

**INVESTIGATION ON WATER-BORNE  
INTUMESCENT FIRE PROTECTIVE  
COATINGS FOR STEEL**

**YEW MING CHIAN**

**FACULTY OF ENGINEERING  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2011**

**INVESTIGATION ON WATER-BORNE  
INTUMESCENT FIRE PROTECTIVE  
COATINGS FOR STEEL**

**YEW MING CHIAN**

**DISSERTATION SUBMITTED IN FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF MASTER OF  
ENGINEERING**

**FACULTY OF ENGINEERING  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2011**

UNIVERSITI MALAYA

**ORIGINAL LITERARY WORK DECLARATION**

Name of Candidate: Yew Ming Chian (I.C/Passport No: 830513-08-5461)

Registration/Matric No: KGA 080061

Name of Degree: Master's Degree

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

Investigation on Water-borne Intumescent Fire Protective Coatings for Steel

Field of Study: Structural Fire Protection Engineering

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work;
- (2) This Work is original;
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature

Date

Subscribed and solemnly declared before,

Witness's Signature

Date

Name:

Designation:

## ABSTRACT

This research studies the efficiency of different water-borne intumescent formulations which incorporate chicken eggshell (CES) as a novel bio-filler, designed to protect steel in the event of a fire. The coating is based on these three flame-retardant additives: ammonium polyphosphate phase II, melamine and pentaerythritol (combination referred to as AMP). CES, silica fume (SF) and epoxy emulsion were incorporated either individually or in combination into the flame-retardant additives. The first part of the study develops and evaluates AMP, AMP+SF and AMP+SF+CES intumescent formulation systems, respectively. The best formulation produced was the AMP+SF+CES system which was subsequently selected for the next part of the study that investigates the effect of epoxy emulsion on the coating performance. The influence of (i) binder, (ii) combination of binder and filler; and (iii) combination of filler and two binders on the properties and fire-resistive performance of the coatings were investigated by using thermogravimetric analysis (TGA), scanning electron microscope (SEM), Instron microtester, field emission scanning electron microscope (FESEM), small scale Bunsen burner test and furnace test. The thermal stability of CES was compared with that of commercial calcium carbonate filler by using TGA. CES was shown to have higher thermal stability. TGA results showed that addition of CES and SF increases the residual weight and anti-oxidation of the coatings. The combination of 25 wt.% CES and 10 wt.% SF added into the flame retardant additives led to the best fire resistance performance, highest thermal stability, densest surface structure and greatest expansion, while showing improved char cohesion and sufficient adhesion to the steel substrate during fire exposure. The second part of the study attempts to investigate the effect of water-borne epoxy resin on the fire protection performance and bonding strength of the coating to the steel. Addition of 10 wt.% epoxy resulted in significant improvement in fire protection performance and foam structure of the

coating. The results of Instron microtester indicated that the bonding strength of the coatings was improved with the increase of epoxy content.

