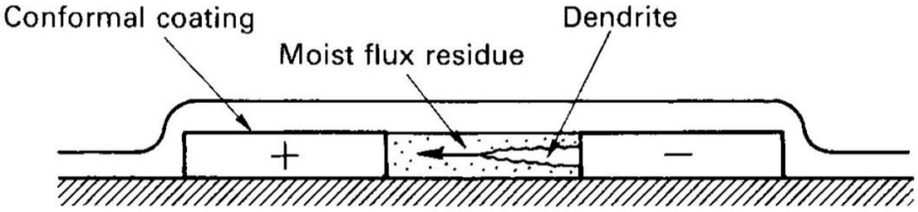


Figure 2. 15 Formation of dendrites (10).

2.2.4.2.2.3 Problems arising with follow-on processes

Flux residue can be responsible for bad adhesion of conformal coatings, lacquers or potting compounds. Some classes of electronic product require the highest possible degree of reliability, and hence cleanliness, which can only be achieved by a cleaning procedure after soldering, irrespective of the flux or soldering method used. These classes include professional electronic equipment which falls under categories I, II and sometimes III (10).

2.2.4.2.3 Environmental acceptability

When judging the environmental acceptability of a cleaning solvent for industrial use, its potential to cause damage can be quantified by four principal parameters. Its maximum allowable concentration (MAC) quantifies the harm which it might cause to the persons working with it. Its ozone depletion potential (ODP) and its global warming potential (GWP), or in popular parlance its ‘greenhouse effect’, quantify the threat which the substance poses to life on our planet if it escapes into the atmosphere. Its photochemical ozone creation potential (POCP), a relative newcomer to the list of environmental villains, relates to the threat to the quality of life in our cities and industrial areas from the phenomenon of man-made ‘photochemical smog’ (10).

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

2.4 Literature review

In 1979, Thompson et. al. (11) developed water soluble soldering flux compositions, and provided methods of making. The compositions contain, as the fluxing agent, an effective amount to cause fluxing, at or below the soldering temperature of the piece to be soldered, of a water-soluble ester of phosphoric acid.

In 1981, Hugh et al. (12) developed a rosin flux with water soluble rosin derivatives replacement the rosin otherwise a typical rosin flux such that residues of solder flux be completely removable with either a water based or solvent based cleaning substance.

In 1991, Gutierrez et al (13) developed a water soluble soldering flux is shown which includes gum arabic, modified polysaccharides and other natural resins as the carrier, an organic activator and water. The carrier provides a tacky, yet fluid medium capable of holding precisely aligned electrical components during solder reflow and allows aqueous removal of the flux after reflow. The flux composition can be used to solder precisely aligned integrated circuit chips onto a circuit board

In 1993 Raymond, et al. (14) developed a non-toxic, non-corrosive water soluble flux for cored solders comprises citric acid. The flux of the invention produces solder joint of high metallic luster and excellent quality. Clean-up of the flux residues is accomplished using only water.

In 2001 Saikawa, et al. (15) developed a water-soluble flux composition which comprises a water-soluble binder and an activator comprising at least one compound selected from the group consisting of sulfonic acid compounds, sulfuric acid compounds, sulfamic acid compounds, polycarboxylic acid compounds, and persulfuric acid compounds; and a process for producing a soldered part such as a part for electronic appliances, IC part, or electronic part, characterized in that the water-soluble flux composition was used.

In 2004 Satturwar, et al. (16) studied rosin and rosin-based polymers for diversification of drug delivery applications achieving sustained/controlled release profiles. Two new Rosin derivatives were synthesized and evaluated for physicochemical properties, molecular weight, polydispersity and glass transition temperature. The films showed low tensile strength and high percent elongation values achieving smooth and uniform surface.

In 2006 Nande, et al. (7) synthesized ester-adduct derivatives of rosin by reacting of rosin with polyethylene glycol 200 (PEG 200) and maleic anhydride (MA) at elevated temperature. The derivatives were soluble in organic solvents; aqueous solubility was pH dependent. All results support applications of these rosin derivatives in different drug delivery systems.

In 2011 Wang, et al. (19) tested the wettability and corrosiveness of some organic acids to choose an appropriate activator. Then orthogonal design method was used to determine the proportion among the components of the activator. The final soldering flux for Sn-0.7Cu welding wire caters to the demands of welding process such as good weld ability, good liquidity, less smoke, full and shiny welding spot.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and Material

China WW rosin was purchased from Pet Thai Chemical Co., Ltd. and hydrogenated rosin was purchased from Arakawa Chemical Industries, Ltd.

PEGs such as PEG 1000, PEG1500, PEG2000, PEG3000 were purchased from Merck Co., Ltd. Activators such as succinic acid, adipic acid, octaindioic acid, dimethylammonium chloride and diethyl ammoniumbromide were purchased from Merck Co., Ltd. All other chemicals were synthetic grade and were used as received.

3.2 Instruments and apparatus

The Heating Mantle with stirrer, MTOP MS-Series Model MS-ES-302 and 250 ml flat bottom Florence flasks were used for synthetic reaction of rosin-polyethylene glycol derivatives.

The melting points of rosin-PEG derivatives were determined using a differential scanning calorimeter (DSC 204 F1 Phoenix, Netzsch-Gerätebau). A Fourier transform infrared (FT-IR) spectrophotometer (Spectrum One, Perkin Elmer) was used to determine the functional groups of the rosin-PEG derivatives. A carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrometer (Bruker Avance III HD 500 MHz, Bruker) was used to confirm ester bonding of the rosin-PEG derivatives. Molecular weights and polydispersity were measured using gel permeation chromatography with a differential refractometer (model RI-10A, Shimadzu). An X-ray fluorescence (XRF) spectrometer (XRF Tiger S8, Bruker) was used to confirm the presence of Zn in the product.

3.3 Experimental procedure

3.3.1 Part 1: Optimized conditions for the synthesis of rosin-polyethylene glycol derivatives (rosin-PEG)

Reaction conditions for synthesis reaction of rosin-PEG derivatives were optimized. The effect of catalyst type, reaction temperature, concentration of catalyst on rosin concentration and ratio of rosin and polyethylene glycol were studied. In this optimizing condition, the obtained product was monitored by acid value titration and water solubility.

3.3.1.1 The procedure of synthesis reaction of rosin-PEG derivatives

Rosin was placed in a boiling flask and heated to a temperature between 100 °C and 150 °C on a heating mantle with a stirrer. PEG and catalyst were added and mixed with molten rosin under continuous stirring until the completion of reaction. The temperature of the reaction varied from 100 °C to 250 °C. In this research, zinc dust, zinc oxide, and tin chloride were used as catalysts and their concentrations varied from 0.5% to 3.0%. The acid number was measured after completion of the reaction using a KEM Automatic Potentiometric Titrator (AT-510) with 0.1 M KOH. The molten PEG-rosin was poured into an aluminum foil cup, allowed to solidify, and used as the sample for subsequent testing. The reaction conversion percentage is defined as the change in acid value between the start and end of the reaction of rosin and PEG. It can be determined from the following equation

$$\% \, conversion = \frac{|(Si - S0)| \times 100}{S_0} \qquad \text{Equation 3. 1}$$

in which, S0 refers to initial acid value and Si refers to the acid value at some reaction time (20).

3.3.1.2 Study on influence of catalyst type on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.1 shows the reactant concentration.

Table 3. 1 The amount of reactant used for studying influence of catalyst type on rosin-PEG derivatives synthesis reaction.

Entry	Catalyst Name	Amount of Reactant (gram)		
		Rosin	PEG1500	Catalyst
1	Zn dust	24.16	120.00	0.12
2	ZnO	24.16	120.00	0.12
3	Tin Chloride	24.16	120.00	0.12

3.3.1.3 Study on influence of catalyst concentration on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.2 shows the reactant concentration.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 3. 2 The amount of reactant used for studying influence of catalyst concentration on rosin-PEG derivatives synthesis reaction.

Entry	Catalyst Conc.	Amount of Reactant (gram)		
		Rosin	PEG1500	ZnO
1	0 %	24.16	120.00	0.00
2	0.5%	24.16	120.00	0.12
3	1.0%	24.16	120.00	0.24
4	1.5%	24.16	120.00	0.36
5	2.0%	24.16	120.00	0.48
6	3.0%	24.16	120.00	0.72

3.3.1.4 Study on influence of the rosin:PEG ratio on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.3 shows the reactant concentration.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 3. 3 The amount of reactant used for studying influence of rosin: polyethylene glycol ratio on rosin-PEG derivatives synthesis reaction.

Entry	Rosin:PEG ratio	Amount of Reactant (gram)		
		Rosin	PEG1500	ZnO
1	1.00:1.00	18.12	90.00	0.36
2	1.25:1.00	22.65	90.00	0.45
3	1.50:1.00	27.18	90.00	0.54
4	1.75:1.00	31.71	90.00	0.63
5	2.00:1.00	36.24	90.00	0.72

3.3.1.5 Study on Influence of temperature on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.4 shows the reactant concentration.

Table 3. 4 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction.

Entry	Temperature, ^{O}C	Amount of Reactant (gram)		
		Rosin	PEG1500	ZnO
1	100	36.24	90.00	0.72
2	150	36.24	90.00	0.72
3	200	36.24	90.00	0.72
4	225	36.24	90.00	0.72
5	250	36.24	90.00	0.72

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

3.3.1.6 Study on influence of the reaction time on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.5 shows the reactant concentration.

Table 3. 5 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction.

Entry	Temperature, ^{O}C	Amount of Reactant (gram)		
		Rosin	PEG1500	ZnO
1	250	36.24	90.00	0.72

3.3.1.7 Study on influence of PEG type on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.6 shows the reactant concentration.

Table 3. 6 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction.

