ปุ๋ยที่เคลือบด้วยน้ำมันชักแห้งเพื่อการปลดปล่อยแบบควบคุม

นางสาววริษฐา แสงฤทธิ์

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FERTILIZERS COATED WITH DRYING OILS FOR CONTROLLED RELEASE

Miss Waristha Saengrith

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By Miss Waristha Saengrith
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Thesis Advisor Associate Professor Amorn Petsom, Ph.D.

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

……………………………………Dean of the Faculty of Science
(Professor Piamsak Menasveta, Ph.D.)

Thesis Committee

……………………………………Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

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

……………………………………..Member
(Professor Sophon Roengsumran, Ph.D.)

……………………………………..Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……………………………………..Member
(Associate Professor Chaiyo Chaichantipayuth, Ph.D.)

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การศึกษาการเตรียมปุ๋ยควบคุมการปลดปล่อยโดยการเคลือบด้วยน้ำมันชักแห้งชนิดต่างๆคือ น้ำมันลินสีด น้ำมันทัง และน้ำมันถั่วเหลืองโดยใช้เครื่องมือในการเคลือบคือ ฟลูอิไดซ์ เบด และหม้อเคลือบ พบว่าเครื่องมือที่มีความเหมาะสมในการเคลือบปุ๋ยเพื่อควบคุมการปลดปล่อยคือ หม้อเคลือบ และศึกษาปัจจัยที่มีผลต่อการเคลือบพบว่าปุ๋ยจะเคลือบได้ดีที่สุดเมื่อใช้โคบอลต์ แนพทีเนต 1% เป็นตัวเร่งปฏิกิริยาที่ อุณหภูมิ 80^{0}ซ โดยเม็ดปุ๋ยที่เคลือบได้จะมีลักษณะมันวาว ผิวเรียบและสม่ำเสมอ ชนิดของน้ำมันที่เหมาะสมในการเคลือบปุ๋ย คือน้ำมันลินสีด และน้ำมันถั่วเหลือง ส่วนน้ำมันทังไม่เหมาะสมในการเคลือบปุ๋ยโดยใช้หม้อเคลือบ และปริมาณของน้ำมันชักแห้งที่เหมาะสมในการเคลือบโดยใช้หม้อเคลือบคือ 10 ส่วนในร้อยส่วน

จากการศึกษาการปลดปล่อยโพแทสเซียมโดยใช้เทคนิคอะตอมมิกแอบซอร์บชัน สเปกโตรสโกปี และศึกษาอัตราการปลดปล่อยยูเรีย โดยใช้เทคนิค ยูวี วิสิเบิล สเปกโตรโฟโตเมตรี พบว่าปุ๋ยที่เคลือบด้วยน้ำมันลินสีดมีความสามารถในการควบคุมการปลดปล่อยธาตุอาหารได้ดีที่สุด รองลงมาคือ น้ำมันถั่วเหลืองและน้ำมันลินสีดผสมน้ำมันถั่วเหลือง และพบว่าเมื่อความหนาของฟิล์มหรือจำนวนชั้นของฟิล์มมีจำนวนมากขึ้นจะทำให้อัตราการปลดปล่อยสารอาหารลดลง เมื่อทำการเปลี่ยนแปลงสภาวะในการทดสอบปุ๋ยที่เคลือบได้ พบว่าเมื่อเพิ่มอุณหภูมิจะทำให้ปุ๋ยมีการปลดปล่อยธาตุอาหารเพิ่มขึ้น ช่วงภาวะความเป็นกรดที่สูงจะเพิ่มการปลดปล่อยธาตุอาหาร

สาขาวิชา…ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ …ลายมือชื่อนิสิต……………………………….

