การเตรียมอนุภาคทนไฟด้วยวิธีอิมัลชันเพื่อการเคลือบผิวที่ขยายตัวได้

นางสาว วาสนา กมลมาลย์นิวัฒน์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550

PREPARATION OF FIRE RETARDANT PARTICLES BY EMULSION METHOD FOR INTUMESCENT COATING

Miss Vasana Kamonmanniwat

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2007

Thesis Title	PREPARATION OF FIRE RETARDANT PARTICLES BY EMULSION METHOD FOR INTUMESCENT COATING
By	Miss Vasana Kamonmanniwat
Field of study	Chemical Engineering
Thesis Advisor	Associate Professor Tawatchai Charinpanitkul, D. Eng.
Thesis Co-advisor	Nattaporn Tonanon, D. Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

……………………………………………… Dean of the Faculty of Engineering

(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

……………………………………………… Chairman

(Associate Professor Seeroong Prichanont, Ph.D.)

……………………………………………… Thesis Advisor

(Associate Professor Tawatchai Charinpanitkul, D. Eng.)

……………………………………………… Thesis Co-advisor

(Nattaporn Tonanon, D. Eng.)

……………………………………………… External Member

(Assistant Professor Cattaleeya Pattamaprom, Ph.D.)

……………………………………………… Member

(Assistant Professor Thanyawat Pothisiri, Ph.D.)

วาสนา กมลมาลย์นิวัฒน์: การเตรียมอนุภาคทนไฟด้วยวิธีอิมัลชันเพื่อการเคลือบผิวที่ขยายตัวได้ (PREPARATION OF FIRE RETARDANT PARTICLES BY EMULSION METHOD FOR INTUMESCENT COATING). อ. ที่ปรึกษา : รศ. ดร. ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาร่วม: อ. ดร. ณัฐพร โทณานนท์ , 47 หน้า

โดยส่วนใหญ่ในอาคารสิ่งก่อสร้างมักใช้วัสดุที่เป็นเหล็กซึ่งสมบัติเชิงกลจะเปลี่ยนแปลงไปเมื่อได้รับความร้อน มีการหาแนวทางเพื่อลดการถูกทำลายของโครงสร้างลงด้วยการปกคลุมพื้นผิวด้วยวัสดุทนไฟ ในงานวิจัยนี้ การเตรียมอนุภาคทนไฟสามารถเตรียมได้จากแหล่งของกรด (แอมโมเนียม โพลีฟอสเฟต) แหล่งของคาร์บอน (เซลลูโลส) และสารช่วยการขยายตัว (เมลามีน) โดยการใช้วิธีอิมัลชัน ส่วนสารเคลือบผิว จะทำการเตรียมโดยนำอนุภาคทนไฟที่เตรียมได้ไปผสมกับสารยึดติด การลดปริมาณก๊าซออกซิเจนในบริเวณพื้นผิวที่ต้องการป้องกันโดยอาศัยหลักการทำงานของชั้น char ซึ่งจะเกิดขึ้นเมื่อพื้นผิวที่ปกคลุมได้รับความร้อน งานวิจัยนี้ได้ทำการศึกษาผลของอัตราส่วนของสารตั้งต้น ชนิดของสารยึดติดและความหนาของการเคลือบผิวที่มีต่อการทนไฟ การทดสอบคุณสมบัติการทนไฟของสารเคลือบผิวที่ขยายตัวได้จะใช้เตาเผา โดยควบคุมอุณหภูมิตาม ASTM E119 โดยที่อัตราส่วนของ เซลลูโลส: แอมโมเนียม โพลีฟอสเฟต: เมลามีน ที่ได้ผลดีที่สุดคือ 1:9:1 มีเวลาการทนไฟเท่ากับ 33.15 นาทีที่ความหนาของการเคลือบผิว 3.0 มิลลิเมตร

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต..
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา..
ปีการศึกษา 2550 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..

4970565721: MAJOR CHEMICAL ENGINEERING
KEY WORD: FIRE RETARDANT/ INTUMESCENT COATING/ BINDER

VASANA KAMONMANNIWAT : PREPARATION OF FIRE RETARDANT PARTICLES BY EMULSION METHOD FOR INTUMESCENT COATING. THESIS ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng, THESIS COADVISOR : NATTAPORN TONANON, D. Eng, 47 pp.

Metal structure in various typical building will lose its mechanical property under severe heating by fire incident. An alternative way to reduce the possibility of fire destruction is to cover building structure surface with a fire-resistant material. Fire retardant particles are made of an acid source (Ammonium polyphosphate), a carbon source (Cellulose), and a blowing agent (Melamine) by emulsion method. The fire-retardant particles are mixed with a specific binder for preparing intumescent coating agent. In general, the hindrance of oxygen penetration into the fired structure could be achieved by the formation of char layers which could be generated after the coated particle layer is exposed to the fire. In these work the effects of fire-retardant particles content, binder content, and intumescent layer thickness on fire rating were experimentally investigated. The standard furnace control (ASTM E 119) was applied for fire retardant testing of intumescent. The suitable condition weight ratio of Cellulose: Ammonium polyphosphate: Melamine in fire retardant particles is 1:9:1 which could result in 33.18 min fire endurance. The minimal thickness of intumescent coating is 3.0 mm.

Department...............Chemical Engineering..........Student’s signature..................................

Field of study............Chemical Engineering……..Advisor’s signature...................................

Academic year ……………..2007.........................Co-advisor’s signature................................

ACKNOWLEDGEMENT

I am very thankful to my advisor, Assoc. Prof. Tawatchai Charinpanitkul, Center of Excellence in Particle Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, for his introducing me to this interesting project. I am also very thankful to my co-advisor, Dr. Nattaporn Tonanon, for her helpful and stimulated suggestions, deep discussion and encouraging guidance throughout the course of this work. Furthermore, I am also thankful to Assist. Prof. Thanyawat Pothisiri, Assist. Professor Cattaleeya Pattamaprom and Assoc. Prof. Seeroong Prichanont for their stimulative comments and participation as my thesis committee.

I would like to acknowledge Ajarn Pricha Sangthirapithikul, for his useful guidance, comments, research assistance, and kindness. It has been a great experience learning a lot of things from him.

Furthermore, I would like to acknowledge Permpoon Pattana Industry Co., Ltd. support cotton, Clariant Chemicals (Thailand) Co., Ltd. support Ammonium polyphosphate and binder, Thai KK Industry Co., Ltd support melamine, and Allied Products (Thailand) Ltd. support raw materials. Financial support form MINE TECH Co.Ltd

Moreover, I would like to thank Fire Safety Research Center member for their kind and helpful suggestion.

This thesis has received a partial support from the Centennial Fund of Chulalongkorn University.

In addition, I am also thankful to all members of the Center of Excellence in Particle Technology for their help, kindness and warm collaborations.

Last but not least, I would like to express my cordial and deep thank to my parents and my friends for their love and encouragement.

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Page

CHAPTER I

INTRODUCTION

1.1 Background

It could often be observed that constructions and buildings are destroyed and harmed by the hand of fires. Since the main structures of building are consists of mainly of metal, which could lose its mechanical property, once intensely heated. Heat from fire will destroy such structure and make it collapsed. An alternative way to reduce the possibility of fire destruction is to cover exposed area of building with a fire resistant which will help resist the destruction of fire and increase escaping time of inhabitants. Three main factors for the fire are energy source, oxygen supply, and fuel. There are several methods which can minimize risk, for instance, dilution of the combustible mass, endothermic decomposition, char layer formation (intumescent) and radical scavenging. This research focuses on an obstruction of oxygen penetration by a formation of char layer.

The intumescent will expand and increase its volume after being exposed to fire. An increase in temperature results in a chemical reaction. Phosphoric acids and ammonia gas can be generated from ammonium polyphosphate decomposition. After that, the structure of cellulose reacts with phosphoric acids and ammonia gas followed by a reaction with oxygen gas and steam in the air. This reaction generates nitrogen gas which can dilute oxygen gas in the surrounding of fire. As a result, char or carbon layer will be coated on the metal surface and acts as thermal insulation and oxygen gas barrier as well.

In previous work, the intumescent coating is developed by using a thermoset epoxy-amine resin system into which fire retardant agents, boric acid and ammonium polyphosphate derivative has been incorporated [1]. The intumescent flame retardant system is microcapsules of di-ammonium hydrogen phosphate (DAHP) with polyurethane shell for flame retardant textile [2]. The intumescent flame retardant coating was prepared by unsaturated polyester resin and epoxy resin as two component matrix resin. The main ingredients of intumescent systems are ammonium polyphosphate (APP) as acid source, Melamine (Mel) as the blowing agent and Pentaerythriol (PER) as carbon agent, expandable graphite as synergistic agent, adding titanium dioxide (TiO_2) [3]. In general, the reactants will be added into a binder of intumescent coating but in this work, fire retardant particles will be prepared before adding into binder.

Fire retardant particle in this work will mainly be prepared by emulsion method. Synthesized fire retardant particles used as a coating material in fire protection or are known as intumescent coating. Intumescent coatings contain main ingredients bound together by a binder. Three main ingredients are used an acid source (ammonium polyphosphate or a mineral acid), a carbon source (such as char forming polymers) and a blowing agent.

The output of this research can be beneficially applied and then developed to other work such as fire retardant fabric or other fire retardant construction materials. Furthermore, preparation of fire retardant particles and intumescent coating can promote domestic preparation and development of intumescent particles and coating.

1.2 Objectives of study

The objective of this research is to prepare fire retardant particles by emulsion method and to compare intumescent coatings with commercial paints available in the market.