Entry	PEG Type	Amount of Reactant (gram)		
		Rosin	PEG	ZnO
1	PEG1000	48.71	80.86	0.97
2	PEG1500	37.15	92.25	0.74
3	PEG2000	30.20	100.00	0.60
4	PEG3000	21.73	107.91	0.43

3.3.1.8 Study on influence of resin type on the esterification reaction

The influence of catalyst type on rosin-PEG derivatives synthesis reaction was studied using experiment procedure 3.3.1.1. In this experimental catalyst concentration was 0.5% of rosin. Table 3.7 shows the reactant concentration.

Table 3. 7 The amount of reactant used for studying influence of reaction temperature on rosin-PEG derivatives synthesis reaction.

Entry	Rosin Type	Molecular Weight, g/mol	Acid Value, mg.KOH/g	Amount of Reactant (gram)		
				Rosin	PEG3000	ZnO
1	Rosin	302	170.4	26.3	130.4	0.526
2	Tetrahydroabietic acid	306	167	26.7	130.4	0.534
3	Maleic anhydride modified rosin	401	170-220	32.7	122.4	0.65

3.3.2 Part 2: Preparation of water-soluble solid soldering flux

3.3.2.1 Selection of activators for water-soluble rosin soldering fluxes

To optimized preparation condition for effect of varying activator type, activator concentrations and rosin-PEG derivatives were investigated. In this optimizing condition, the obtained product was characterized by JIS Z 3197 and J-STD-004.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 3. 8 The formula of sample for spreading factor test by various the concentration of acid and amine halide.

Activator Name	Formulas No./Reactant Conc.(%)									
	1	2	3	4	5	6	7	8	9	10
Ethylammonium chloride	0.1									
Dimethylammonium chloride		0.1								
Diethylammonium chloride			0.1							
Diethylammonium bromide				0.1						
Pyridine hydrobromide					0.1					
Succinic acid						5				
Glutaric acid							5			
Oxalic acid								5		
Pimelic acid									5	
Malonic acid										5
Rosin-PEG3000	24.9	24.9	24.9	24.9	24.9	20	20	20	20	20
Water	75	75	75	75	75	75	75	75	75	75
Total	100	100	100	100	100	100	100	100	100	100

The sample was prepared using the below procedure.

1. All chemicals were weighted in to 100 ml. glass beaker and put on hotplate and stirrer.
2. The mixture was stirred by magnetic bar until all chemicals completely dissolved.
3. This sample was used for spreading ratio test.

3.3.2.2 Preparation of water-soluble solid soldering flux

Table 3. 9 The amount of activator for water soluble rosin soldering fluxes (WSRFs).

Flux Code	Composition (% mass)				
	Ethylamine hydrochloride	Diethylamine hydrochloride	Succinic acid	Glutaric acid	Water Soluble Rosin 3000
WSRF01	0.20	0.12	0.00	0.00	99.68
WSRF02	0.20	0.12	2.50	0.00	97.18
WSRF03	0.20	0.12	5.00	2.50	92.18
WSRF04	0.20	0.12	5.00	5.00	89.68
WSRF05	0.20	0.12	5.00	5.00	89.68
WSRF06	0.20	0.12	2.50	5.00	92.18
WSRF07	0.20	0.12	2.50	7.50	89.68
WSRF08	0.20	0.12	0.00	10.00	89.68
WSRF09	0.00	0.00	5.00	2.50	92.50
WSRF10	0.00	0.00	5.00	5.00	90.00
WSRF11	0.11	0.00	5.00	5.00	89.89
WSRF12	0.11	0.00	2.50	5.00	92.39
WSRF13	0.00	0.15	2.50	5.00	92.35
WSRF14	0.00	0.15	5.00	5.00	89.85
WSRF15	0.06	0.00	5.00	5.00	89.94
WSRF16	0.00	0.08	5.00	5.00	89.93

3.3.2.3 Characterization of water-soluble rosin soldering fluxes

3.3.2.3.1 Acid value of reaction and WSRFs

The acid value of reaction and WSRFs were tested using Potentiometric automatic titrator (KEM AT510). This test is conformed to JIS Z 3197-1999 (21) and calculated using equation 3.2 and 3.3.

$$f = \frac{m_S}{V_{EP1} \times c(KOH) \times M_S}$$ Equation 3. 2

f : Titer of the selected titrant

Ms : Mass of standard in mg

VEP1 : Titrant consumption until the first equivalence point in mL

c(KOH) : Concentration of titrant in mol/L; here c(KOH) = 0.1 mol/L

MS : Molecular weight of the standard; here 112.12 g/mol

$$AV = \frac{V_{EP1} \times f \times c(KOH) \times MA}{m_s}$$ Equation 3. 3

AV : Acid value of the sample in mg KOH / g

VEP1 : Titrant used until the first equivalence point in mL

c(KO H): Concentration of titrant in mol/L; here c(KOH) = 0.1 mol/L

f : Correction factor («titer») without unit

MA : Molecular weight of KOH; 56.11 g/mol

Ms : Sample size in g

3.3.2.3.2 Solubility of rosin-PEG and water soluble rosin soldering fluxes

Solubility of the rosin-PEG derivatives and WSRFs in water was gravimetrically determined. Approximately 5 g of derivative was placed in 5 g of water for testing in different test tubes and then sonicated in an ultrasonic bath for one hour at 25 ± 0.5

°C. One gram of the sample was placed into a pre-weighed evaporating dish, dried at 85 ± 0.5 °C for one hour, and weighed. The difference in weights was used to calculate the solubility per gram of the sample (7).

3.3.2.3.3 Halide content test of water soluble rosin soldering fluxes

Halide content of WSRFs were tested using Potentiometric automatic titrator (KEM AT510).This test method is designed to determine the halide content of fluxes attributable to chlorides and bromides e made by titration with 0.1mol/L Silver nitrate. This test is conformed to JIS Z 3197-1999 (21).

1) Fluxes was weighted into a 100 ml. beaker.

2) DI water or 2-propanol was added in the beaker.

3) The beaker was placed on the station of titrator and titrated with 0.1mol/L Silver nitrate to obtain concentration of Halide.

4) Halide content was calculated as chloride content using equation 3.4.

$$Halide\ (\%) = \frac{(EP1 - BL1) \times FA1 \times C1 \times K1}{SIZE} \qquad \text{Equation 3. 4}$$

EP1 : Titration volume (mL)

BL1 : Blank level (mL)

FA1 : Factor of titrant (1.00)

C1 : Concentration conversion coefficient (0.355 mg/mL)

(Chorine in mg equivalent to 1mL of 0.01mol/L AgNO3)

K1 : Coefficient (1000)

SIZE : Sample size (g)

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

3.3.2.3.4 Spreading ratio test of water soluble rosin soldering fluxes

A certain volume of solder and flux was placed and heated for a fixed time on an oxidation treated copper plate. After fusing, evaluate the effect of flux was measured and calculated using equation 3.5 and 3.6. This procedure shall be carried out on the 5 test pieces and the mean value were obtained as the spreading ratio of the specimen. This test is conformed to JIS Z 3197-1999 (21).

$$SR = (\frac{D-H}{D})\ x\ 100 \qquad \text{Equation 3. 5}$$

Where, SR : spreading raito (%)

H : height of the spread solde r(mm)

D : diameter of the solder, when it is assumed to be a sphere (mm)

$$D = 1.24V^{1/3} \qquad \text{Equation 3. 6}$$

V : mass/density of tested solder

3.3.2.3.5 Copper plate corrosion test of water soluble rosin soldering fluxes

This test is standard method to evaluate the existence of corrosion due to the flux residue after soldering under moisture. Using preconditioned steel plate, test piece shall be prepared on which plate solder is fused with flux. After this soldering, the test piece shall be left under humidified condition which is specified, and evaluate the corrosion by discoloring the flux residue. This test is conformed to JIS Z 3197-1999 (21).

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

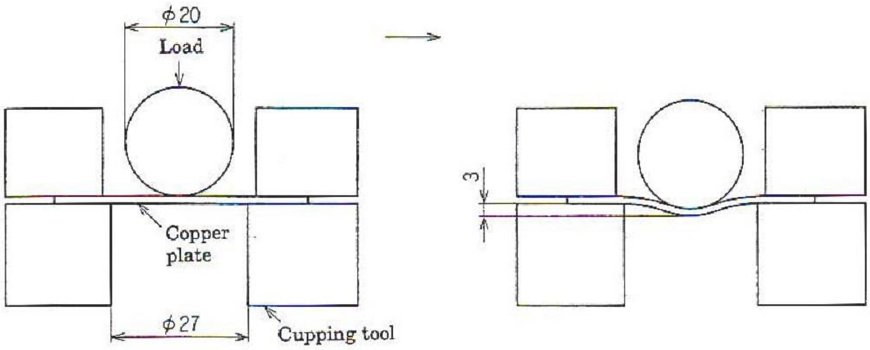


Figure 3. 1 Copper plate for testing (21).

3.3.2.3.6 Insulation Resistance test of water soluble rosin soldering fluxes

This test used a printed circuit board with a comp pattern as picture showed below as a test pieces. 25% Flux solution was applied to a test board and soldered at 270 ± 5 ^{O}C. Insulation resistance was measured by 1865 Megohmmeter (Quadtech) after precondition of soldering board at 40 ± 2 ^{O}C, 90-95 RH % for 168 hours. This test is conformed to JIS Z 3197-1999 (21).

3.3.2.3.7 Resistivity test of aqueous solution of water soluble rosin soldering fluxes

Resistivity test of aqueous solution shall be tested as follow. Specified quantity of flux solution (0.100 ± 0.005 ml) was boiled]; with the purified water of its quantity known (50 ml), and measured the resistivity of this solution by conductivity meter at room temperature. This test is conformed to JIS Z 3197-1999 (21).