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KEY WORDS: DRYING OIL, AUTOOXIDATION, POLYMERIZATION, LINSEED OIL, TUNG OIL, SOY BEAN OIL, FLUIDIZED BED, PAN COATING

WARISTHA SAENGRITH: FERTILIZERS COATED WITH DRYING OILS FOR CONTROLLED RELEASE. THESIS ADVISOR: ASSOCIATE PROFESSOR AMORN PETSOM, Ph.D., 121 pp. ISBN 974-17-6965-2

The preparation of controlled-release fertilizer coated with drying oil i.e. linseed oil, tung oil, and soybean oil was investigated. The fluidized bed and pan coating were used for coating process. It was observed that pan coating was appropriate in the preparation of controlled-release fertilizer. It was found that factors that influence fertilizer coating process in pan coating method were 80^0C temperature using 1 % cobalt naphthenate as catalyst. Products from this coating process were smooth, sparkle and water resistant. In this experiment linseed oil and soybean oil were appropriate to be used as coating material but tung oil was not suitable. The optimum amount of drying oil for coating by pan coating method was 10 pph.

Atomic absorption spectroscopy and UV-Visible spectrophotometry were used to investigate the releasing rate of potassium from NPK fertilizer and urea from urea fertilizer, respectively. It was found that linseed oil coated fertilizers were slowest in nutrient release, while soybean oil and a mixture of linseed oil and soybean oil were inferior. When thickness of the coating film was increased, the releasing rate of nutrient decreased and increasing ambient temperature resulted in increasing of releasing rate. Furthermore, low pH was found to increase releasing rate of nutrient.

Field of study..Petrochemistry and Polymer Science..Student's signature……………...

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LIST OF ABBRIVIATIONS AND SYMBOLS

g	Grams
^{O}C	Degree Celsius
cm	Centimeter
ml	Mililitre
m^2	Square meter
min	Minute
SEM	Scanning Electron Microscope
AAS	Atomic absorption spectroscopy
SCU	Sulfur-coated urea
IBDU	Isobutylidene diurea
UF	Ureaformaldehyde
pph	Part Per Hundred

CHAPTER I

INTRODUCTION

1.1 Introduction

Fertilizers are one of the most important products of the agrochemical industry. They are added to soil to release nutrients necessary for plant growth. Synthetic fertilizers are made from chemical materials. The three major nutrients are based on Nitrogen (N), Phosphorus (P), and Potassium (K). It is well-known fact that no fertilizer, of whatever composition, is ever utilized by the plant with a complete efficiency. The main reason for this deficiency is the rapid dissolution of the fertilizer in the soil, where only part thereof is actually utilized, the balance being lost in the draining of rain or irrigation water. It results in water pollution and environment problems. One method to effectively reduce losses of nutrient components is to use controlled-release fertilizer.

The basic concept of controlled-release fertilizers is that they release their nutrient contents at more gradual rates that permit maximum uptake and utilization of the nutrient while minimizing losses due to leaching, volatilization or excessive turf growth.There are several ways to prepare controlled-release fertilizer. Coating process is particularly useful in that a coating process is relatively simple. The general idea is to provide an insoluble coating on granules of water-soluble fertilizers.

Various materials were found to be suitable for coating purpose. The most important of these include wax and sulfur and organic polymers. However, the main disadvantage of the organic polymers is their relatively high costs, which render them not to be economically feasible to use for a cheap product such as fertilizer. Sulfur coated fertilizer was found not to be adequately resistant to moisture penetration and sulfur can not be utilized in fertilizers containing nitrate where explosive composition might result. The use of drying oil is suggested as a coating film to provide an effective controlled-release fertilizer.

Drying oil is a kind of vegetable oil when exposed to the air, is oxidized to form a tough, elastic film. The common drying oils are tung oil, linseed oil and soybean oil. Drying oils are used mainly in paints, waterproof coating and drying agent in varnishes and inks. Drying oil is consisted of triglycerides that polymerization to hard gel on heating. Controlled-release by using drying oil method is often applied to nutrients controlled release studies.

1.2 Objectives of the research

1. To prepare controlled-release fertilizers coated with drying oils.
2. To study factors effecting nutrients releasing of controlled-release fertilizers.