## ABSTRAK

Penyelidikan ini mengkaji kecekapan beberapa jenis rumusan lapisan penahan api berasaskan air yang menggunakan kulit telur ayam (CES) sebagai 'bio-filler' terkini. Lapisan penahan api ini dirumus untuk melindungi keluli apabila kebakaran berlaku dan berasaskan tiga aditif penahan api: ammonium polifosfat fasa II, melamin dan pentaeritritol (kombinasi dikenali sebagai AMP). CES, 'silica fume' (SF) dan emulsi epoksi digabung secara berasingan atau sebagai campuran ke dalam aditif penahan api. Bahagian pertama penyelidikan ini menghasil dan menilai rumusan AMP, AMP+SF dan AMP+SF+CES. Rumusan yang terbaik merupakan sistem AMP+SF+CES yang dipilih untuk bahagian penyelidikan selanjutnya yang melibatkan kajian kesan emulsi epoksi ke atas kecekapan lapisan penahan api. Pengaruh (i) 'bio-filler' (ii) kombinasi pengikat dan 'bio-filler', dan (iii) kombinasi 'bio-filler' dan dua pengikat terhadap sifat dan prestasi lapisan penahan api diuji dengan menggunakan analisis termogravimetri (TGA), 'scanning electron microscope' (SEM), 'Instron microtester', 'field emission scanning electron microscope' (FESEM), ujian penunu Bunsen skala kecil dan ujian 'furnace'. Kestabilan terma 'bio-filler' CES dibandingkan dengan filler kalsium karbonat komersil dengan menggunakan ujian TGA. CES terbukti mempunyai kestabilan terma yang lebih tinggi. Keputusan TGA menunjukkan bahawa penambahan CES dan SF meningkatkan berat baki pembakaran dan anti-pengoksidaan lapisan penahan api. Kombinasi 25 wt.% CES dan 10 wt.% SF dengan aditif penahan api menghasilkan prestasi ketahanan api terbaik, kestabilan terma yang tertinggi, struktur permukaan terpadat, pengembangan terbesar dan pada masa yang sama menunjukkan peningkatan daya lekitan 'char' dan daya lekatan pada keluli apabila didedah kepada api. Bahagian kedua penyelidikan mengkaji pengaruh resin epoksi berasaskan air terhadap prestasi menahan api dan kekuatan lekatan lapisan penahan api pada keluli. Penambahan 10 wt.% epoksi menyebabkan peningkatan kecekapan perlindungan api

dan struktur busa lapisan penahan api yang ketara. Keputusan 'Instron microtester' menunjukkan bahawa kekuatan lekatan lapisan penahan api pada keluli dapat ditingkatkan dengan penambahan kandungan epoksi.

## ACKNOWLEDGEMENT

I would like to thank my supervisor Dr. Nor Hafizah Ramli@Sulong for giving me the opportunity to carry out research work related to the field of structural engineering and fire protection. I am highly indebted to her for her valuable thoughts and contributions towards the development of my thesis and also for providing me with an ample amount of knowledge about the field of fire protection engineering.

I would also like to thank the entire laboratory assistant for their guidelines and support as a senior to help me carry out appropriate research strategies for facilitating this thesis project.

I would like to thank the suppliers from local and international companies. Also, the contributions and support provided by WELLCHEM Company Inc. have been highly significant without which this project would not have been possible.

My special thanks to all the other staff members at the Civil and Environmental Engineering Department of University of Malaya whose contributions and supports have been invaluable.

I would like to deliver my thankfulness to acknowledge the help given by Perpustakaan Utama (PUM) and Perpustakaan librarians, and friends who involved directly or indirectly to the success of this thesis.

Finally, thanks goes to my personal editor, Liew Fong Yin and my family who provided me the encouragement, love, guidance and support needed to complete this thesis.

## TABLE OF CONTENTS

Title Page	i
Declaration	ii
Abstract	iii
Abstrak	v
Acknowledgement	vii
Table of Contents	viii
List of Figures	xi
List of Tables	xiv
List of Symbols and Abbreviations	xv
<b>1.0 INTRODUCTION</b>	<b>1</b>
1.1 Background and Problem Statement	1
1.2 Research Objectives	5
1.3 Scope of the Thesis	6
1.4 Organization of the Thesis	7
<b>2.0 LITERATURE REVIEW</b>	<b>8</b>
2.1 General	8
2.2 Thermal Degradation, Flame Retardancy and Flammability	8
2.3 Fire Protective Surface Coatings	13
2.4 Intumescent Coatings	14
2.5 Intumescent Flame Retardants	20
2.5.1 Chemical Mechanism of Intumescence	21
2.5.2 Physical Model of Intumescence	24
2.5.3 Phosphorus-based Flame Retardants	26
2.6 Flame Retardant Fillers	30
2.6.1 Chicken eggshell (CES) as Bio-filler	33
2.7 Binder in Intumescent Coatings	33
2.7.1 Silica Fume as Binder	34
2.8 Temperature Effects on Steel	35
2.9 Standard Time-temperature Fire Tests on Steel	39
2.9.1 The Eurocode Parametric Time-temperature Curve	39
2.9.2 ASTM-119 Time-temperature Curve	40
2.9.3 ISO 834 Standard Time-temperature Curve	41