3.3.2.3.8 Ionic Residue Test of water soluble rosin soldering fluxes

This test method obtain the amount of ionic residue remained on printed circuit board by measuring resistivity of the washing agent after washing and by converting the value into NaCl volume per unit area. Evaluation shall be done by comparing this with the value of the reference board converting the resistivity into μg. NaCl/cm^2. This test is conformed to JIS Z 3197-1999 (21).

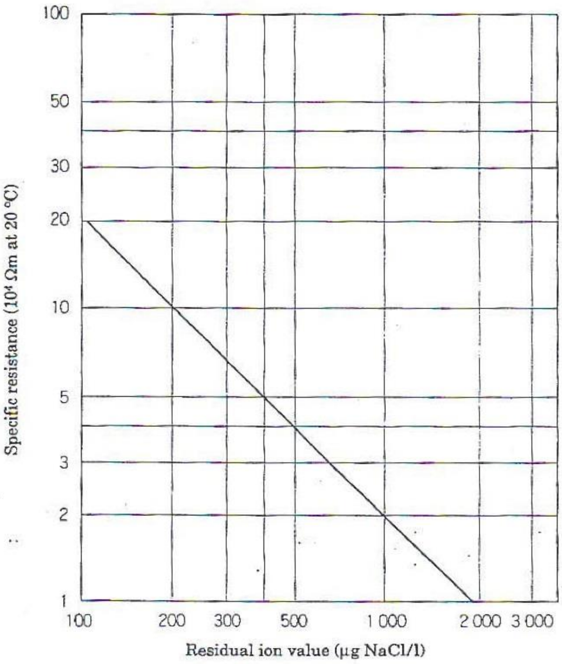


Figure 3. 2 Relation between ionic residue and resistivity by NaCl conversion (21).

Table 3. 10 Test methods and residual ion value (21).

(in terms of Nacl/cm^2)

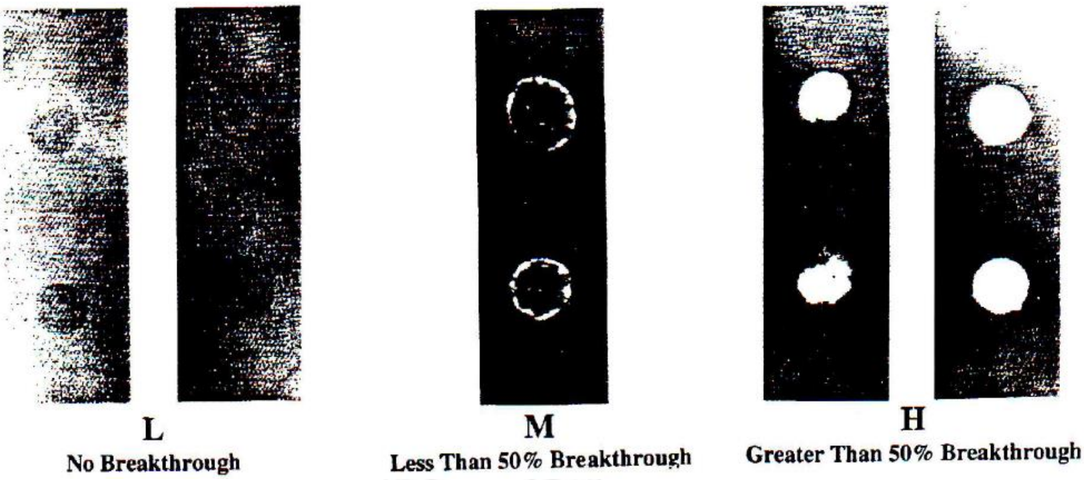
Test methods	Specified values of residual ion (for information) μgNaCl/cm^2
Conductimetric bridge	1.56 max.
Static method	2.2 max.
Dynamic method	3.1 max.

3.3.2.3.9 Flux Induced Corrosion (Copper Mirror Method) test of water soluble rosin soldering fluxes

One drop of the control standard flux was placed adjacent to the test flux. The test panel was placed in a horizontal position in the dust free cabinet at 23 ± 2 °C [73.4 ± 3.6 °F] and 50 ± 5% relative humidity for 24 ± 1/2 hours.

At the end of the 24 hour period, the test panel was removed from the cabinet. The test flux and control standard flux was removed by immersion in clean 2-propanol.

The test panel was carefully examined for possible copper removal or discoloration. The evaluation criteria showed below picture.



L
No Breakthrough

M
Less Than 50% Breakthrough

H
Greater Than 50% Breakthrough

Figure 3. 3 Flux type classification by copper mirror test (22).

3.3.3 Production of water soluble cored flux solder wire

1. Raw materials rosin-PEG3000 were weighted in to beaker 2000 ml.
2. The mixture was heated and stirred for 9 hours until the reaction completely.
3. Acid value was checked as the method 3.3.2.3.1. and activators were added in to WSR3000.
4. The mixture was heated until all materials completely melted.
5. The extrusion machine was set up.
6. The temperature of WSRF was reduced to 100 ^{O}C and poured in to flux tank.
7. The flux core solder wire was extruded into 9 mm diameter, using ultracore extrusion machine as show in figure 3.4 and flux content was checked.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Figure 3. 4 Extrusion machine used for production of water soluble rosin flux cored solder wire.

8. The flux cored solder wire was drown 9 mm. to 1.0, 1.2 mm. diameter.
9. Solder wire was wined in to the bobbin.
10. Flux content was measured conform to JIS Z 3197
11. Solderability of products were tested using automatic soldering machine. Figure 3.5 shows the soldering equipment for solder ability test. Test condition @ 380 ^{O}C.

Figure 3. 5 Solderability test equipment for water soluble rosin soldering fluxes cored solder wire.

CHAPTER IV

RESULTS AND DISSCUSSION

4.1 Optimized conditions for synthetic reaction of rosin-PEG derivatives

In this reaction, carboxylic groups in abietic acid were reacted with hydroxyl groups of PEG to form an ester and water in the presence of a catalyst. The effects of catalyst type, catalyst concentration, rosin concentration, reaction temperature, reaction time, and PEG type on the reaction performance were investigated. The reaction conversion (%) was determined from the acid value of the product.

4.1.1 Influence of catalyst type on the esterification reaction

The esterification reaction of rosin and PEG to rosin-PEG derivatives was carried out in the presence of various kind of catalyst. In this research, Zn-dust, ZnO, and Tin chloride were used for study on catalytic performance of esterification reactions and the results are illustrated in Figure 4.1.

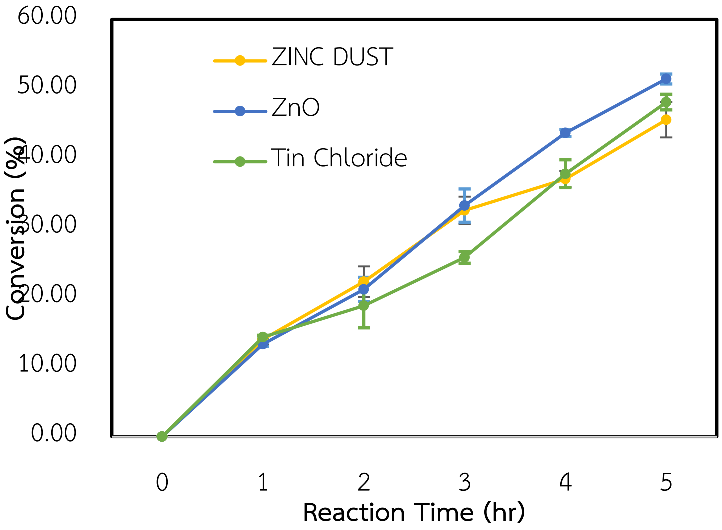


Figure 4. 1 Conversion percentage of reaction versus time for the esterification reaction between rosin and PEG1500 using Zn dust, ZnO, and Tin Chloride as catalysts.

The catalytic performances of Zn dust, ZnO, and tin chloride on the esterification reactions of rosin and PEG were studied and compared (Figure 4.1). Zinc oxide was the most effective catalyst as it resulted in the highest conversion to ester (at 5 hours) due to the Lewis acid performance of this catalyst. ZnO showed higher catalytic performance than metallic zinc in agreement with findings previously reported by Hattori (23). Even though ZnO and tin chloride are both Lewis acids, ZnO had a higher reaction rate than that of tin chloride which was consistent with results previously reported (24, 25). ZnO was therefore selected as the catalyst for this esterification reaction.

4.1.2 Influence of catalyst concentration on the esterification reaction

The concentration of ZnO was varied and the effect on reaction conversion of rosin and PEG to rosin-PEG derivatives was studied. The result was shown in Figure 4.3.

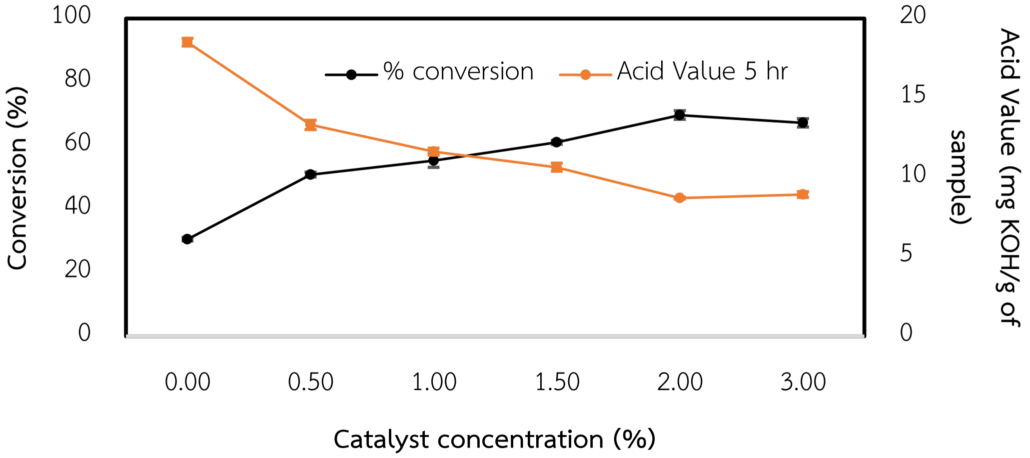


Figure 4. 2 Conversion percentage of reaction and acid value (mg.KOH/g of sample) versus catalyst concentration (%) for the esterification reaction between rosin and PEG1500 using ZnO catalyst.