1.3 Scopes of the research

1. Preparation of controlled-release fertilizers from NPK and urea fertilizers using various drying oil by fluidized bed and pan coating method.
2. Investigation of controlled-release fertilizer morphology by Scanning Electron Microscope (SEM).
3. Determination of release rate of controlled-release urea by spectrophotometric technique and potassium by atomic absorption spectroscopy (AAS).
4. Investigation of factors effecting nutrients releasing of controlled-release fertilizers ex. temperature, pH, and number of coating layer.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Fertilizers (Ahn, 1993)

Fertilizers are material given to plants with the intention of promoting growth. Fertilizers can be divided into two types as natural organic fertilizer and chemical fertilizer.

- Natural organic fertilizers use organic materials such as carcass, manure, dried blood or bone meal. They are popular with organic gardeners who object to chemical fertilizer or water-soluble forms. They have a low level of nutrients compared to most granular chemical fertilizers.

- Inorganic or chemical fertilizers is made from chemical materials. The three major nutrient of fertilizer are nitrogen, phosphorus and potassium and three numbers indicating the ratios in that order.

2.2 Nutrients function

Plants require 17 elements for normal growth. Carbon, hydrogen, and oxygen are found in air and water. Nitrogen, potassium, magnesium, calcium, phosphorous, and sulfur are absorbed from the soil. The latter six elements are used in relatively large amounts by the plant and are called **macronutrients**. There are eight other elements that are used in much smaller amounts; these are called **micronutrients** or trace elements. The micronutrients include iron, zinc, molybdenum, manganese, boron, copper, cobalt, and chlorine. The nutrients that are most likely to limit plant growth are nitrogen, phosphorus, and potassium.

2.2.1 Nitrogen

Plants usually receive most of their nitrogen in the form of nitrate. In general the nitrogen fertilizers used are in the form of an ammonium salt or urea. In the moist soil, catalyzed by the enzyme urease, they will give ammonium (NH_4^+) which is rapidly oxidized to nitrate in the presence of oxygen and the nitrifying bacteria.

$$\begin{tikzcd} CO\,(NH_2)_2 \quad + \quad H_2O \arrow[r, "\text{Enzyme urease}"] & H_2NCOONH_4 \arrow[d] \\ & 2NH_3 + \; CO_2 \quad \underline{\qquad}(1) \end{tikzcd}$$

Equation (1) is normally converted, in the moist soil to ammonium ions by hydrolysis. Then two reactions are as follow. First, *nitrosomonas* bacteria convert ammonia to nitrite:

$$2NH_3 \quad + \quad 3O_2 \longrightarrow 2NO_2^- \; + \; 2H^+ \; + \; 2H_2O \quad \text{———} \quad (2)$$

Secondary, *nitrobacter* converts nitrite into nitrate:

$$2NO_2^- \quad + \quad O_2 \longrightarrow 2NO_3^-$$

Nitrate ions are most readily absorbed by the crop through plant roots. During wet season, they are not able to retain in the soil because both soil and nitrate are negative charged. If there is sufficient rainfall, the nitrate which is far from the root zones of the plant will move downwards through the soil or be washed away into the ground or water ways, thus creating environmental problems.

Nitrogen may be lost to the atmosphere by denitrification or by volatilization where ammonia is produce at or near the soil surface. Leaching of nitrates, primarily from light soils may move nitrogen below the root zone where it cannot be utilized by crops. Erosion of surface soil may also carry nitrogen from fields in to streams and lakes or to the oceans.

Symptoms of nitrogen deficiency in plants

- Slow growth, stunted plants.
- Yellow-green color (chlorosis).
- Firing of tips and margins of leaves beginning with more mature leaves.