## TABLE OF CONTENTS

<b>3.0 MATERIALS AND METHODOLOGY</b>	43
3.1 Introduction	43
3.2 Materials	44
3.3 Sample Preparation	50
3.3.1 AMP System	52
3.3.2 AMP+SF System	54
3.3.3 AMP+SF+CES System	55
3.3.4 AMP+SF+CES+ER System	56
3.4 Characterization and Measurement Techniques	57
3.4.1 Bunsen Burner Test	58
3.4.2 Furnace Test	59
3.4.3 Thermogravimetry Analysis (TGA)	60
3.4.4 Scanning Electron Microscope (SEM)	61
3.4.5 Field Electron Scanning Electron Microscope (FESEM)	62
3.4.6 Instron Microtester	63
<b>4.0 RESULTS AND DISCUSSION</b>	65
4.1 Introduction	65
4.2 Investigation of Flame Retardant Additives	65
4.2.1 Thermal Stability of AMP System	65
4.3 Investigation of Flame Retardant Fillers	69
4.3.1 Thermal Stability of CES and Calcium Carbonate	70
4.3.2 Decarbonation and Recarbonation of CES	72
4.4 Fire Protection Test of Intumescent Coatings on Steel	73
4.4.1 AMP+SF Coating System	75
4.4.2 AMP+SF+CES Coating System	77
4.4.3 AMP+SF+CES+ER Coating System	78
4.4.4 Comparison of Intumescent Coating System (A2, B2, C3 and D2)	79
4.4.5 Evolution of Fire Performance Using Small Scale Furnace Test	85
4.5 Thermal Analysis of Intumescent Coatings	89
4.5.1 Influence of Silica Fume as Binder	89
4.5.2 Influence of CES as Filler	90
4.5.3 Influence of Epoxy Resin	91

## TABLE OF CONTENTS

4.6	Surface Morphology of Intumescent Coatings	92
4.6.1	Influence of Binder and Filler	92
4.6.2	Influence of Epoxy Resin	93
4.7	Bonding Strength of Intumescent Coatings	95
<b>5.0</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	99
5.1	Conclusion	99
5.2	Recommendations	102
	<b>REFERENCES</b>	103
	<b>APPENDICES</b>	111

## LIST OF FIGURES

<b>Figure</b>	<b>Caption</b>	<b>Page</b>
Figure 2.1	Emman's fire triangle (Wolf and Lal Kaul, 1992)	9
Figure 2.2	A simplified model for combustion and flame retardancy	10
Figure 2.3	Sequence of intumescent reaction process (Vanderall, 1971)	16
Figure 2.4	Intumescent coating (a) before fire testing and (b) after fire testing (Anderson et al., 1985)	18
Figure 2.5	Composition of the back-face time-temperature profiles of a composite panel with and without an intumescent coating when exposed to fire	19
Figure 2.6	Chemical mechanism of intumescence	22
Figure 2.7	Schematic diagrams of the different layers during the burning process (Gilman and Kashiwagi, 1997)	26
Figure 2.8	Pyrophosphate structure formations from phosphoric acid condensation	27
Figure 2.9	Formation of double carbon-carbon bonds after dehydration of alcohol and groups	27
Figure 2.10	Chemical structure of APP I and APP II (Camino et al., 1978)	29
Figure 2.11	Stress-strain relationships for carbon steel at elevated temperatures (EC3, 2005)	37
Figure 2.12	Reduction factors for the stress-strain relationship of carbon steel at elevated temperature (EC3, 2005)	38
Figure 2.13	Eurocode parametric time-temperature curve (EC1, 2002)	40
Figure 2.14	ASTM-119 time-temperature curve (ASTM, 1988)	41
Figure 2.15	ISO 834 time-temperature curve (ISO, 1975)	42
Figure 3.1	Flow chart of sample preparation and characterization of the four different intumescent coating systems	44
Figure 3.2	APP II structure	45
Figure 3.3	SEM image of ammonium polyphosphate phase II	46
Figure 3.4	SEM image of melamine	47
Figure 3.5	SEM image of pentaerythritol	48