1.3 Scopes of Research

1. To prepare fire retardant particles by emulsion method.
    1.1 To study the effect of reactant ratios.
    1.2 To study the effect of other additives.
2. To develop effective intumescent coating.
    2.1 To study the effect of binder.
    2.2 To study the effect of intumescent thickness.

1.4 Expected Benefits

1. To have a new study on preparation of fire retardant particles used an acid source, a carbon source and a blowing agent by emulsion method.

2. To have more understanding on the effect of reactant ratios, binder and other additive and intumescent thickness on the properties of fire retardant particle.

CHAPTER II

FUNDAMENTAL KNOWLEDGE AND LITERATURE REVIEW

2.1 Intumescent system and mechanism

2.1.1 Intumescent system

The majority of intumescent systems are based on an acid source (normally ammonium polyphosphate or a mineral acid), a carbon source (such as char forming polymers or polyols) and a blowing agent (e.g. melamine) [1]. In this work, ammonium polyphosphate (APP), cellulose and melamine were used.

2.1.1.1 Ammonium polyphosphate (APP)

Ammonium polyphosphate is an inorganic salt of polyphosphoric acid and ammonia. The chain length (n) of this polymeric compound is both variable and branched and can be greater than 1000. Structure of ammonium polyphosphate are shown in Figure 2.1

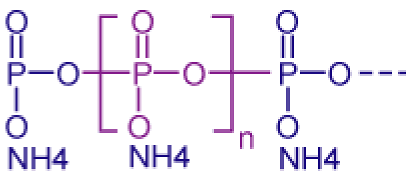


Figure 2.1 Structure of ammonium polyphosphate

APP is a stable, non-volatile compound. Higher temperatures and prolonged exposure to water will accelerate its hydrolysis. Long chain APP starts to decompose at temperatures above 300°C to polyphosphoric acid and ammonia. Short chain APP will begin to decompose at temperatures above 150 °C [4].

2.1.1.2 Cellulose

Cotton is known as the purest form of cellulose in nature. Linking two molecules of sugar produces a disaccharide called cellobiose. Cellulose is a polysaccharide produced by linking additional sugars in exactly the same way. The length of the chain varies greatly, from a few hundred sugar units in wood pulp to over 6000 for cotton. Structure of cellulose are shown in Figure 2.2

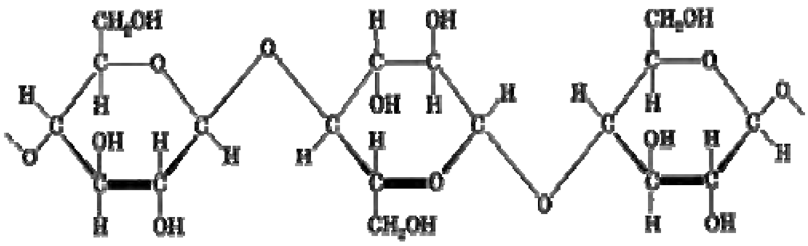


Figure 2.2 Structure of cellulose

The cellulose chain bristles with polar -OH groups. These groups form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The chains also pack regularly in places to form hard, stable crystalline regions that give the bundled chains even more stability and strength [5].

2.1.1.3 Melamine

Melamine (2,4,6-triamino-1,3,5 triazine, CAS nr. 106-78-1) is a white crystalline powder with a melting point of approximately 354°C and a density of 1.573grams/cc.Far below its melting point, already at >200°C, melamine is known to vaporize or sublime (diluting the fuel gases and oxygen near the combustion source) [6]. Structure of melamine are shown in Figure 2.3

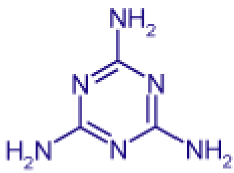


Figure 2.3 Structure of melamine

2.1.2 Intumescent mechanism

When other materials which contain APP are exposed to an accidental fire or heat, the flame retardant starts to decompose, commonly into polymeric phosphoric acid and ammonia. The polyphosphoric acid reacts with hydroxyl or other groups of a synergist to a non stable phosphate ester. In the next step the dehydration of the phosphate ester follows. Carbon foam is built up on the surface against the heat source (charring). The carbon barrier acts as an insulation layer, preventing further decomposition of the material [4]. Mechanism of reaction are shown in Figure 2.4

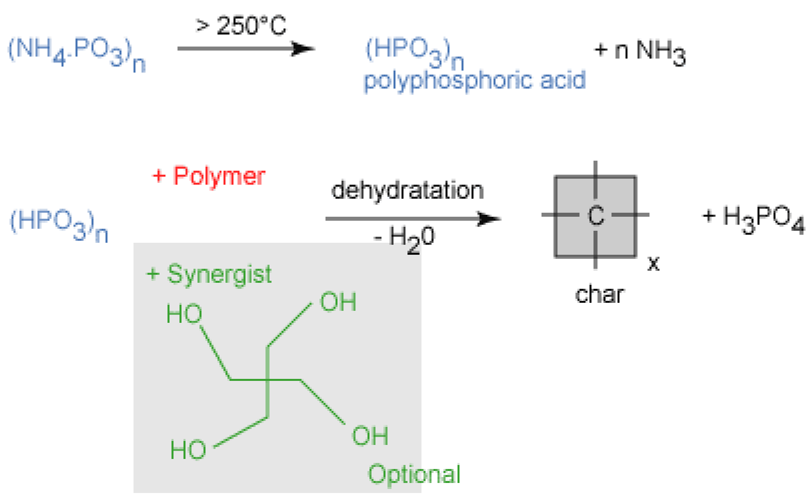


Figure 2.4 Mechanism of reaction [4]

Jimenez et al. [7], study the mechanism of action of boric acid and coated ammonium polyphosphate (pure ammonium polyphosphate coated with tris-(2-hydroxyethyl) isocyanurate) used as flame retardants in a commercial intumescent epoxy-based formulation was investigated using analytical techniques including thermo gravimetric analyses (TGA) and solid-state NMR. APP begins to lose ammonia at a temperature slightly above 200°C, resulting in a highly condensed polyphosphoric acid.

Jimenez et al. [1], explain the formation of the effective char occurs via a semi-liquid phase, which coincides with gas formation and the expansion of the surface. The degradation of the intumescent material and in particular of the blowing agent, have to be trapped and to diffuse slowly in the highly viscous melt degraded material in order to create a layer with appropriate morphological properties as shown in Figure 2.5

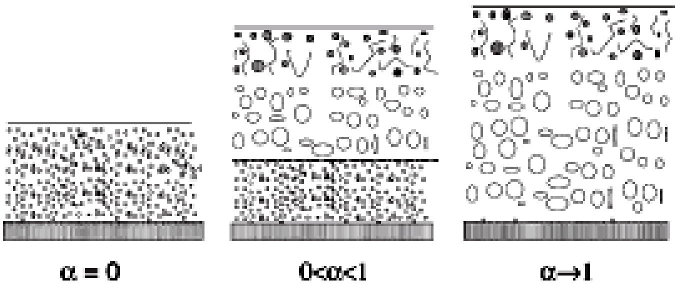


Figure 2.5 Development of the intumescence (α=conversion degree) [1]

A. Richard Horrocks [8] explains intumescent mechanism in the following stages: (1) APP starts to decompose at 210°C on wards and phosphorylation of the polyol present (e.g. pentaerythritol) occurs without elimination of gaseous products. (2) Subsequent phosphorylation yields cyclic phosphate esters which eliminate water and ammonia which remain with unreacted pentaerythritol in the reaction products. The exact character of the products is determined by the APP: polyol ratio. (3) Between 280 and 330°C, the polyolphosphates decompose to char with considerable formation of phosphoric acid, water and ammonia and maximum swelling of the mass. Polymerisation of released phosphoric acid to polyphosphoric acid will occur with evolution of water. (4) Presence of blowing agents like melamine which volatilise and subsequently decompose in the range 270-400°C adds to the swelling effect. (5) APP which does not directly participate in phosphorylation will undergo decomposition via cross-linking reactions with loss of ammonia and water within the temperature range 280-400°C. Above 500°C, crosslinked residues start to fully volatilize, probably after complete conversion to P_2O_2. The advantage of melamine as a blowing agent is that it sublimes at about 250°C before releasing ammonia over the range 250-380°C; it thus creates a continuous blowing action over the char-forming temperature range. Incompatible blowing action occurs with agents like urea which show significant gasification in the range 150-240°C before char formation occurs in the range 280-330°C.

2.2 Intumescent coating

Intumescent coating was composed of three ingredients: acid source, carbon source and blowing agent linked together by binder. Binder is a main ingredient in paint which helps bind together two or more other materials in mixtures to the substrate. Its two principal properties are adhesion and cohesion [9]. Intumescent coatings provide an appearance similar to that of a paint finish and remain stable at ambient temperatures. However, in a fire situation the increase in temperature causes a chemical reaction and the intumescent coating expands to many times its original thickness. This provides an insulating foam-like coating or 'char' which protects the substrate. The intumescent coating is designed to insulate the steel and prevent the temperature of the steel from rising above a certain point [10].

2.3 Additive

Aluminium and Titanium dioxide was investigated in this work. Aluminium (atomic number 13; melting point: 660.32°C, boiling point: 2519°C) have silvery colors. When being deposited, a fresh, pure aluminium film serves as a good reflector (approximately 92%) of visible light [11]. Another additive is titanium dioxide which has white solid molar mass 79.87; melting point: 1870°C, boiling point: 2972°C). When being used as a pigment, it is called titanium white [12].

2.4 Three component of a fire

The concept of fire symbolized by the triangle of combustion in which, fuel, heat, and oxygen are represented in Figure 2.6.