2.2.2 Phosphorus

Phosphorus is required in much lesser amounts than nitrogen, to the extent that only about one-tenth as much is found in plants. Phosphorus is absorbed by plants as $H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-} depending upon soil pH. Most of the total soil phosphorus is tied up chemically in compounds of limited solubility. In neutral to alkaline soils, calcium phosphate is formed, while in the acid soils, iron and aluminum phosphates are produced. Phosphorus is also necessary for the health of the plant; it is a constituent of nucleic acids, phytins, and phospholipids, and in the early life of the plant contributes to the formation of the reproductive parts. It is essential to seed formation and is found in large quantities in seed and fruit.

Symptoms of phosphorus deficiency in plants

- Slow growth, stunted plants.
- Purplish coloration on foliage of some plants.
- Dark green coloration with tips of leaves dying.
- Delay maturity.
- Poor grain, fruit and seed development.

2.2.3 Potassium

Potassium is taken up by plants in the form of potassium ion (K^+). It is not synthesized into compounds such as occurs with nitrogen and phosphorus but tends to remain in ionic form within cell and tissue. Potassium is essential for trans location of sugar and for starch formation. Potassium encourages root growth and increase crop resistance to decease. Furthermore, it increases size and quality of fruit and grains and is essential for high quality forage crop.

Symptoms of phosphorus deficiency in plants

- Tip and marginal burn starting on more mature leaves.
- Weak stalks, plants lodge easily.
- Small fruit or shriveled seeds.
- Slow growth.

Because of the relatively large consumption of macronutrients in agriculture, a discussion of fertilizer technology must be devoted mainly to nitrogen, phosphorus, and potassium

2.3 Physical form of fertilizer

Fertilizers are made in one of several forms:

2.3.1 Granulated fertilizers

Granulated fertilizers are manufactured for easy spreading and mixing into soil. They can be broadcast by hand or with a spreader, or incorporated into soil when potting or tilling planting beds. The highest-quality granules are even in particle size, free of dust, and deliver a mix of quick-release and slow-release nutrients.

2.3.2 Liquid fertilizers

Liquid fertilizers are usually diluted in water and applied with the water. They are usually quick-acting, without sustained release or persistence in the soil. They can be applied with a watering can, through a garden hose, or injected into a drip irrigation system.

2.3.3 Powdered fertilizers

Powdered fertilizers are soluble powders that, like liquid fertilizers, are delivered in water. They can be used in any way liquid fertilizers can be used. Before using them in a drip irrigation system, be sure they dissolve completely, without leaving a residue that will plug up the fine pores.

2.3.4 Pelleted fertilizers

Pelleted fertilizer looks like granules, but the pellets are very round and uniform in size and shape. They are composed of pieces of soluble fertilizer coated with sulfur and/or polymers to slow the rate of release. This is one type of slow-release fertilizer, made to be mixed into the soil within the root zone.

2.3.5 Tablets

Tablets are another slow-release fertilizer. They are buried in the soil within the root zone of plants. Most last for several months to a couple of years, releasing nutrients slowly.

2.3.6 Spikes

Spikes are similar to tablets. These slow-release forms are made to be pressed into planted soil or driven in with a hammer.

2.4 Controlled- release fertilizers (Sartain, 2002)

Controlled- release fertilizers are either inorganic fertilizers made up of larger molecules that require microbial action for degradation or regular fertilizers such as urea that are coated in some way to reduce solubility. Like organic fertilizers they have a low burn potential. They also release fertilizer over a longer period of time. Many formulations are now available that have release rates of 50 days to over one year. They are particularly useful on sandy soils where leaching of nitrogen is a concern. Higher rates of fertilizer can be applied without the fear of losing nitrate with excessive rainfall.

The main disadvantages of slow-release fertilizers are the high cost compared to quick-release fertilizer and the release rate maybe too slow for fast-growing crops.

Controlled-release fertilizers differ from conventional forms of fertilizer (for example, urea and water-soluble products) in that the majority of nutrients are not available immediately following application but release slowly over time. Two primary distinctions between individual controlled-release fertilizers products are the technology associated with encapsulating or binding fertilizer nutrients and the environmental mechanism by which these nutrients are released into the soil solution.