Figure 4.3 shows the percentage conversion of different reactions, along with their acid values, versus catalyst concentration (%) for the esterification reaction of PEG1500 and 0.5% ZnO at 250°C for 5 hours. The data show that increasing the concentration of the catalyst from 0.5% to 2.0% increased the reaction conversion from 30.2% to 69.4%; however, the conversion decreased slightly to 67.0% when the catalyst concentration was increased to 3.0%. This finding suggests that increasing catalyst concentration had a noticeable effect on the conversion rate of the rosin into ester derivatives. This fact can be attributed to the higher number of molecules of substrate activated by polarization of the carbonyl in the presence of the Zn^{2+} catalyst. Thus, the nucleophilic attack by hydroxyl groups of PEG becomes more favourable which results in the increase of ester formation. These results were consistent with those previously reported (26, 27). Therefore, the optimum catalyst concentration was chosen as 2.0%.

4.1.3 Influence of the rosin:PEG ratio on the esterification reaction

The molar ratio of rosin: PEG was varied and the effect on reaction conversion was studied. The result was shown in Figure 4.8.

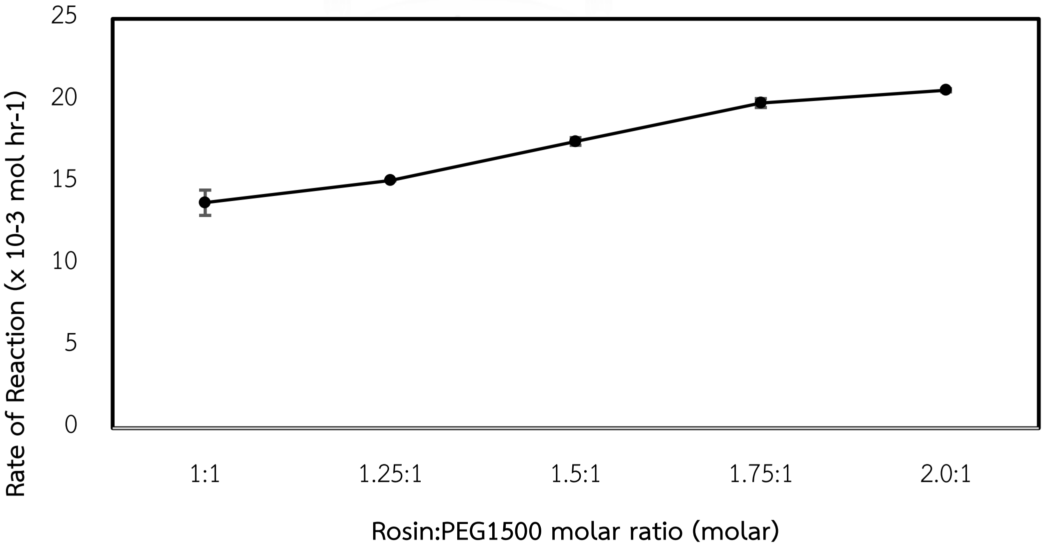


Figure 4. 3 Rate of reaction of rosin-PEG derivatives using different molar ratios of rosin:PEG1500.

The rosin:PEG ratio is one of the most important parameters that affects the conversion of rosin to rosin-PEG derivatives. The effect of the rosin:PEG ratio on the conversion of rosin was investigated at 250 °C with a catalyst concentration of 2%. Figure 4.3 represents the rate of the esterification reactions at various rosin:PEG ratios. The reaction rate at a 2:1 ratio was the highest. It could be suggested that the reaction is driven forward by using a large excess of rosin to PEG due to the reversible nature of the esterification reaction. This result is consistent with those previously reported (7, 17, 28). The optimal ratio of rosin to PEG was therefore chosen as 2:1.

4.1.4 Influence of temperature on the esterification reaction

Reaction temperatures of 100 °C, 150 °C, 200 °C, 225 °C, and 250 °C for 5 hours were investigated for completion of the reaction. Table 4.1 shows the results of reaction at each temperature and indicates that the acid value of the mixture did not change at 100°C but dropped when the reaction temperature was increased to 150 °C, 200 °C, 225 °C, and 250 °C. From the experimental data it can be concluded that at 100 °C the reaction of rosin and PEG did not occur. However, the reaction rate increased with increase in the reaction temperature because water molecules were eliminated more effectively from the reaction to form PEG esters of rosin. The product obtained at 250 °C showed the highest water solubility at 0.96 mg/ml. This result was consistent with those shown in previous studies (Cardoso *et al*., 2008; Morkhade *et al*., 2008; Liu *et al*., 2006). The optimum reaction temperature was therefore chosen as 250 °C.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

Table 4. 1 Acid value, conversion percentage, and water solubility of reaction product at temperatures of 100°C, 150°C, 200°C, 225°C, and 250°C.

Reaction Temperature (°C)	Acid Value (mg KOH/g of sample)		% conversion	Water solubility (g/L)
	start	5 hrs		
100	46.53 ± 0.19	47.04 ± 084	No Reaction	324.89 ± 3.42
150	47.00 ± 0.02	43.95 ± 0.75	6.50 ± 1.55	244.84 ± 8.79
200	48.96 ± 0.22	45.34 ± 0.66	7.29 ± 0.93	3.07 ± 1.62
225	50.03 ± 0.67	40.66 ± 0.86	18.74 ± 0.62	8.50 ± 9.31
250	47.55 ± 0.14	16.37 ± 0.01	65.57 ± 0.09	971.88 ± 15.89

4.1.5 Influence of the reaction time on the esterification reaction

The conversion of rosin and PEG to the rosin-PEG derivative was expected to be time-dependent so the effect of increasing reaction time was investigated. The results in Figure 4.4 show that increasing the reaction time from one to eight hours significantly increased reaction conversion, which then became constant from nine to ten hours. The reaction time of nine hours was therefore optimal with 95% reaction conversion.

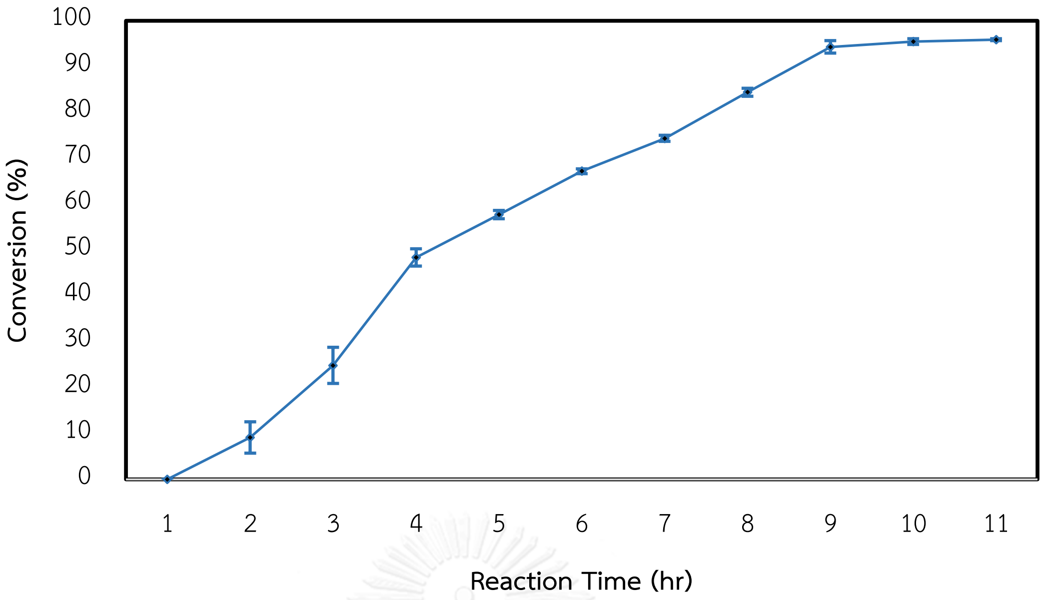


Figure 4. 4 Conversion percentage of rosin-PEG derivatives using ZnO 2%, rosin 2 mol : PEG 1 mol at 250°C for 10 hr.

4.1.6 Influence of the resin type on the resin type

In this study three kinds of rosin was used and the results show in table 4.3

Table 4. 3 Characteristics of rosin-PEG3000 derivatives using difference kind of resin.

Rosin Type	% conversion	Color and appearance	Melting Point, ^{O}C
Rosin	84.54	Black	55.2
Tetrahydroabietic acid	74.93	Black	47.1
Maleic anhydride modified rosin	73.06	Black	56.0

From test data it can be conclude that rosin-PEG3000 derivative is the most appropriated for solid flux production due to % conversion of reaction and melting point were the highest.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

4.2 Characterization of rosin-PEG derivatives

4.2.1 FT-IR and ^{13}C NMR spectroscopy measurement

FT-IR and ^{13}C-NMR were used to characterize and confirm the ester bond formation in the rosin-PEG derivatives. Figure 4.5 presents the IR spectra of rosin, PEG, and the rosin-PEG1500 derivative at 0, 5, and 10 hours. The IR spectrum of rosin shows a peak at 1691 cm^{-1} (C=O stretching) and one at 3568 cm^{-1} (O–H stretching), indicating the presence of the carboxylic acid group in rosin (29). The IR spectrum of the derivative at hour zero showed peaks at 1693 cm^{-1} (C=O stretching, carboxylic group) and 1721 cm^{-1} (C=O stretching, ester group). The peak ratio 1693/1721 decreased when the reaction time was increased, suggesting that the conversion of acid to ester increased with increasing reaction time. This finding is consistent with that reported previously (Morkhade *et al*., 2008). Overall, the results suggested that the ester group was present in all rosin-PEG derivatives (Figure 4.6). The ^{13}C-NMR spectra of all Rosin-PEG derivatives are presented in Figure 4.7 with the chemical shift around 180 ppm supporting the existence of the ester bond (C=O). These findings are consistent with those previously reported (30-32).