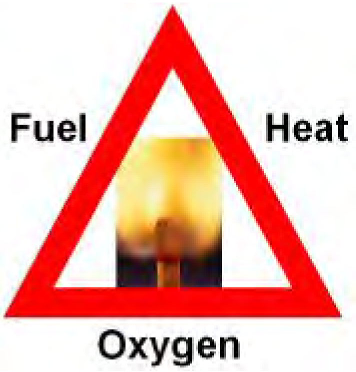


Figure 2.6 The triangle of combustion

- **Fuel** -- For a fire to start there must be something to burn. The physical state of the fuel may be gases (natural gas, propane, butane, hydrogen, etc.); liquids (gasoline, kerosene, turpentine, alcohol, paint, varnish, lacquer, etc.) or solid (coal, wood, paper, cloth, grease, etc.)

- **Heat** -- For a fire to start there must be a source of ignition, usually heat or a spark. Heat sources include: open flame, hot surfaces, sparks and arcs, friction-chemical action, electrical energy and compression of gases

- **Oxygen** -- A source of oxygen is needed. Approximately 16% is required. Normal air contains 21% oxygen. Some fuels contain enough oxygen within their make-up to support burning [13].

2.5 Test Method of Building Construction and Material (ASTM E 119)

ASTM is well known as Acronym of American Society of Testing and Materials ASTM E119. That is Test Methods of Building Construction and Materials. This test is used to evaluate the fire resistive construction that contains though-penetrations or joints which controlled by the standard time-temperature curve. Figure 2.7 demonstrates standard time-temperature curve of ASTM E119 [14].

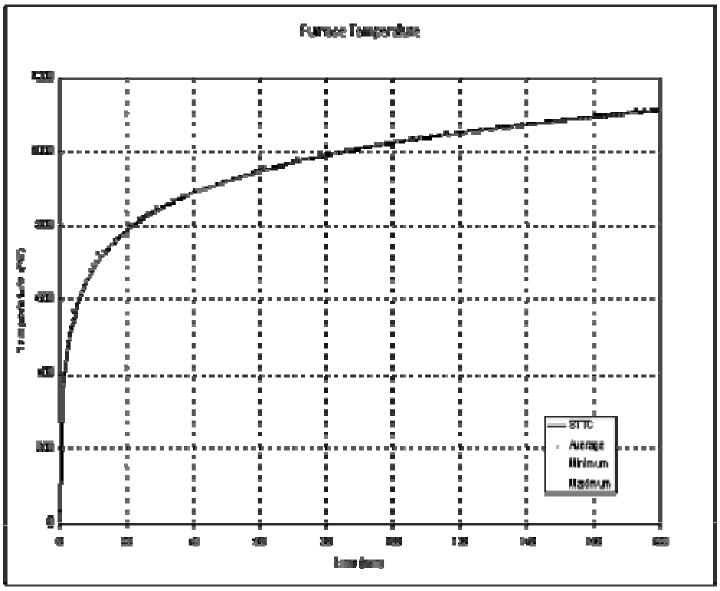


Figure 2.7 Standard time-temperature curve of ASTM E119 [15]

2.6 Literature review

In order to grasp the present situation of new development of fire retardant particle, some available literatures have been reviewed as follows.

Jimenez et al. [1] investigated different intumescent formulation designed for steel protection. The coating was prepared from a thermoset epoxy-amine resin system into which fire retardant agents, boric acid and ammonium polyphosphate derivative has been incorporated. The efficiency of intumescent coatings on steel was investigated by using a fire test. The combination of different intumescent ingredients in a thermoset epoxy resin is examined. It was observed that their combination inside the resin resulted in the formation of a hard char which exhibits a good adhesion onto steel surface.

Giraud et al. [2] investigated a novel intumescent flame retardant system which is microcapsules of di-ammonium hydrogen phosphate (DAHP) with polyurethane shell. The developed systems were evaluated as intumescent flame retardant (FR) in a commercial polyurea coating for textiles. The expected advantages of this new concept of encapsulated FR agent are to be compatible with a polymeric matrix which could give a permanent FR effect for many materials.

Ping Zhu et al. [16] investigated thermal decompositions of cotton and flame-retardant cotton fabrics by using analytical techniques including thermo gravimetric analyses (TGA) and differential scanning calorimeter (DSC). The pyrolysis of cellulose fiber includes three stages: initial, main, and char decomposition. In the initial stage, where the temperature range is below 300°C, the most important changes of the fibers are some physical properties and little weight loss. Here, the damage of the cellulose occurs mostly in amorphous polymers. The main pyrolysis stage occurs in the temperature range of 300–380°C. Most of pyrolysis products are produced in this stage. The major products are l-Glucose, together with all kinds of combustible gases. Finally state, char pyrolysis occurs at the temperature above 430°C. During this process, dewatering and charring reactions compete with the production of l-glucose, with the dewatering and charring reactions being more obvious. The pyrolysis of the flame-retardant cellulose fiber shows the similar three stages but with lower decomposition temperatures and weight loss than that of the untreated cellulose.

CHAPTER III

EXPERIMENTAL

3.1 Raw Materials

Ammonium polyphosphate (APP) (supported by Clariant, product name:Exolit AP 422), cellulose, melamine (supported by Thai KK Industry Co., Ltd), surfactant A, surfactant B, silicone and mineral oil. In addition are main ingredients for fire retardant particles preparation. Aluminium powders (Al) and Titanium dioxide (TiO_2) used as refection for heat radiation.

Three binders were used for the preparation of intumescent coating. The compositions of binders were reported in table 3.1.

Table 3.1 Composition of binder

Binder	Composition
A	Vinyl acetate and acrylic acid ester
B	Styrene and acrylic acid ester
C	Acrylic and methacrylic acid esters and styrene

3.2 Preparation

3.2.1 Preparation of fire retardant particles

Fire retardant particles can be prepared by using two difference dispersants.

3.2.1.1 Using mineral oil as a dispersant.

This diagram shows the preparation of fire retardant particles by using mineral oil as a dispersant.

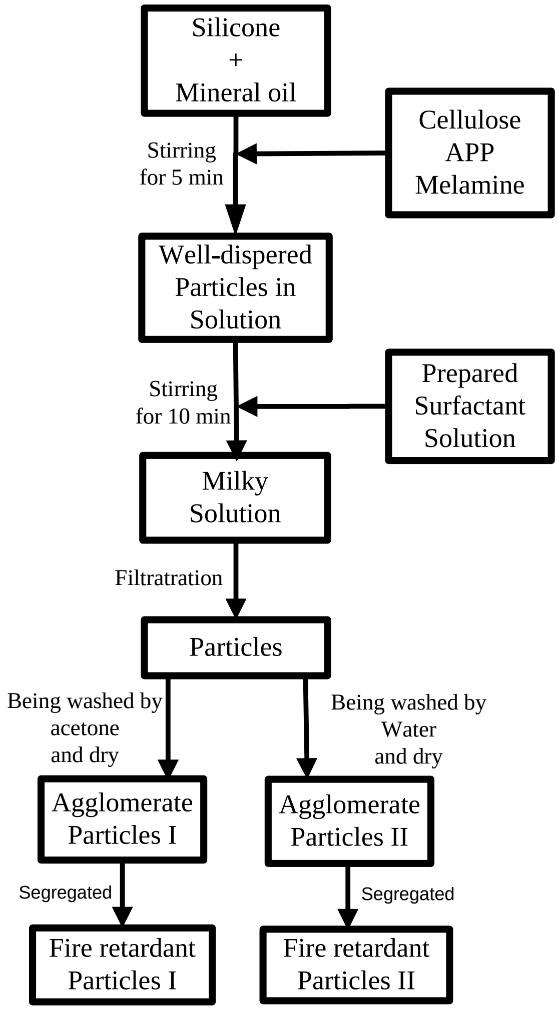


Figure 3.1 The preparation of fire retardant particles by using mineral oil as a dispersant.

From Figure 3.1, the silicone and mineral oil were added to the reactants (Cellulose: APP: Melamine) at different ratios, 1:1:1, 1:3:1 and 1:6:1, respectively. They were stirred for five minute to well disperse. Surfactant solution was added to the solution and followed by stirring for ten minutes. Then, milky solution was obtained. The particles were separated from the solution by filtration. The particles were cleaned with acetone (Particles I) and water (Particles II) to get rid of excess mineral oil on the surface.

3.2.1.2 Using surfactant solution as a dispersant.

This diagram shows the preparation of fire retardant particles by using surfactant solution as a dispersant.

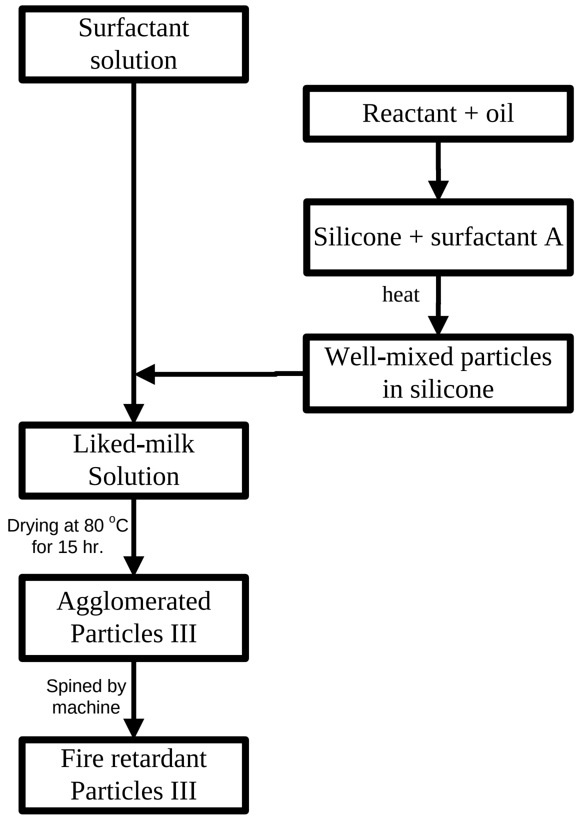


Figure 3.2 The preparation fire retardant particles by using surfactant solution as a dispersant.