## LIST OF FIGURES

<b>Figure</b>	<b>Caption</b>	<b>Page</b>
Figure 3.6	TGA curve of silica fume	49
Figure 3.7	Dispersion of silica fume after (a) 1 hour, (b) 2 hours, (c) 12 hours and (d) 24 hours in water	49
Figure 3.8	SEM image of chicken eggshell	50
Figure 3.9	Flow chart of chicken eggshell powder preparation	51
Figure 3.10	High speed disperse mixer	53
Figure 3.11	The flow diagram for the preparation process of AMP system	54
Figure 3.12	The flow diagram for the preparation process of AMP+SF system	55
Figure 3.13	The flow diagram for the preparation process of AMP+SF+CES system	56
Figure 3.14	The flow diagram for the preparation process of AMP+SF+CES+ER system	57
Figure 3.15	The Bunsen burner test (a) virgin steel plate and (b) coated steel plate	58
Figure 3.16	Furnace test	59
Figure 3.17	Thermogravimetry Analysis (TGA)	60
Figure 3.18	Scanning Electron Microscope (SEM)	62
Figure 3.19	Field Emission Scanning Electron Microscope (FESEM)	63
Figure 3.20	Instron Microtester	64
Figure 4.1	TGA curves of the AMP system	66
Figure 4.2	TGA curve of pentaerythritol	68
Figure 4.3	TGA curve of ammonium polyphosphate phase II	69
Figure 4.4	TGA curve of melamine	69
Figure 4.5	TGA curves of chicken eggshell and commercial CaCO <sub>3</sub>	71
Figure 4.6	TGA graphs of CES at 20°C/min heating and cooling ramp under air flow and chemical changes that occur during the two ramps	73
Figure 4.7	The time-temperature curve of uncoated steel plate under fire test	74
Figure 4.8	Evolution of temperature on the back of the steel plates of AMP+SF system	75

## LIST OF FIGURES

<b>Figure</b>	<b>Caption</b>	<b>Page</b>
Figure 4.9	Evolution of temperature on the back of the steel plates of AMP+SF+CES system	78
Figure 4.10	Evolution of temperature on the back of the steel plates of AMP+SF+CES+ER system	79
Figure 4.11	Evolution of temperature on the back of the steel plates coated with the best formulations of intumescent coating system	80
Figure 4.12	The steel plate coated with A2 formulation during fire test	81
Figure 4.13	The steel plate coated with B2 formulation during fire test	83
Figure 4.14	The steel plate coated with C3 formulation during fire test	84
Figure 4.15	The steel plate coated with D2 formulation during fire test	85
Figure 4.16	Time-temperature curves of protected and unprotected steel plates	86
Figure 4.17	Deformation of the steel plates after fire test (a) protected and (b) unprotected	86
Figure 4.18	Residues obtained after the furnace test	87
Figure 4.19	TGA curves of samples A2 and B2	89
Figure 4.20	TGA curves of samples B2 and C3	90
Figure 4.21	TGA curves of samples D1, D2, D3 and D4	91
Figure 4.22	SEM micrographs of A2, B2 and C3 coatings	92
Figure 4.23	FESEM micrographs of the foam structure of D1, D2, D3 and D4	94
Figure 4.24	Coating sample D1 with 5 wt.% ER	96
Figure 4.25	Coating sample D2 with 10 wt.% ER	96
Figure 4.26	Coating sample D3 with 15 wt.% ER	97
Figure 4.27	Coating sample D4 with 20 wt.% ER	98