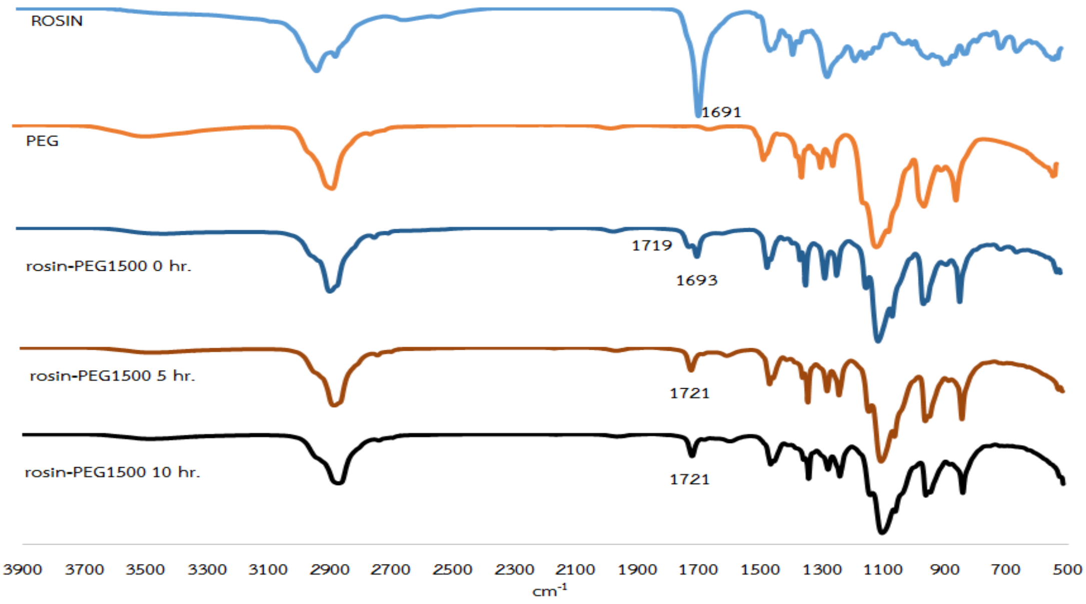


Figure 4. 5 Infrared spectra of China rosin, PEG and the rosin-PEG1500 derivative at 0 hour, 5 hours, 10 hours.

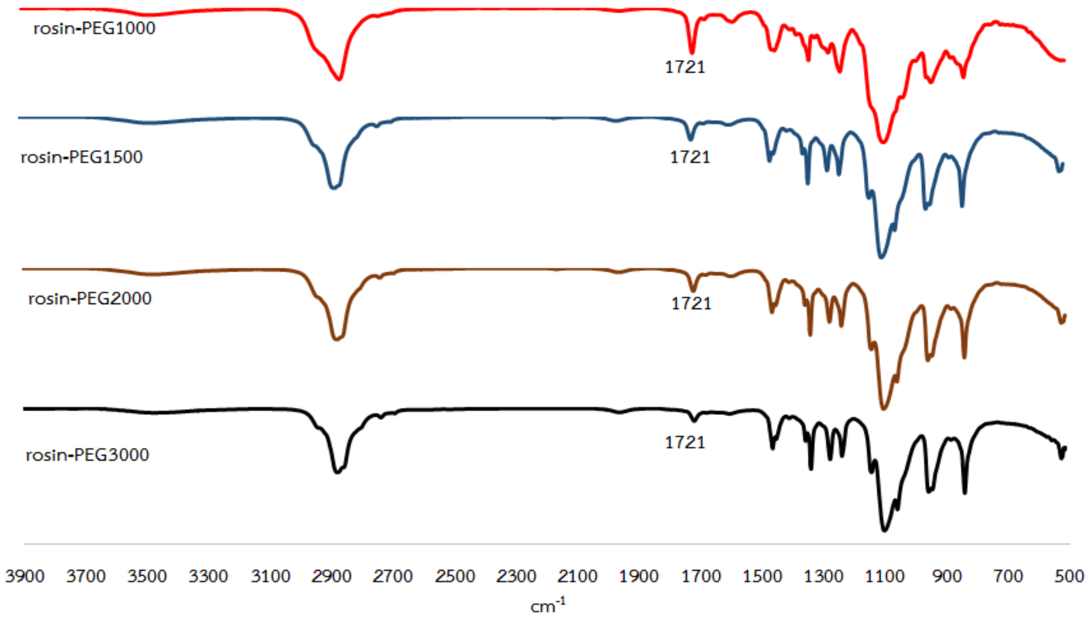


Figure 4. 6 Infrared spectra of rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000.

From FTIR and ^{13}C-NMR data, it can confirmed that esterification reaction of carbonyl group from rosin and hydroxyl group from PEG occurred and formed ester group lead to water soluble material (17, 30, 31). The reaction scheme can be proposed as shown in scheme 4.8.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

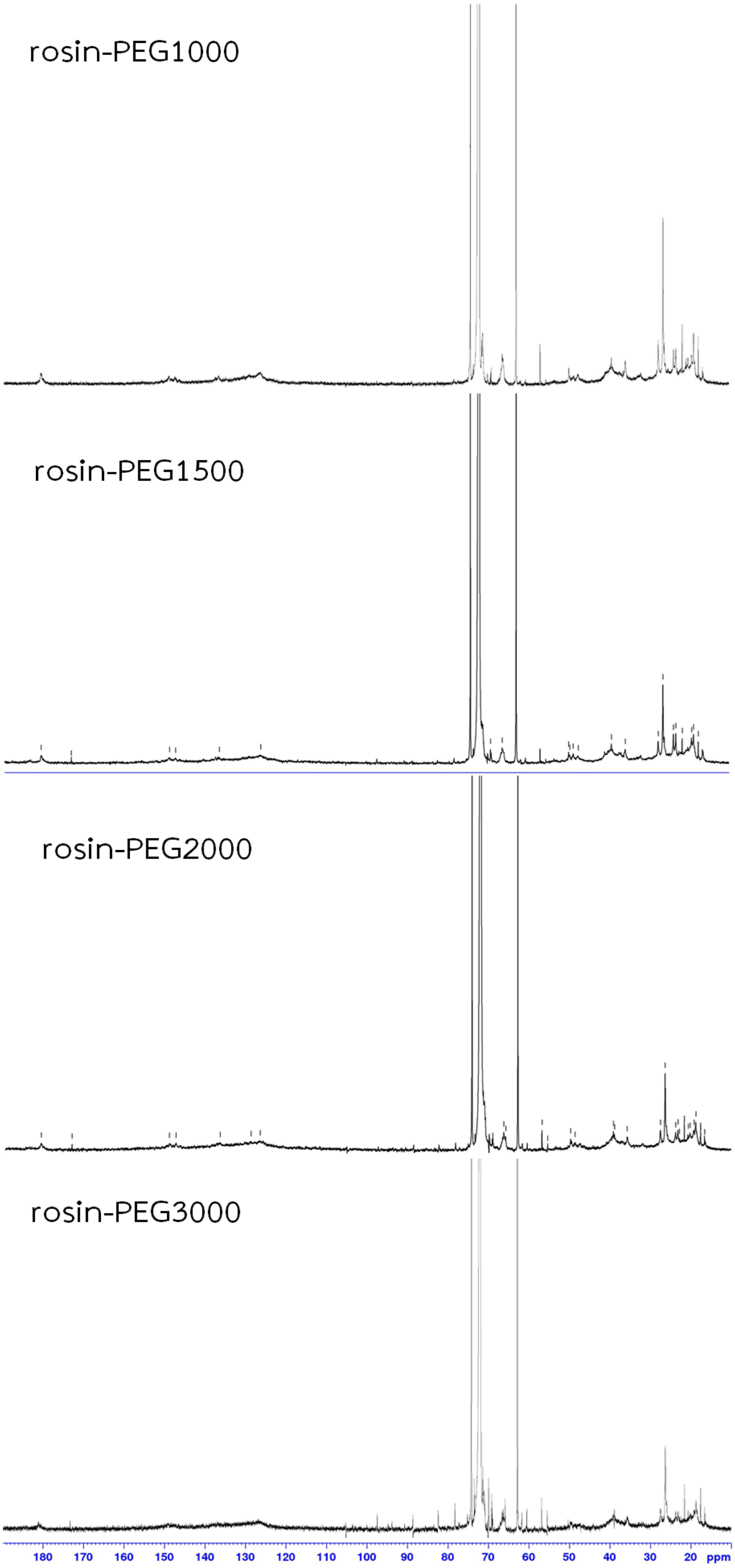


Figure 4. 7 ^{13}C-NMR spectra of rosin-PEG derivatives (rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000).