From Figure 3.2, first the well-mixed particles in silicone were prepared by mixing between reactants with oil and silicone with surfactant A under slow heating. Surfactant B solutions were added to well-mixed compound in silicone. The mixture was stirred for five minute to well disperse. After that, the milky solution was obtained. The mixture was dried at 80°C for fifteen hours. After that, the particles were segregated, fire retardant particles III obtained. This method was used to study the effect of reactants ratios, and other additive. Formulations have been studied in this work were reported in Table 3.2.

Table 3.2 Fire retardant particles formulation

Ratio (Cellulose:APP:Melamine)	**Total weight of ingredients**
1:6:1	30
1:6:1	60
1:6:1	90
1:6:1	120
1:3:1	90
1:9:1	90
1:12:1	90

The fire retardant particles were prepared by 60g of silicone. The ratio of cellulose: APP: melamine was fixed at 1:6:1. The total weight of the ingredients was varied into 30, 60, 90 and 120g. After the suitable formulation of fire retardant particles were obtained. Then, the effect of binder and intumescent thickness were investigated.

3.2.2 Preparation of intumescent coating.

Intumescent coating is prepared by mixing fire retardant particles with binder at different types. The binders used in this study are reported in table 3.1.

3.2.3 Testing

Intumescent coating was applied onto the metal plate surface (30×30 cm^2). Thermocouples were attached to front and backside on the metal plate surface which are shown in Figure 3.3. Four thermocouples were used on each metal plate surface, so that an average temperature can be obtained. After that, the coated steels were set in fire test using a standard furnace of Fire Safety Research Center at Department of Civil Engineering, Chulalongkorn University. Fire testing is according to ASTM E 119 standard which was controlled by the standard time-temperature curve as showed in Figure 2.7. The furnace works until the thermocouples reach an average temperature higher than 538°C or the temperature rise of any thermocouple on the metal plate surface is higher than 649°C. Controller and furnace are shown in Figure 3.4 and Figure 3.5.

.

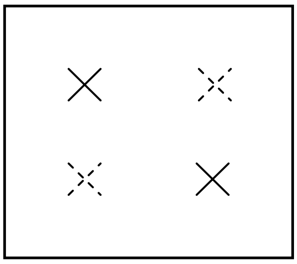


Figure 3.3 Location of thermocouples on the metallic support

Figure 3.4 Controller of furnace

Figure 3.5 Furnace

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of fire retardant particles

Fire retardant particles can be prepared by using two different dispersants.

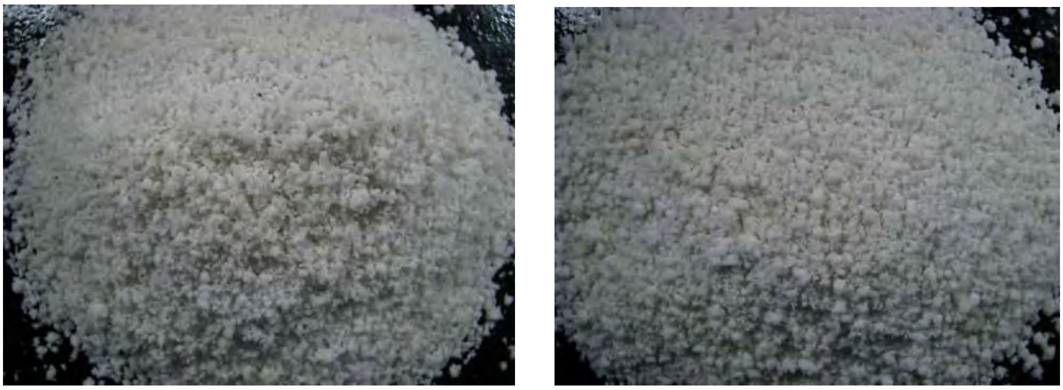
4.1.1 Using mineral oil as a dispersant

In this part, the comparison of particles with acetone washing (Particles I) and without washing (Particles II) is conducted. From the Table 4.1, the range of particles size from sieve analysis is demonstrated. Smaller size particles can be obtained by cleaning the primary particles with acetone (particles I).

Table 4.1 Range of particles size from sieve analysis

Range of particles (mm)	% By weight	
	Cleaning with acetone (Particles I)	**Cleaning without acetone (Particles II)**
More than 1.18	11.88 %	48.59 %
0.600 - 1.18	50.56 %	28.96 %
0.425 - 0.600	17.78 %	4.20 %
Less than 0.425	19.78 %	18.25 %

The shape of fire retardant particles cleaned with and without acetone are demonstrated in Figure 4.1(a) and Figure 4.1(b), respectively.



(a) (b)

Figure 4.1 Morphology of fire retardant particles (a) cleaned with acetone (b) cleaned without acetone**.**

4.1.2 Using surfactant solution as a dispersant.

Triton X 100 was used as dispersant surfactant in this method. By using this method larger number of smaller particles (0.6 -1.18 mm) compared with that in 4.1.1 were obtained and their properties were summarized in Table 4.2. The shapes of fire retardant particles III are demonstrated in Figure 4.2.

Table 4.2 Range of particles size from sieve analysis

Range of particles (mm)	**% By weight**
More than 1.18	5.67 %
0.600 - 1.18	70.26 %
0.425 - 0.600	17.98 %
Less than 0.425	5.97 %

Figure 4.2 Morphology of fire retardant particles III

4.2 Fire testing

4.2.1 With mineral oil as a dispersant.

Fire retardant particles are prepared from various ratios of cellulose: APP: melamine (1:1:1, 1:3:1 and 1:6:1) followed by cleaning with and without acetone. Binder A was mixed with particles for coating on metal substrate. The fire rating results are summarized in Table 4.3.

Table 4.3 Fire rating of intumescent coating cleaned with and without acetone

Ratio (Cellulose:APP:Melamine)	**Time (min:sec)**
1:1:1	16.51
1:3:1	17.27
1:6:1	19.03
1:1:1 (no acetone)	20.03
1:3:1 (no acetone)	20.15
1:6:1 (no acetone)	21.09

* The thickness of intumescent coating is 3.0 mm

Figure 4.3 shows time dependence of average temperature of samples cleaned with acetone while Figure 4.4 showed time dependence of average temperature of samples without cleaning. All samples compared with uncoated metal substrate. Visual evidences of chars sample mentioned in Table 4.3 are demonstrated in Figure 4.5 and Figure 4.6, respectively.

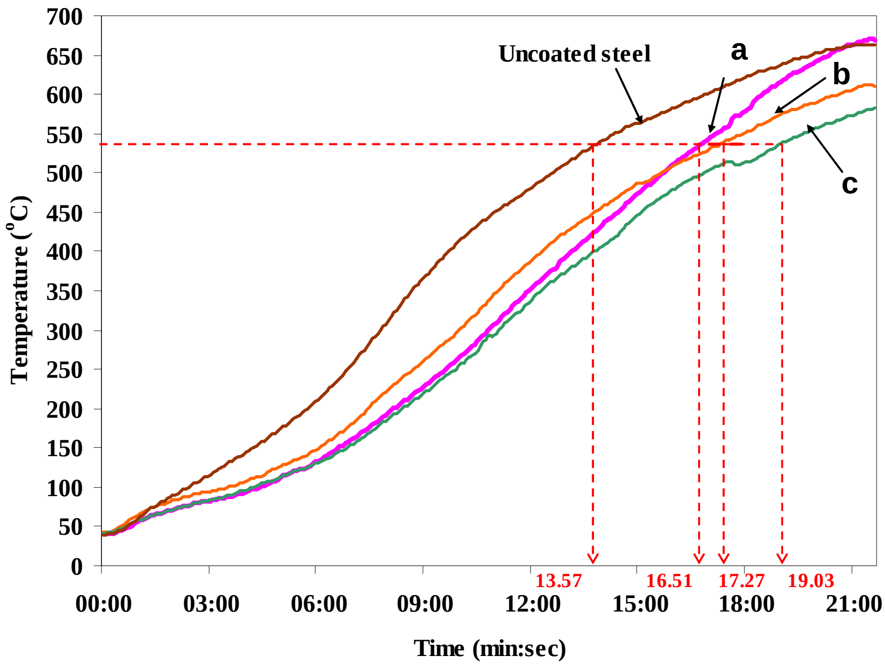


Figure 4.3 Time dependence of average temperature of sample cleaned with acetone (a) 1:1:1 (b) 1:3:1 (c) 1:6:1