2.4.1 Uncoated organic materials

Several different nitrogen reaction products are produced for use as controlled-release fertilizer. These involve reacting low-cost urea with the one of several aldehyde to form a compound that is sparingly soluble in water. These compounds then slowly release nitrogen into the soil solution by chemical and/or biological activity. A disadvantage as compared to polymer-coated fertilizers is that independently, these products release only nitrogen, and supplemental products may be needed to provide additional macro and micronutrients. A potential advantage is that nutrient release controlled by factors other than soil temperature; soil moisture being the most notable. Two common examples of uncoated organic controlled release fertilizer are urea-formaldehyde (ureaform) and isobutylidene diurea (IBDU).

2.4.1.1 Ureaform

Ureaform is a form of slow release nitrogen technology and is product of the reaction of urea and formaldehyde in presence of catalyst. An example is Nitroform. The urea-formaldehyde reaction produces methylene urea polymers of varying molecular weights and chain lengths. The chain lengths is the technological mechanism by which nutrient release is controlled; a longer chain length is less water soluble and require more time to breakdown. Microbial decomposition is the primary mechanism by which ureaform is converted to plant available forms of nitrogen in the soil. Thus, the numerous environmental conditions that regulate microbial activity (for example, soil moisture, temperature, pH, aeration, and so on) also control the rate of nutrient release.

2.4.1.2 Isobutylidene diurea

Another nitrogen reaction product is IBDU, which is the condensation product of urea and isobutyraldehyde. Commercially, Woodace uses IBDU as a nitrogen source. This compound is relatively insoluble (<0.1%) in water and a commercial product may contain roughly 31% nitrogen. As compared to ureaform, water is the primary mechanism for nutrients release as nitrogen from IBDU become available to plant strictly through hydrolysis. In the presence of water the compound hydrolyzes to urea and isobutyraldehyde and this process is accelerated at low pH and high temperatures. Smaller particles tend to hydrolyze faster.

2.4.2 Coated materials

Coated controlled-release fertilizer products currently represent the most widely expanding form of controlled-release technology due to the flexibility in patterns of nutrient release and the capacity to release nutrients other than nitrogen. Coated controlled-release fertilizer products usually involve the encapsulation of soluble fertilizer nutrients within a water-insoluble coating, creating a 2 to 3 mm granule commonly referred to as a prill. The variability and unevenness of an individual prill makes attaining a complete and uniform coating difficult. Many different types of coatings have been used experimentally and it is likely that the ideal material has yet to be discovered. Some materials release nutrients too rapidly while others never effectively release nutrients. Two common controlled release fertilizer coatings used commercially are sulfur and polymer.

2.4.2.1 Sulfur coated

Sulfur was one of the first materials used as coating for controlled-release fertilizer due to its low cost and value secondary nutrient. Sulfur coated urea (SCU) is often marketed for use in the turf grass industry Following the coating of urea particles with sulfur, a wax sealant may be used to close sulfur pores. Nutrients are release from SCU by water penetration through micropore or inconsistencies in the sulfur coating. Urea inside the prill dissolves and is rapidly released into the soil solution. The release rate of SCU is controlled by modifying the quality and thickness of the sulfur coating. Environmental conditions, such as high temperatures and exposure to relatively dry soils, act to further degrade the coating and accelerate nutrient release. A disadvantage to SCU is the potential for urea to be released at a rapid initial rate and then quickly taper off. An advantage is the lower cost. Lesco is an example of a SCU on the market.

2.4.2.2 Polymer coated

Polymer-coated controlled-release fertilizers are considered the most technically-advanced form of controlled-release fertilizer due to the considerable ability to control product longevity and subsequent efficiency of nutrient delivery. In the most horticultural systems, polymer-coated controlled-release fertilizers have placed SCU because they provide a more gradual and consistent pattern of nutrient release. The mechanism of nutrient release from coated granular of fertilizers is same as following. In the first stage, water penetrates the porous coating. Then the nutrients are successively dissolved in the solution and thereafter diffuse through the coating. The coating consists a barrier for transport of encapsulated nutrients. The release rate of the nutrients through drying oil coating is also limited by rate of the base fertilizer solubility. This process is accelerated at progressively higher soil temperatures, with soil water content providing little influence on release.