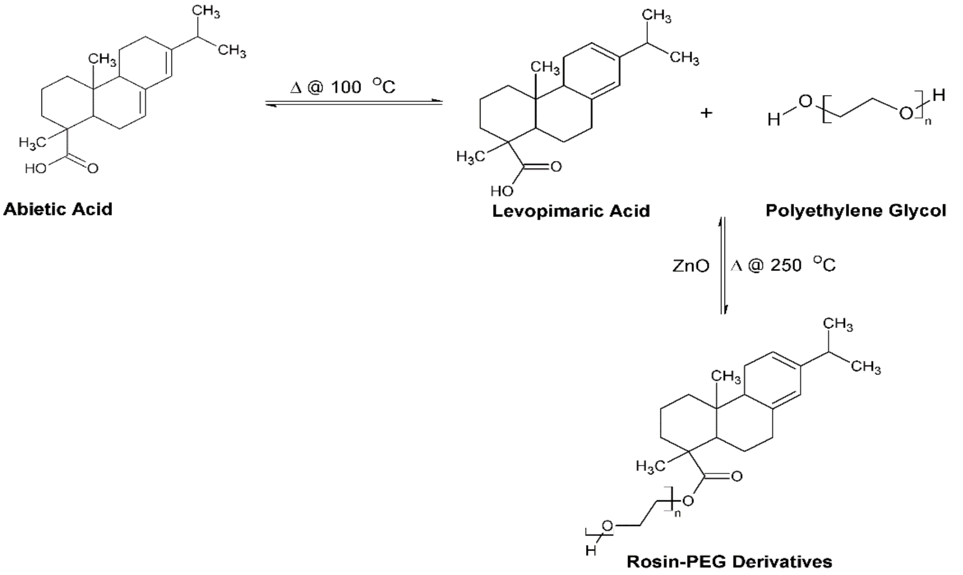


Figure 4. 8 Reaction scheme of rosin-PEG derivatives synthesis.

4.2.2 DSC measurement

Figure 4.9 presents the DSC data of the rosin-PEG derivatives. The melting points of the derivatives were lower than that of native rosin. However, they increased when the molecular weight of PEG increased.

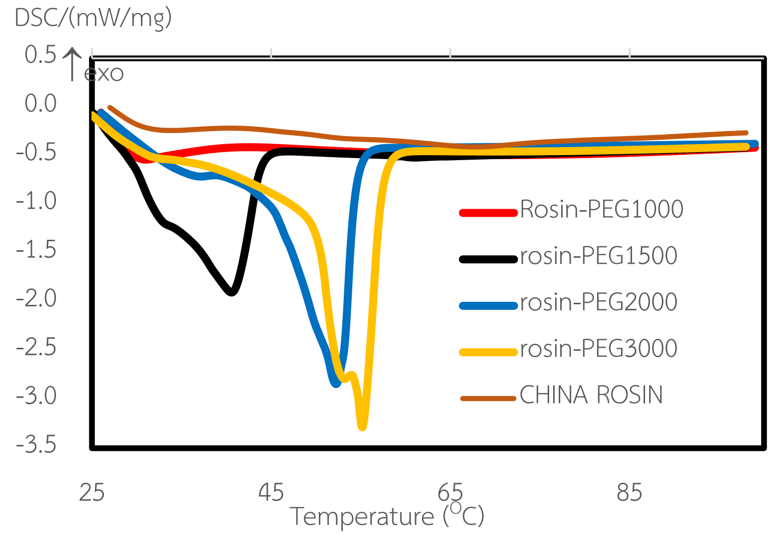


Figure 4. 9 DSC spectrum of rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000.

All rosin-PEG derivatives were completely dissolved in water, suggesting that the carboxylic acid group in rosin reacted with the hydroxyl group in PEG to yield the ester bond and increase the hydrophilicity of rosin. Thus, reaction with PEG increased the water solubility of native rosin.

The physical and chemical properties of rosin-PEG derivatives are summarized in Table 4.2. The results show that all PEGs had excellent water solubility. The water-soluble rosin synthesized from PEG3000 showed the highest melting point at 55.2 °C. These results suggest that the melting point of the rosin-PEG derivatives are influenced by the rosin content and the melting point of the PEG which is consistent with results reported previously (7, 17, 28).

Table 4. 2 Physical and chemical properties of rosin-PEG derivatives.

Items	Rosin-PEG1000	Rosin-PEG1500	Rosin-PEG2000	Rosin-PEG3000
Appearance	Dark brown	Dark brown	Dark brown	Dark brown
Melting point (°C)	< 25.0	40.6	52.2	55.2
Weight-A.M.W. (Mw)/PDI	1141/1.19	1647/1.30	2405/1.36	3198/1.58
Water solubility (g/ml)	Soluble (1.1±0.01)	Soluble (1.07±0.01)	Soluble (1.11±0.02)	Soluble (1.06±0.01)
Acid value (mg KOH/g of sample)	2.73±0.51	2.50±0.31	4.44±0.42	4.37±1.07
Conversion (%)	95.5±0.51	95.0±0.66	88.9±1.29	84.5±3.76

The physical and chemical properties of rosin-PEG derivatives using difference resin type are summarized in Table 4.3. It was found that rosin-PEG3000 showed the highest % conversion at 84.54%.

Table 4. 3 Physical and chemical properties of rosin-PEG derivatives using difference resin type.

Rosin Type	% Conversion	Color	Melting Point, ^{O}C
Rosin	84.54	Black	55.2
Tetrahydroabietic acid	74.93	Black	47.1
Maleic modified rosin	73.06	Black	56

The aim of this research is to find a suitable flux vehicle with water washable characteristics to be used in solid core flux for lead-free solder wire. Since rosin-PEG3000 had an appropriate melting point and could be injected and solidified in cored solder, it was chosen as a representative for further study as a solid, WSRF.

4.2.3 XRF measurement

Zn content in Rosin-PEG derivatives was determined by XRF (Figure 4.10). The results show that the concentration (%) of Zn contained in rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, and rosin-PEG3000 derivatives was 0.80%, 0.60%, 0.34%, and 0.40%, respectively. It was assumed that ZnO used as a catalyst remained in the synthesized product and was changed from ZnO to $Zn(O[CH_2CH_2O]_n)_2$, which enhanced its solubility in water.

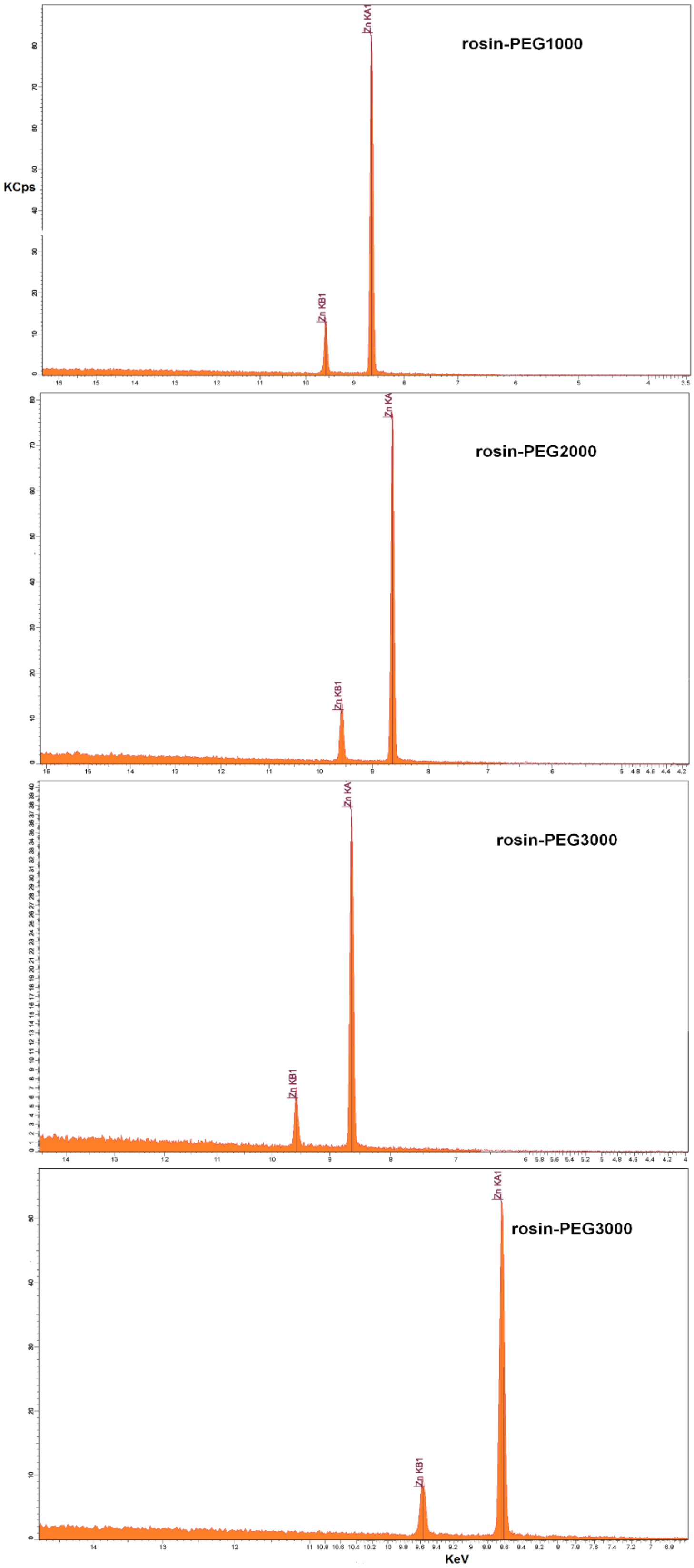


Figure 4. 10 XRF spectra of Zn in rosin-PEG1000, rosin-PEG1500, rosin-PEG2000, rosin-PEG3000.

4.3 Investigations of water-soluble rosin soldering fluxes produced from rosin-PEG derivatives

4.3.1 Selection of activator for production of WSRFs

Dicarboxylic acids and amine hydrohalides with water solubility of at least 50 mg/L and melting points of at least 100 °C were selected as activators for the production of water-soluble soldering fluxes. Table 4.4 shows the spreading ratios of dicarboxylic acids and amine hydrohalides. It was found that amine hydrohalides had higher spreading ratios than dicarboxylic acid. This finding could be explained by the active functional groups of the amine hydrohalides (HCl and HBr) being more active than the carboxylic acid group (-COOH) of the acid activators.