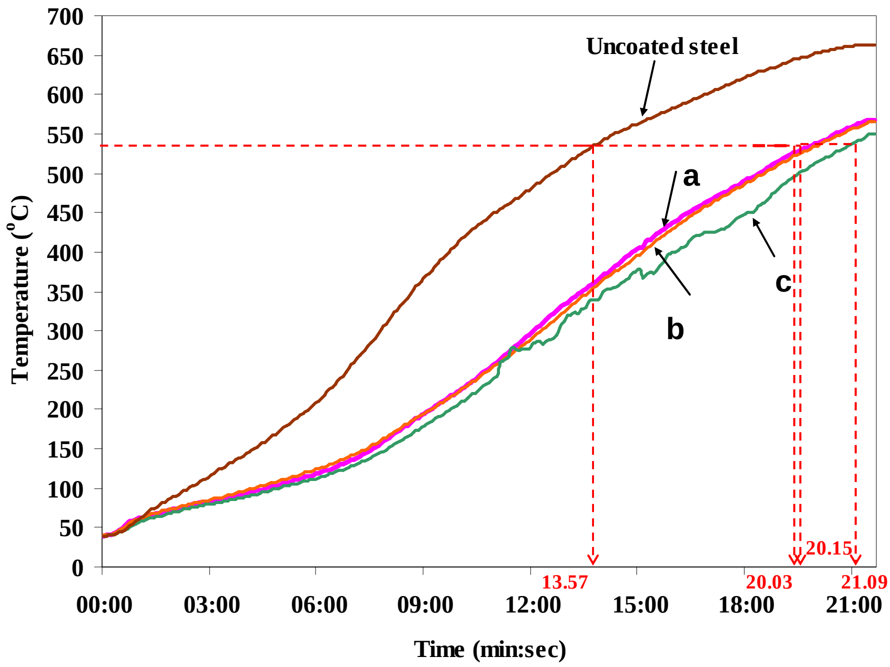
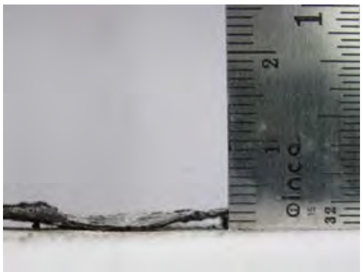
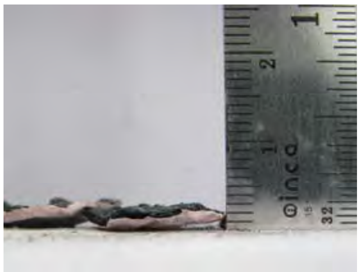


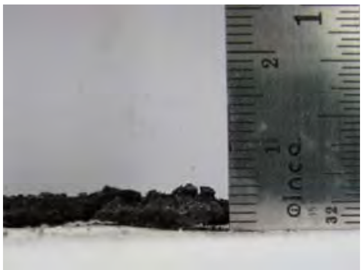
Figure 4.4 Time dependence of average temperature of sample cleaned without acetone (a) 1:1:1 (b) 1:3:1 (c) 1:6:1.



(a)



(b)

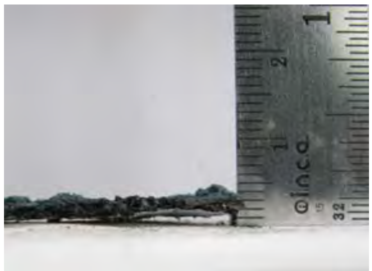


(c)

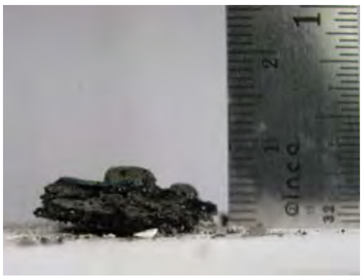
Figure 4.5 Char of samples compose of intumescent particles cleaned with acetone

(a) ratio 1:1:1(b) ratio 1:3:1 (c) 1:6:1.

(a)



(b)



(c)

Figure 4.6 Char of samples compose of intumescent particles cleaned without acetone

(a) ratio1:1:1(b) ratio 1:3:1 (c) 1:6:1.

From this result, the ratio of 1:6:1 (cellulose: APP: melamine) could provide the best fire retarding performance. Although they posses larger particle size an advantage of intumescent particles cleaned without acetone was a higher fire rating compared with those cleaned with acetone. Binder A seems to have poor adhesion on metal surface.

4.2.2 With surfactant solution as dispersant.

The above method in 4.2.1 suggests the suitable ratio of fire retardant which is 1:6:1.Therefore, the ratio was fixed while the quantity of ingredient (30, 60, 90 and 120) was varied. Binder C was introduced as an alternative for coating on metal substrate. The results of fire rating are summarized in Table 4.4.

Table 4.4 Fire rating of intumescent coating with various quantities of main ingredients

Ratio(Cellulose:APP:Melamine)	Total weight of ingredients	Time (min:sec)
1:6:1	30	17.48
1:6:1	60	23.24
1:6:1	90	29.54
1:6:1	120	23.21

* The thickness of intumescent coating 3.0 mm

Time dependence of average temperature of sample in Table 4.4 was plotted in Figure 4.7 for the purpose of comparison of coated and uncoated metal substrate. Char sample from Table 4.3 are demonstrated in Figure 4.8

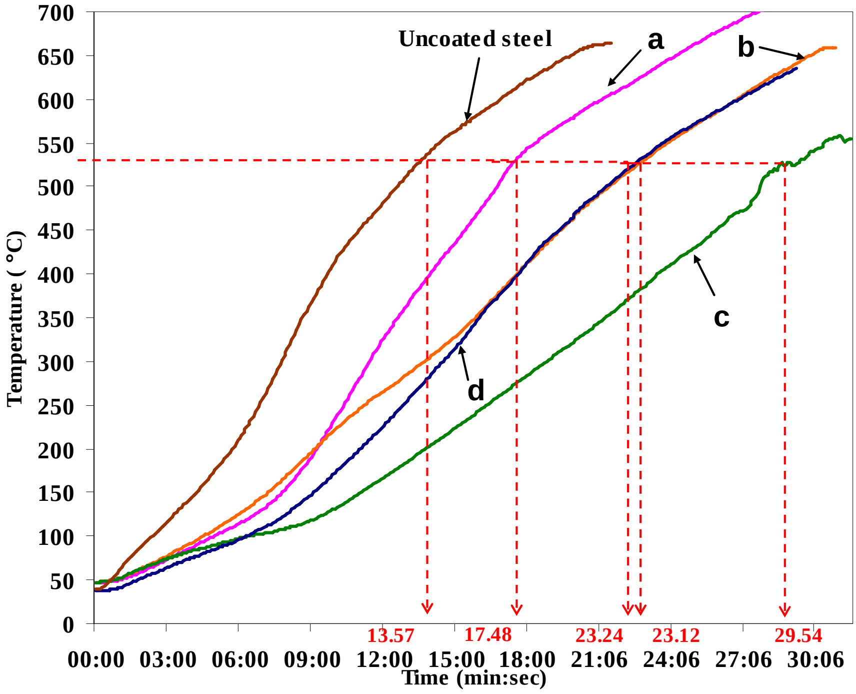
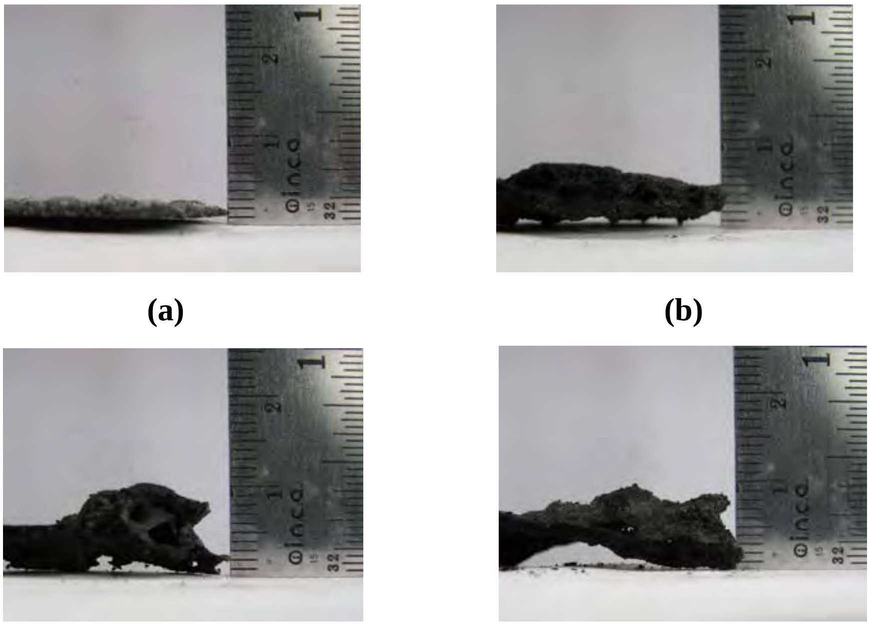


Figure 4.7 Time dependence of average temperature of samples with different amount of active ingredient (a) 1:6:1(30) (b) 1:6:1(60) (c) 1:6:1(90) (d) 1:6:1(60)



(a) (b) (c) (d)

Figure 4.8 Char of samples with different amount of active ingredient
(a) 1:6:1(30) (b) 1:6:1(60) (c) 1:6:1(90) (d) 1:6:1(60)

From the experimental results mentioned above, the suitable ratio of fire retardant amount of active ingredient is 1:6:1 and 90 g, respectively. Effect of binder was also investigated in this work. In the next step, the suitable binder will be determined by using the 1:6:1 and 90 g of active ingredient. The fire rating results can be summarized in Table 4.5.

Table 4.5 Fire rating of intumescent coating with different types of binder

Ratio (Cellulose:APP:Melamine)	Binder type	Time (min:sec)
1:6:1 (90)	A	26.54
1:6:1 (90)	B	29.00
1:6:1 (90)	C	29.54

* The thickness of intumescent coating 3.0 mm

Time dependence of average temperature of sample in Table 5 was showed in Figure 4.9. All samples compared with uncoated metal substrate. Char characteristics of sample in Table 4.5 are demonstrated in Figure 4.10.