## LIST OF TABLES

<b>Table</b>	<b>Caption</b>	<b>Page</b>
Table 2.1	The basic and essential components of intumescent flame-retardant system (Rains, 1994)	23
Table 2.2	Current and potential fire retardant filler (Rothon, 2003)	31
Table 2.3	Physical properties and chemical composition of silica fume	34
Table 2.4	Reduction factors for stress-strain relationship of carbon steel at elevated temperatures (EC3, 2005)	37
Table 2.5	Time-temperature curve as specified by the ASTM E-119 (1988), reported by Buchanan (2002)	41
Table 2.6	Time-temperature curve as specified by the ISO 834 standards (1975), reported by Buchanan (2002)	42
Table 3.1	Physical and chemical properties of ammonium polyphosphate phase II	45
Table 3.2	Physical and chemical properties of melamine	46
Table 3.3	Physical and chemical properties of pentaerythritol	47
Table 3.4	Properties of water-borne epoxy resin	48
Table 3.5	Physical properties of silica fume	49
Table 3.6	Composition and sample name of intumescent coating	52
Table 3.7	Constituents of the AMP samples	52
Table 3.8	Constituents of the AMP+SF samples	54
Table 3.9	Constituents of the AMP+SF+CES samples	55
Table 3.10	Constituents of the AMP+SF+CES+ER samples	56
Table 4.1	Thermal stability of sample A2	67
Table 4.2	Thermal stability of CES and commercial CaCO <sub>3</sub>	72
Table 4.3	Char thickness and equilibrium temperature of AMP+SF coating system	75
Table 4.4	Char thickness and equilibrium temperature of AMP+SF+CES coating system	78
Table 4.5	Char thickness and equilibrium temperature of AMP+SF+CES+ER coating system	79
Table 4.6	Mechanical properties of coatings	95

## LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Description	Unit
$A$	Cross section area	$m^2$
$f_b$	Bonding strength	Pa
$F$	Force	N
$f_{y,\theta}$	Effective yield strength	Pa
$f_{p,\theta}$	Proportional limit	Pa
$E_{a,\theta}$	Slope of the linear elastic range	Pa
$\varepsilon_{p,\theta}$	Strain at the proportional limit	-
$\varepsilon_{y,\theta}$	Yield strain	-
$\varepsilon_{t,\theta}$	Limiting strain for yield strength	-
$\varepsilon_{u,\theta}$	Ultimate strain	-
$\theta_a$	Steel temperature	$^{\circ}C$
$k_{y,\theta}$	Reduction factor (relative to $f_y$ ) for effective yield strength	-
$k_{p,\theta}$	Reduction factor (relative to $f_y$ ) for proportional limit	-
$k_{E,\theta}$	Reduction factor (relative to $E_a$ ) for the slope of the linear elastic range	-

## LIST OF SYMBOLS AND ABBREVIATIONS

<b>Abbreviation</b>	<b>Compound</b>
AISC	American Institute of Steel Construction
Al <sub>2</sub> O <sub>3</sub>	Aluminum oxide
APP	Ammonium polyphosphate
ATH	Aluminum trihydroxide or aluminum trihydrate
CaCO <sub>3</sub>	Calcium carbonate
CaO	Calcium oxide
CO <sub>2</sub>	Carbon dioxide
CES	Chicken eggshell
CuO	Copper (II) oxide
e.g.	Exempli gratia (for example)
EG	Expandable graphite
et al.	et alibi (and elsewhere)
EVA	Ethylene vinyl acetate
Fe <sub>2</sub> O <sub>3</sub>	Iron (III) oxide
FESEM	Field emission scanning electron microscope
FTIR	Fourier transform infrared spectroscope
H <sub>2</sub> O	Water
ISO	International Organization for Standardization
K <sub>2</sub> O	Potassium oxide
LDPE	Low density polyethylene
MDH	Magnesium di-hydroxide
MEG	Modified expandable graphite
MEL	Melamine
MF	Melamine-formaldehyde
MgCO <sub>3</sub>	Magnesium carbonate
NH <sub>3</sub>	Ammonia
NMR	Nuclear magnetic resonance
(O)P(O)(OH)	Metaphosphoric acid
PA	Polyamide
PEG	Polyethylene glycol

## LIST OF SYMBOLS AND ABBREVIATIONS

<b>Abbreviation</b>	<b>Compound</b>
PER	Pentaerythritol
PET	Polyester
PH <sub>3</sub>	Phosphine
rpm	Revolutions per minute
SEM	Scanning electron microscope
SF	Silica fume
SiO <sub>2</sub>	Silicon dioxide
SnO <sub>2</sub>	Stannous oxide
SSA	Self-crosslinked siliconeacrylate
TGA	Thermogravimetry analysis
THEIC	Tris-2-hydroxyethyl isocyanurate
TiO <sub>2</sub>	Titanium dioxide
XRD	X-ray diffraction
XRF	X-ray fluorescence