Table 4. 4 Spreading ratio of various amine hydrohalides and various dicarboxylic acids using Sn-0.7Cu at 270°C.

Formulas No.	Spreading ratio (%)
1	70.6
2	65.8
3	59.7
4	61.9
5	60.4
6	73.1
7	76.3
8	47.9
9	70.7
10	65.0

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

For the amine hydrohalide activators, ethylamine hydrochloride (ET.HCl) and diethylamine hydrobromide (DE.HBr) showed the highest spreading ratio because these chemicals have the lowest melting point and contained the highest total halide content. Therefore, ET.HCl and DE.HBr were selected as the halide activators in this study. Oxalic acid, malonic acid, and pimeric acid were less active compared to glutaric acid (GA) and succinic acid (SA) because the flux's activity was initiated when the acid melts (33). Thus, dicarboxylic acids with lower melting points have more time for the action of the flux to take place. For this reason, GA and SA were selected for production of WSRFs in this research.

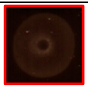
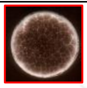
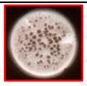
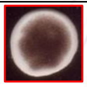
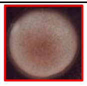
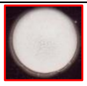
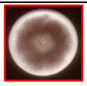
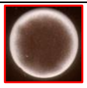
4.3.2 Characteristics of water-soluble rosin soldering fluxes

The target characteristics of WSRFs are low halide content (chloride [Cl$^-$] <1000 ppm and bromide [Br$^-$] < 1000 ppm), low total halide content (combined Cl$^-$ and Br$^-$ less than 1500 ppm), and low corrosion (L and M types) even with the "no-clean" condition.

The flux expansion method was used to determine the flux wettability characteristic at the time of soldering and expressed as a spreading ratio. Table 4.3 shows the characteristics of 16 WSRFs with different concentrations of GA, SA, ET.HCl and DE.HBr.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

Table 4. 5 Characteristics of WSRFs.

No.	Halide Content (as % chloride)	Copper Mirror Corrosion	Flux Category	Copper Corrosion	Spreading Rate (%)	Insulation Resistance (IR) (Ωx10^{12})
WSRF01	0.1205±0.0016		L1	No corrosion	69.2±1.1	1.65±0.38
WSRF02	0.1275±0.0042		M1	No corrosion	70.2±0.9	2.15±0.23
WSRF03	0.1198±0.0082		M1	No corrosion	71.3±1.1	2.75±0.91
WSRF04	0.1150±0.0015		M1	No corrosion	73.3±0.3	2.04±0.38
WSRF05	0.1072±0.0123		H1	Corrosion	74.1±1.6	5.15±1.57
WSRF06	0.1175±0.0071		H1	Corrosion	73.6±0.6	1.39±1.14
WSRF07	0.1208±0.0069		H1	Corrosion	74.4±0.6	1.91±0.58
WSRF08	0.1112±0.0019		H1	Corrosion	74.4±2.7	2.33±1.81
WSRF09	0.0000±0.0000		L0	No Corrosion	69.3±0.4	3.27±1.85
WSRF10	0.0014±0.0020		L0	Corrosion	69.3±3.0	3.49±1.47
WSRF11	0.0407±0.0052		H0	Corrosion	73.3±0.9	4.02±2.31
WSRF12	0.1107±0.0020		H0	Corrosion	71.5±0.8	3.81±1.62
WSRF13	0.0462±0.0004		H0	Corrosion	72.6±0.9	2.09±0.53
WSRF14	0.0495±0.0005		H0	Corrosion	73.2±0.6	2.43±0.77
WSRF15	0.0252±0.0018		H0	Corrosion	72.1±1.9	1.51±0.69
WSRF16	0.0243±0.0022		H0	Corrosion	71.2±1.2	2.23±0.19

An insulation resistance (IR) test was used to examine the insulation resistance of flux residue after soldering under conditions of high temperature and high humidity. This study was performed after the test circuit board passed preconditioning at 85°C and 85% relative humidity for 168 hours. From the test results, the IR of all fluxes was more than 1 x 10^{12} ohms and showed no significant difference because all fluxes were low-halide types which could not induce conductivity in the residue (34).

The copper mirror test was used to examine the corrosion characteristics of flux in accordance with the IPC-TM-650 test method 2.3.32. Flux was classified into three types depending on the degree of removal of the copper film coated on the glass slide. The data led to the classification of WSRFs 01, 09 and 10 as type L (low), WSRFs 02, 03, 04, 06, 11 and 12 as type M (medium), and WSRFs 05, 07, 08, 14, 15 and 16 as type H (high). From the data, WSRFs containing halide showed a greater degree of corrosion than did acid flux due to the fact that halide fluxes generate HCl and HBr in the soldering process and the corrosion of these types of fluxes was much more pronounced than those of organic acids (33).

The copper plate corrosion test was used to examine the corrosion characteristics of flux residue after soldering at 270 °C. These characteristics were evaluated by the discoloration of the flux residue on a copper plate or the presence or absence of corrosion product during exposure to humidity at 90 - 95% and a temperature of 40 ± 2 °C for 72 hours. This test was carried out in accordance with JIS Z 3197-1999. The tests performed on WSRFs 01, 02, 03, 04 and 09 did not change the color of the copper plate with flux residue due to the low halide and acid content of these fluxes. From all of the test results, WSRFs 01, 02, 03, 04 and 09 demonstrated low corrosion to copper. WSRFs 04 and 09 were chosen due to their characteristics.

For ionic residues, a test was used to evaluate the reliability of a printed circuit board after the soldering and cleaning process by measuring the resistivity of the washing agent after washing and expressing in terms of weight of sodium chloride per cm^2. This test was applied for WSRFs 04 and 09 and their results showed the presence of <2.2 μg.NaCl/cm^2 (Table 4.4). These findings confirmed that WSRFs 04 and 09 were completely removable by water and a low residue of conductance material remained on the soldered board after cleaning.

Table 4. 6 Ionic contamination test results of WSRF04 and 09.

Sample Name	Resistivity @ 20 ^{O}C (MΩ)					Residue Ion Value (µg.NaCl/cm^2)
	1	2	3	Average	SD	
Test solution	10.25	10.21	10.51	10.32	0.133	Approx. 1.8
Reference board	9.84	9.58	10.02	9.81	0.181	Approx. 2.1
WSRF04	8.32	10.21	10.53	9.69	0.975	Approx. 2.1
WSRF09	8.67	10.42	10.24	9.78	0.786	Approx. 2.1

Table 4. 7 Water solution resistivity test results of WSRF04 and 09.

Sample Name	Conductivity @ 20 ^{O}C (µS)					Water solution Resistivity, Ωm	Specification , Ωm
	1	2	3	Average	SD		
DI water	0.63	0.61	0.65	0.63	0.016	15873	5000 min
WSRF04	4.91	4.75	4.95	4.87	0.086	2053	500 min
DI water	0.66	0.64	0.74	0.68	0.043	14706	5000 min
WSRF09	4.71	4.56	4.83	4.70	0.110	2128	1000 min

Water solution resistivity test is to be carried out to determine the mass of conductive material in flux, and specifies the procedure of measuring resistivity of extracted water from a solution containing a certain level of density and test result of WSRF04 and 09 show in Table 4.5. From test results indicate that WSRF04 and 09 contain conductive material conform to control standard of JIS Z 3283-2006 type AA and type A.

The water solubility test of WSRFs 04 and 09 were 1.11 and 1.09 g/ml respectively showed that two fluxes completely dissolved in deionized water at 25 °C to 30 °C. This indicated the efficiency of water washing during flux residue cleaning.

From all of the data, it was suggested that the best formulation among the halide-free WSRFs (halide less than 0.05%) was WSRF 09 and the best formulation among the low halide WSRFs (halide less than 0.15%) was WSRF 04.

4.3.2 Water-soluble cored flux solder wire production

In this study water soluble core flux might be extruded in cored solder and halide content, the solderability, flux content and stability of flux and other properties were studied and reported as show in table 4.6, figure 4.13 and 4.14.

Table 4. 8 Summary of test result of water-soluble flux cored lead free solder wire.

Test Item	**Product Name**	
	U5204 WRSF04	**U5204 WRSF09**
Tin (Sn)	Remainder	Remainder
Copper (Cu)	0.698	0.685
Flux content, % mass	3.893 ± 0.071	3.895 ± 0.012
Halide Content, % mass	0.1168 ± 0.001	N.D (< 0.001)
Acid Value, mg.KOH/g	72.404 ± 0.418	74.734 ± 0.534
Spreading Ratio, %	73.3 ± 0.3	69.3 ± 0.4
Soldering time, S	0.78 ± 0.00	1.11 ± 0.00

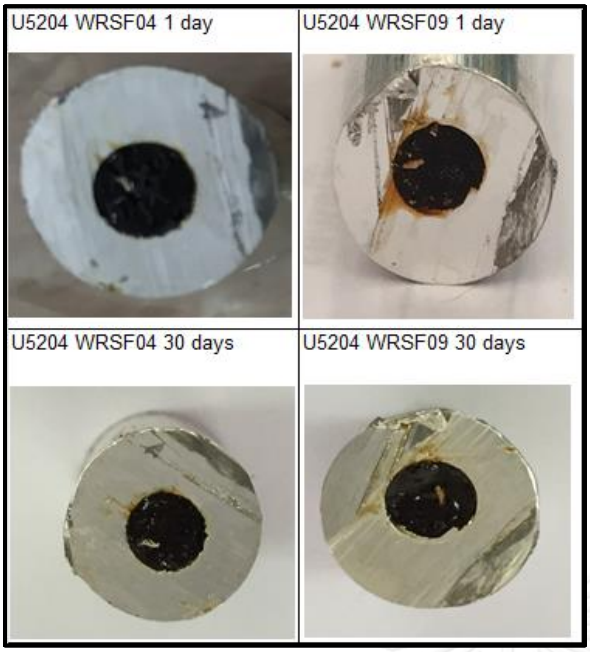


Figure 4. 11 Cross section of water-soluble fluxed core lead free solder wire 11 mm storage at room temp. for 30 days.