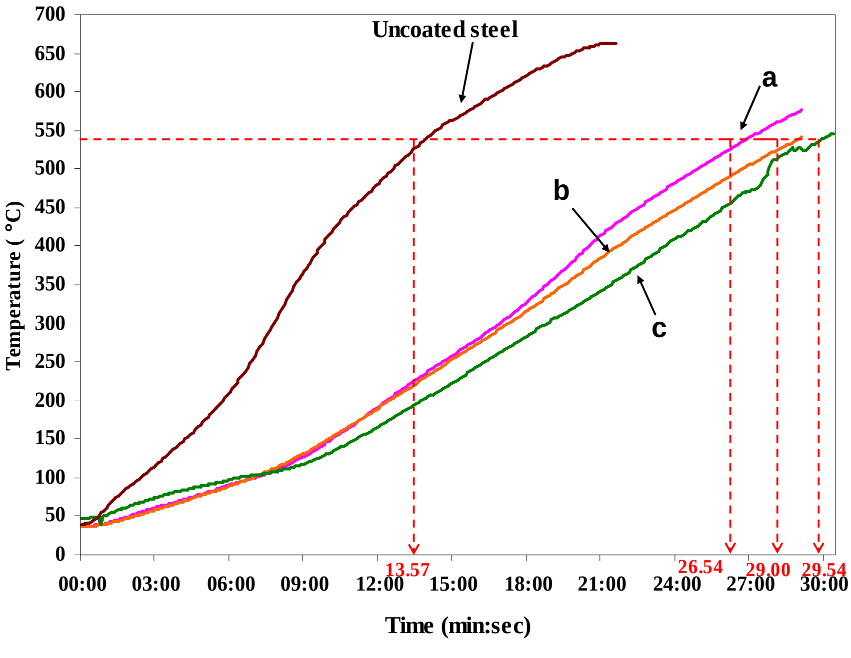
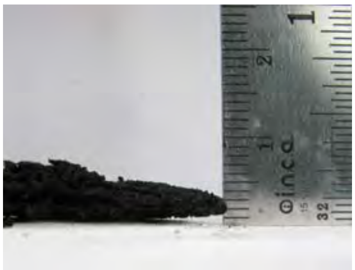


Figure 4.9 Time dependence of average temperature of sample ratio 1:6:1(90) with different binders (a) Binder A (b) Binder B (c) Binder C



(a)

(b)

(b)

Figure 4.10 Char of sample ratio 1:6:1(90) with different types of binder
(a) Binder A (b) Binder B (c) Binder C

It can be concluded that the suitable composition is binder C with 90g as amount of active ingredient. The ratio of (Cellulose: APP: Melamine) 1:3:1, 1:6:1, 1:9:1 and 1:12:1 will be varied in order to determine the optimum conditions. The test results of fire rating are summarized in Table 4.6.

Table 4.6 Fire rating of intumescent coating with different reactant ratios

Ratio (Cellulose:APP:Melamine)	**Time (min:sec)**
1:3:1 (90)	25.24
1:6:1 (90)	29.54
1:9:1 (90)	33.18
1:12:1 (90)	29.54

* The thickness of intumescent coating 3.0 mm

Time dependence of average temperature of sample in Table 4.6 was showed in Figure 4.11. All samples compared with uncoated metal substrate. Char characteristics of sample in Table 4.6 are demonstrated in Figure 4.12.

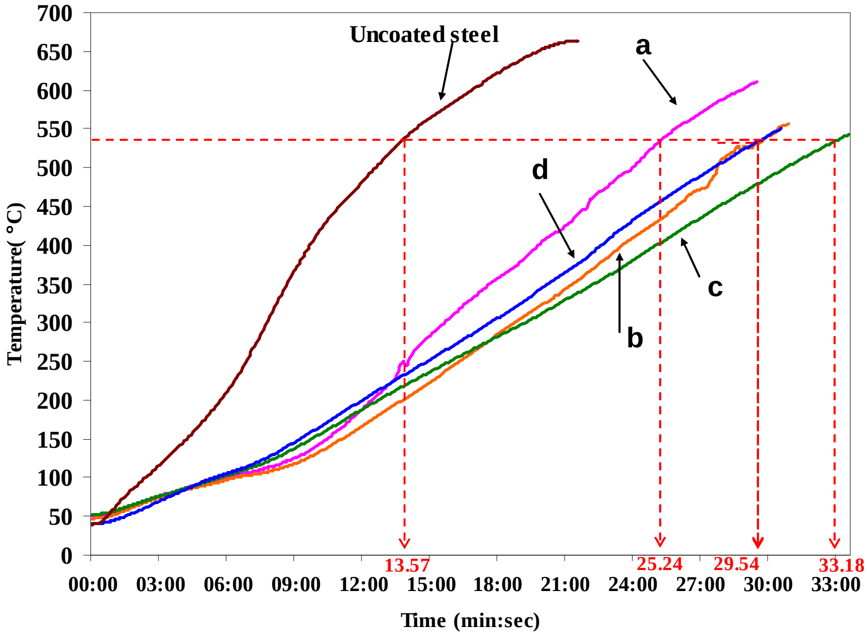
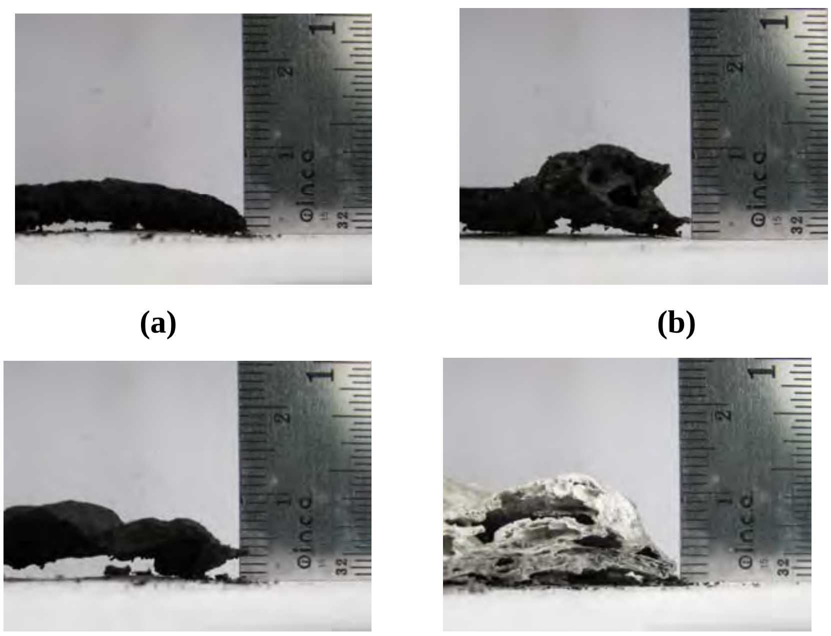


Figure 4.11 Time dependence of average temperature of samples with different reactant ratios (a) 1:3:1(90) (b) 1:6:1(90) (c) 1:9:1(90) (d) 1:12:1(90)



(a) **(b)**

(c) **(d)**

Figure 4.12 Char of samples with different reactant ratios (a) 1:3:1(90) (b) 1:6:1(90) (c) 1:9:1(90) (d) 1:12:1(90)

Based on these experimental results, the optimum condition is 1:9:1 with 90 g of active ingredient and type C binder. The effect of intumescent thickness at 3.0 mm and 5.0 mm was studied. As a result, coating layer with the intumescent thickness of 3.0 and 5.0 mm had acceptable fire rating, which could be assessed by the retarding time of 33.18 min and 36.48 min, respectively. Time dependence of average temperature of sample intumescent thickness at 3.0 and 5.0 mm was showed in Figure 4.13. All samples were compared with uncoated metal substrate. Char layers of intumescent thickness at 3.0 and 5.0 mm were demonstrated in Figure 4.14

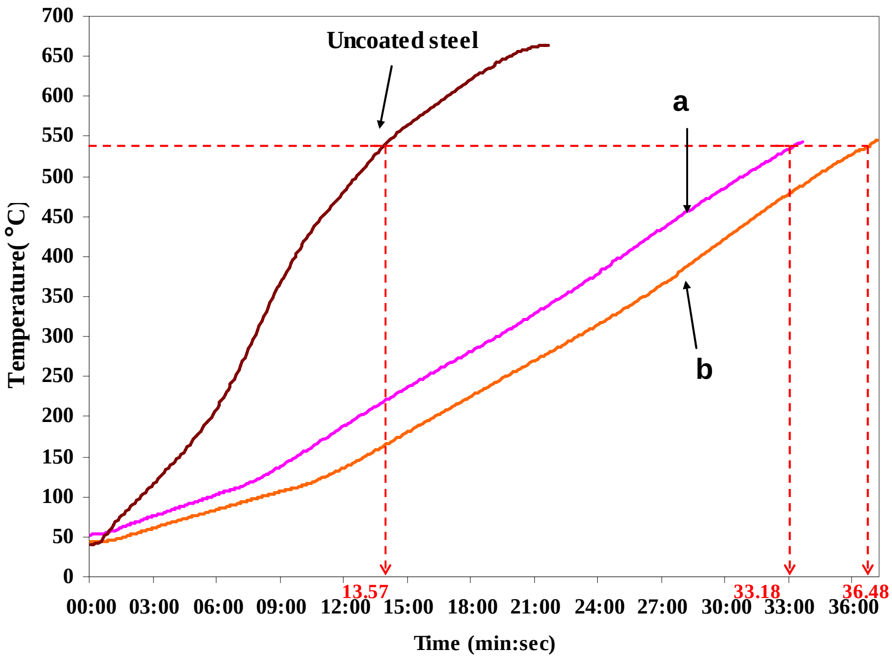
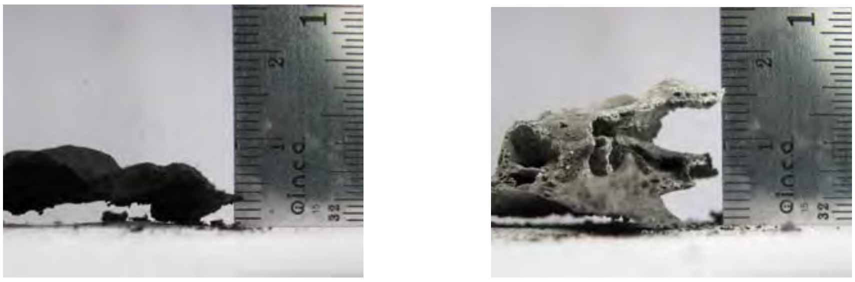


Figure 4.13 Time dependence of average temperature of sample ratio 1:9:1(90) at intumescent thickness (a) 3.0 mm (b) 5.0 mm.



(a) **(b)**

Figure 4.14 Char of samples ratio 1:9:1(90) at intumescent thickness (a) 3.0 mm (b) 5.0 mm

In addition to main active ingredients, Al and TiO_2 are also used as an reflective agents. 10 % Al, Al (Top seal) and TiO_2 were added into intumescent coating for a comparison with that of 1:9:1 (90) with binder C. The result of fire rating can be summarized in Table 4.7. Time dependence of average temperature of sample in table 4.7 was showed in Figure 4.15. Samples of char in table 4.7 intumescent thickness are demonstrated in Figure 4.16

Table 4.7 The effect of reflective additives on fire rating of intumescent coating

Ratio (Cellulose:APP:Melamine)	Additive	Time (min:sec)
1:9:1(90)	no	33.18
1:9:1 (90)	Al	25.12
1:9:1 (90)	Al Top seal	29.54
1:9:1 (90)	TiO_2	22.42

* The thickness of intumescent coating 3.0 mm

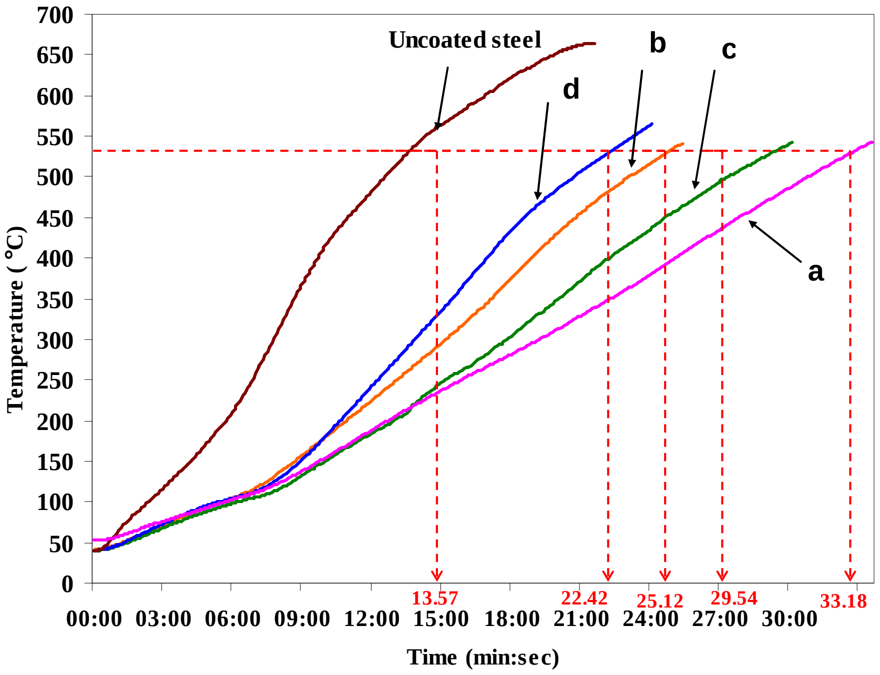
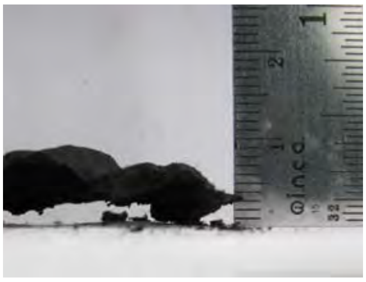
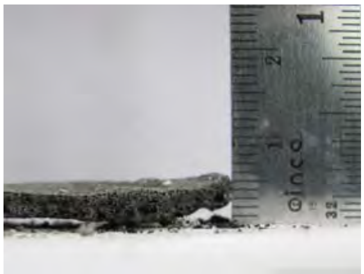


Figure 4.15 Time dependence of average temperature of sample ratio 1:9:1(90)

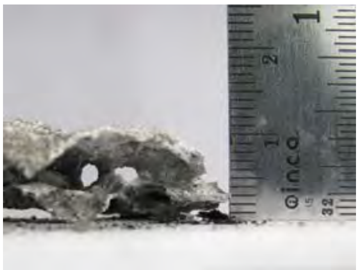
(a) no additive (b) 10 % Al (c) 10 % Al Top seal (d) 10% TiO_2



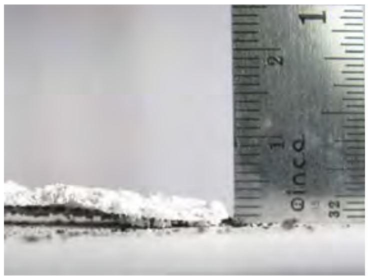
(a)



(b)



(c)



(d)

Figure 4.16 The effect of additives on char of sample ratio 1:9:1(90)

(a) No additive (b) 10% Al (c) 10 % Al Top seal (d) 10 %TiO_2

Furthermore, two types of commercial paints were tested for fire rating. Commercial paint A provided fire rating, regarding to the longer retarding time of 61.42 min which could be compared with commercial paint B providing the retarding time of 54.06 min. Time dependences of average temperature of sample commercial paint A and commercial paint B were showed in Figure 4.17. All samples were compared with uncoated metal substrate. Samples of char of commercial paint A and commercial paint B were demonstrated in Figure 4.18

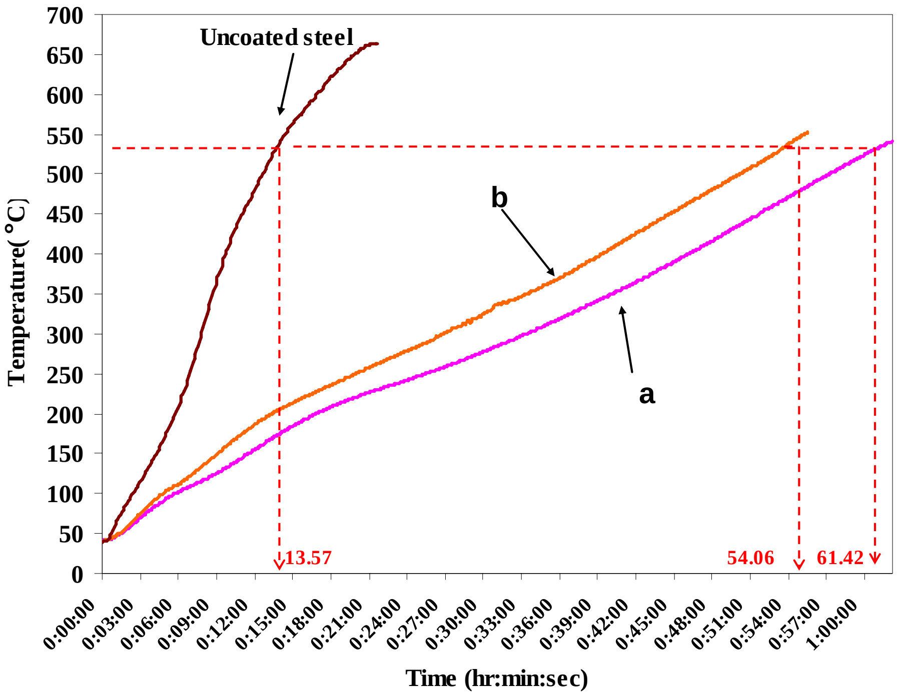
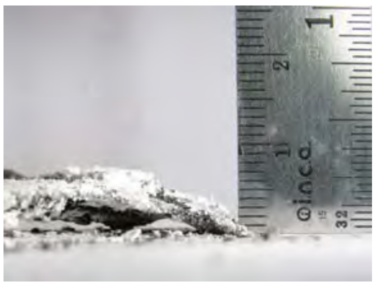


Figure 4.17 Time dependence of average temperature of commercial paint A and commercial paint B

(a)



(b)

Figure 4.18 Char characteristic of sample (a) commercial paint A (b) commercial paint B

A comparison of various percent by weight of APP in silicone was found that fire rating increased as by weight per cent of APP in silicone was increased until achieving the optimum point. With the excessive APP, fire rating decrease. The result was shown in the Figure 4.19