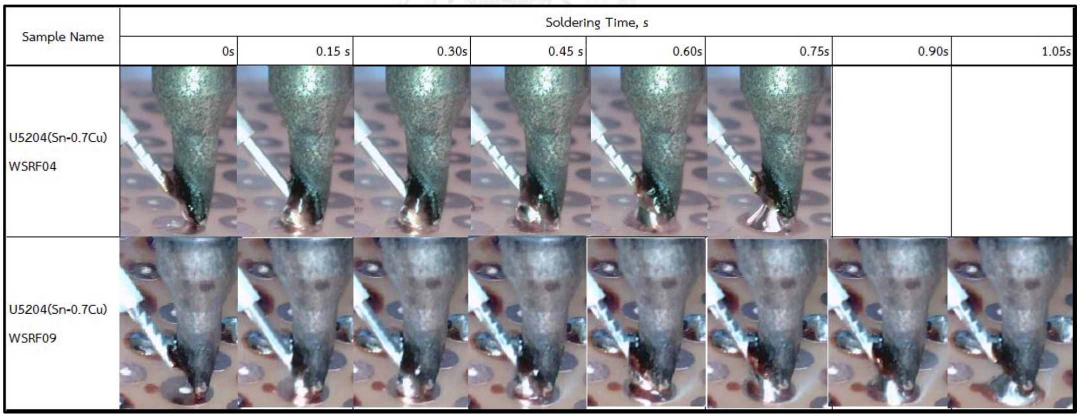


Figure 4. 12 Picture of soldering time of water-soluble flux cored lead free solder wire U5204-WRSF04 and U5204-WRSF09 @ 380 ^{O}C.

CHAPTER V
CONCLUSION AND SUGESTION

5.1 Conclusion

The rosin-PEG derivatives were successfully synthesized from rosin and PEG using 2% ZnO as a catalyst, with a 2:1 ratio of rosin:PEG at a temperature of 250 °C over 9 hours. The rosin-PEG derivatives were completely soluble in water. The rosin-PEG3000 showed the highest melting point at 55.2 °C which was suitable to be applied as a water-soluble solid soldering flux and it was chosen for the investigation of WSRF characteristics. The study revealed that succinic acid, glutaric acid, ethylamine hydrochloride, and diethylamine hydrobromide showed acceptable wetting ability and were chosen for the production of fluxes. WSRFs were prepared and characterized and it was found that WSRF 09 and WSRF 04 were the best water-soluble rosin soldering fluxes with good solderability, low halide content (less than 1500 ppm), high insulation resistance, and low corrosion even though “no-clean” conditions were adopted. Soldering performance was very good using Sn-0.7Cu solder alloy. The flux characteristics complied with type AA and A according to JIS Z 3283. These environmentally friendly, water-soluble PEG-rosins are therefore attractive as water-soluble rosin solid soldering flux vehicles, especially for solid core solder wire for the electronics industry.

5.2 Suggestion for further work

Further studies are necessary on large-scale production and to compare the performance of these fluxes to those from conventional water-soluble soldering fluxes currently available in the market. Moreover, the application of rosin-PEG derivatives for liquid flux and solder paste flux will be investigated.

REFERENCES

1. Klein-Wassink R. Soldering in electronics. 2 ed: Electrochem. Soc.; 1994. 753 p.

2. Cole HF, inventor; US Patent 4290824, assignee. Water soluble rosin flux. US patent 4290824. 1981.

3. Turner RL. Water-soluble flux for cored solder. US Patent 5192360; 1993.

4. Strauss R. Cleaning after soldering. 1998:261-324.

5. Hwang JS. Alkali metal hydroxide in polyol flux, water soluble synthetic wax. US Patent 4460414; 1984.

6. Jacobs W. Water soluble activator is mixture of alkylamine acid salt, lower alkanol amine, organic acid, (poly)ethylene glycols. US Patent 4872928; 1989.

7. Nande VS, Barabde UV, Morkhade DM, Patil AT, Joshi SB. Synthesis and characterization of PEGylated derivatives of rosin for sustained drug delivery. Reactive and Functional Polymers. 2006;66(11):1373-83.

8. Silvestre AJ, Gandini A. Rosin: major sources, properties and applications. Monomers, Polymers and Composites from Renewable Resources. 2008;6:67-88.

9. Inc. M. Rosin grade and rosin type: MiniScience Inc.; 2005 [cited 2015 10-12-2015]. Available from: http://www.rosinproducts.com/.

10. Strauss R. SMT Soldering Handbook: Elsevier; 1998. 20-83 p.

11. Thompson Jr FA. Solder flux. US Patent 4,180,419; 1979.

12. Cole HF. Water soluble rosin flux. US Patent 4,290,824; 1981.

13. Gutierrez BL, Sickler J. Water soluble soldering flux. US Patent 4,994,119; 1991.

14. Turner RL. Water-soluble soldering flux. US Patent 5,452,840; 1995.

15. Saikawa T, Sumi T, Takashou S. Water-soluble flux composition and process for producing soldered part. US Patent 20040069376A1; 2001.

16. Satturwar PM, Fulzele SV, Panyam J, Mandaogade PM, Mundhada DR, Gogte BB, et al. Evaluation of new rosin derivatives for pharmaceutical coating. International Journal of Pharmaceutics. 2004;270(1-2):27-36.

17. Morkhade DM, Nande VS, Barabde UV, Kamble MU, Patil AT, Joshi SB. A comparative study of aqueous and organic-based films and coatings of PEGylated rosin derivative. Drug development and industrial pharmacy. 2008;34(1):24-32.

18. Yang M, Zhang T, Liu X, He S, editors. Water-soluble fluxes for Sn-4Zn-0.89 Cu-3.5 Bi-0.3 Re alloy lead-free solder. Physical and Failure Analysis of Integrated Circuits, 2009 IPFA 2009 16th IEEE International Symposium on the; 2009: IEEE.

19. Wang C, Wang J, Chen L, Li Y, Liu X. Study on soldering flux used for Sn-0.7Cu welding wire. 2011:246-9.

20. Ding J, Xia Z, Lu J. Esterification and Deacidification of a Waste Cooking Oil (TAN 68.81 mg KOH/g) for Biodiesel Production. Energies. 2012;5(12):2683-91.

21. Standard TJI. JIS Z 3197:1999 Testing methods for soldering fluxes. 1999 ed. Japan: Japanese Standards Association; 2000.

22. IPC. Flux Specification Task Group (5-24a). Flux Induced Corrosion (Copper Mirror Method). USA: Association Connecting Electronics Industries 2004.

23. Hattori H, Misono M, Ono Y. Acid-base Catalysis II: Elsevier; 1994.

24. Tamaddon F, Amrollahi MA, Sharafat L. A green protocol for chemoselective O-acylation in the presence of zinc oxide as a heterogeneous, reusable and eco-friendly catalyst. Tetrahedron Letters. 2005;46(45):7841-4.

25. Kulkarni P. $Al2(SO_4)_3$ is an efficient and mild acid catalyst for the one-pot, four-component synthesis of polyhydroquinoline. Journal of the Chilean Chemical Society. 2014;59(1):2319-21.

26. Uddin MR, Ferdous K, Uddin MR, Khan MR, Islam MA. Synthesis of Biodiesel from Waste Cooking Oil. Chemical Engineering and Science. 2013;1(2):22-6.

27. Cardoso AL, Neves SCG, da Silva MJ. Esterification of Oleic Acid for Biodiesel Production Catalyzed by SnCl2: A Kinetic Investigation. Energies. 2008;1(2):79-92.

28. Morkhade D, Nande V, Barabde U, Patil A, Joshi S. PEGylated rosin derivatives: novel microencapsulating materials for sustained drug delivery. AAPS PharmSciTech. 2006;8(2):Article 47-Article

29. Institute of Chemistry UoT, Estonia. IR spectrum of Rosin (also called colophony) 2015 [cited 2015 9-06-2015]. Available from:

http://tera.chem.ut.ee/IR_spectra/index.php?option=com_content&view=article&id=98&Itemid=66.

30. Tavares MIB, Mendes LC, Cardoso RS, Sanches NB, Chagas BS. 13C NMR Study PP/ROSIN Blends. International Journal of Polymeric Materials. 2000;46(3-4):793-9.

31. Hess SC, Farah MIS, Eguchib SY, Imamura PM. Synthetic studies with Pinus elliottiis rosin derivatives. Oxidation of maleopimaric anhydride methyl ester and trimethyl fumaropimarate. Journal of the Brazilian Chemical Society. 2000;11(1):59-63.

32. Smith WB. The ^{13}C NMR spectrum of abietic acid and its methyl ester. Organic Magnetic Resonance. 1978;11(8):427-8.

33. Singler TJ, Meschter SJ, Spalik J. Solder Wetting and Spreading. Handbook of lead-free solder technology for microelectronic assemblies. 2004:331.

34. Lee N-C. Reflow soldering processes and troubleshooting: SMT, BGA, CSP, and flip chip technologies: Newnes; 2002.

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University

VITA

Miss Kanlaya Phaphon was born on September 1, 1977. She received her Bachelor’s Degree of Science in Chemistry from Faculty of Science, Chulalongkorn University in 1999. She began her Master study in the program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2002, and completed the program in 2004. She began her a Ph.D degree in the program of Petrochemistry, faculty of Science in 2011 and completed the program in 2015. Her current address is 222/232 passorn-28, Tambon Bangpleeyai, Amphoe Bangplee, Samutprakarn Province, 10540.

จุฬาลงกรณ์มหาวิทยาลัย
Chulalongkorn University