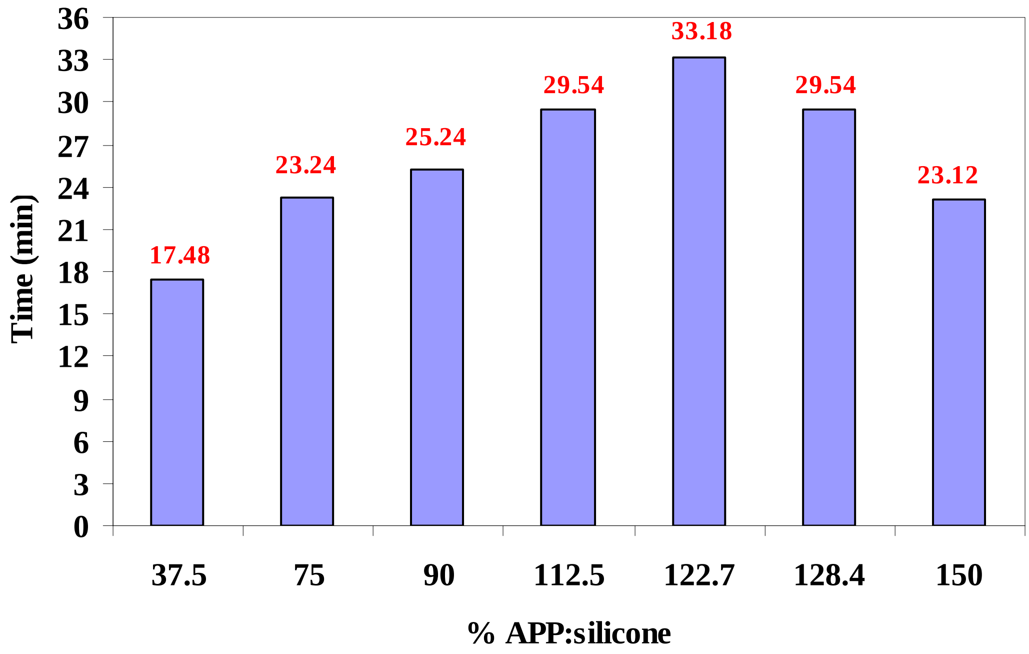


Figure 4.19 Relation between Time and percent APP with silicone

Then, intumescent coating was compared with the other intumescent coating containing the same amount of APP. In order to compare particles system (add fire retardant particles from emulsion method into binder) with another powder system (directly add all reactant in powder form into binder). The testing results of fire rating are summarized in Table 4.9. Time dependence of average temperature of sample in Table 4.8 was shown in Figure 4.20

Table 4.8 Comparison between powder system and particles system

Sample	% APP	Time (min:sec)
3:5:8 (30) (powder)	50	21.21
1:6:1 (120) (particles)	50	23.12
1:9:1 (90) (particles)	49.5	33.18

* The thickness of intumescent coating 3.0 mm

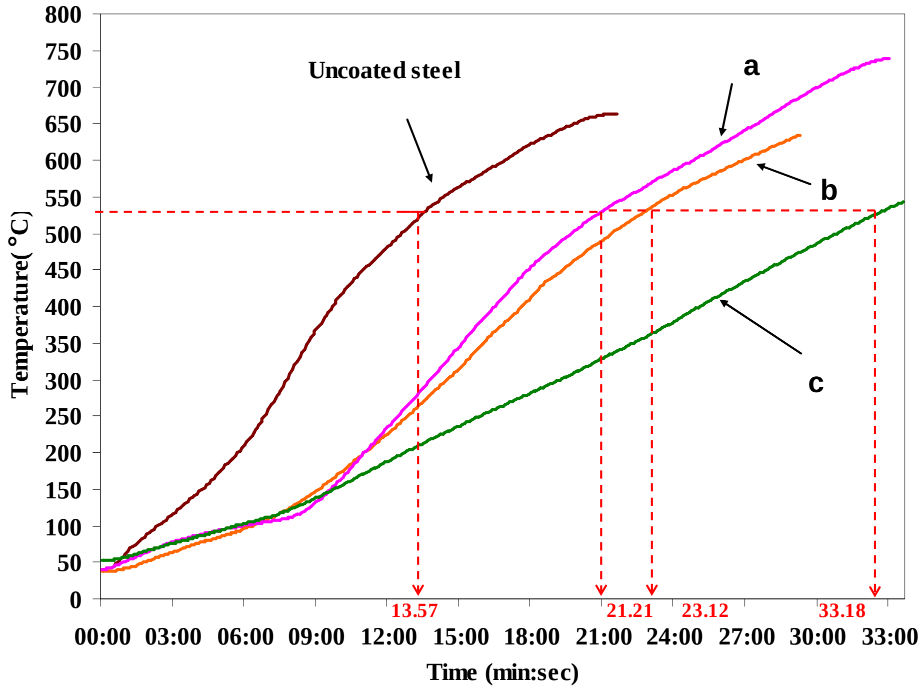


Figure 4.20 Time dependence of average temperature of powder system and particles system (a) 3:8:5 (powder) (b) 1:6:1 (120) (particles) (c) 1:9:1 (90) (particles)

From the result above, at the same amount of %APP the particles system (add fire retardant particles from emulsion method into binder) showed much higher fire rating than that of the powder system (directly add all reactant in powder form into binder).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this work, fire retardant particles can be prepared by using two different dispersants. Fire retardant particles prepared by surfactant solution showed better results. The advantages of this method are no acetone used in the process and smaller particle size distribution.

The suitable ratio of cellulose to APP to melamine is 1:9:1, respectively. 90 g of active ingredient with type C binder with coating thickness of 3.0 mm which results in retarding time of 33.2 min. Furthermore, the 5.0 mm thickness of coating can increase the fire endurance to 36.48 min

With a comparison of various weight per cent of APP in silicone, it was found that fire rating increased as by weight per cent of APP in silicone was increased until achieving the optimum point. With the excessive APP, fire rating decrease.

This work has revealed that the particles system, add fire retardant particles from emulsion method into binder, gave a significant effect on fire rating of intumescent coating compared with that of the powder system, directly add all reactant in powder form into binder, but the same amount of APP.

5.2 Recommendations for future work

1. More studies on the effect of APP/Cellulose, APP/Melamine, APP/Cellulose/Melamine are required.
2. It is interesting to try other carbon source such as pentaerythritol.
3. Study another additive which used in intumescent coating such as alumina (Al_2O_3), etc.

REFERENCES

1. Jimenez, M., Duquesne, S., and Bourbigot, S. Characterization of the performance of an intumescent fire protective coating. Surface & Coatings Technology 201 (2006): 979–987.
2. Girauda, S., Bourbigot, S., Rochery , M., Vroman, I., Tighzert, L., Delobel, R. and Poutch, F. Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating. Polymer Degradation and Stability 88 (2005): 106-113
3. Gu, J., Zhang, G., Dong, S., Zhang, Q. and Kong, J. Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. Surface & Coatings Technology 201 (2007): 7835–7841
4. Bernard, H. Additive center [online] .2000.Availible from: http://www.specialchem4polymers.com/tc/ammoniumpolyphosphate/index [2007]
5. Senese, F. [online] .1997.Availible from: http://antoine.frostburg.edu/chem/senese/101/consumer/faq/what-is-cellulose.shtml [2007]
6. Bernard, H. Additive center [online] .2000.Availible from: http://www.specialchem4polymers.com/tc/Melamine-Flame-Retardants/index. [2007]
7. Jimenez, M., Duquesne, S., and Bourbigot, S. Intumescent fire protective coating: Toward a better understanding of their mechanism of action. Thermochimica Acta 449 (2006):16-26
8. A. Richard. Developm ents in flame retardants for heat and fire resistant textiles - the role of char formation and intumescence. Polymer Degradation and Stability 54 (1996):143-154
9. http://en.wikipedia.org/wiki/Binder_(material)
10. http://www.nullifire.com/intumescent_coating/index.htm
11. http://en.wikipedia.org/wiki/Aluminium
12. http://en.wikipedia.org/wiki/Titanium_dioxide

13. Kerns. S. [online]. University of Wisconsin – Milwaukee: Availible from: http://www.uwm.edu/Dept/EHSRM/FIRE/fireinfo.html [2007]

14. [Online]. Specified Technologies Inc: Availible from: http://www.stifirestop.com/technical_library/glossary

15. Bennetts I. D., and Goh C. C. Fire behaviour of steel members penetrating concrete walls. Electronic Journal of Structural Engineering 1 (2001): 38-51

16. Zhua, P., Sui, S., Wang, B., Sun, K., and Sun, G. A study of pyrolysis and pyrolysis products of flame-retardant cotton fabrics by DSC, TGA, and PY–GC–MS. Anal. Appl. Pyrolysis 71 (2004): 645–655

APPENDIX

Appendix A

Sieve Analysis Test

1. Weight of fire retardant particles Retained

Weight of fire retardant particles Retained

= (Wt. Sieve + fire retardant particles) - (Wt. Sieve)

Example;

Weight of fire retardant particles Retained = (376.45g + 5.94g)-376.45g

= 5.94g

2. Percent Retained

Percent Retained = $\frac{\text{Wt. of fire retardant particles Retained}}{\text{Wt. of sample}} x100$

Example;

Percent Retained = $\frac{5.94\text{ g}}{50} x100$ = 11.88%

Sieve No.	Sieve Opening	Weight Sieve	Weight of particle	Weight Sieve+ particle	Percent
	(mm)	(g)	(g)	(g)	%
16	1.18	376.45	5.94	382.39	11.88
30	0.6	328.31	25.27	353.58	50.54
40	0.425	316.41	8.89	325.3	17.78
Pan		262.32	9.89	272.21	19.78

VITA

Miss Vasana Kamonmanniwat was born on June 25, 1984 in Bangkok, Thailand. She studied in primary and secondary educations at Khajornroaj Wittaya School and Chinorodwitthayalai Secondary School, respectively. In 2005, she received the Bachelor Degree of Engineering (Chemical Engineering) from King Mongkut's University of Technology North Bangkok. After that, she continued to study in Master program in Center of Excellence in Particle Technology (CEPT) at Chemical Engineering Department, Faculty of Engineering, Chulalongkorn University with the master thesis entitled “Preparaion of fire retardant particles by emulsion method for intumescent coating”.