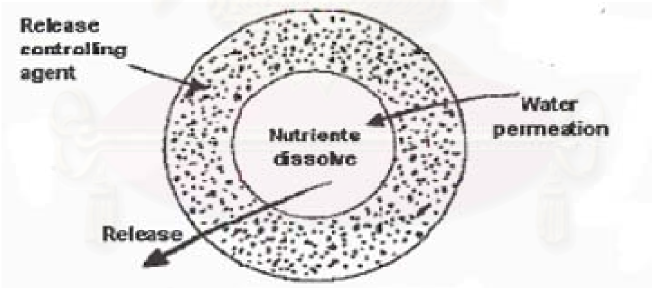


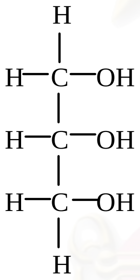
Figure 2.1 Mechanism of nutrient release from coated granule of fertilizer.

The terms slow-release fertilizer (SRF) and controlled release fertilizer (CRF) are often used synonymously, but technically they distinguish different fertilizer materials. Slow-release fertilizer is used to define organic fertilizer materials like hoof and horn and urea formaldehyde, as well as chemical fertilizers of low solubility like dicalcium phosphate and magnesium-ammonium phosphate. On the other hand, the term controlled-release fertilizer is used for inorganic fertilizers that have been coated by materials (acrylic resins, polyethylene, waxes and sulfur) that reduce their immediate solubility and availability to plants. Examples of CRF include the popular Osmocote and Nutricote formulations.

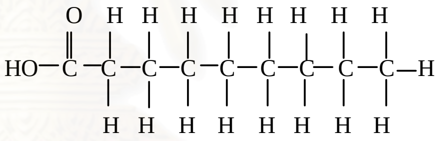
2.5 Drying oils (Martens, 1968)

Drying oils are liquid products of vegetable, animal, mineral, and synthetic origin. Chemically they are triglycerides, i.e., compounds of one molecule of glycerin and three molecules of long chain fatty acids.

Triglycerides have the following composition

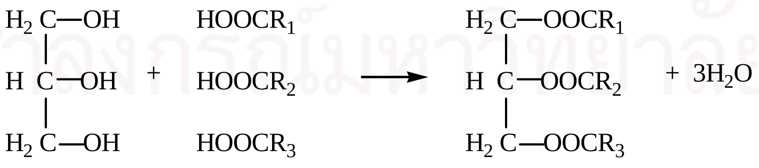


Glycerol



Fatty Acid

Fatty acid chain length can vary from C_9 to C_{22}



1 Moles of Glycerol

3 Moles of Fatty Acids

Triglyceride

3 Moles of Water

In the formulas show above, R_1, R_2 and R_3 stand for fatty acid chains. If R_1, R_2 and R_3 are the same, a simple triglyceride results. If they are not the same, the triglyceride is mixed. Triglycerides occurring in nature are usually of this type. This is a reversible reaction so that if we hydrolyze oil we obtain glycerin and fatty oil.

The nature of fatty acid present in oil determines its characteristics. The fatty acid consists of a carboxyl group attached to a hydrocarbon chain. Saturated fatty acids have hydrocarbon chains containing no double bonds, each carbon having a least two hydrogen atoms. Fatty acids with chains containing double bonds are termed unsaturated. They may have one, two, three or more double bonds, whose position in the chain may vary. Two double bonds separated by a single bond are called conjugated.

The double bonds in unsaturated fatty acids are chemically reactive sites. The reaction of oxygen with the oil molecule at the double bond results in drying; usually the greater the unsaturation, the better is the drying. Saturated fatty acids are nondrying. Fatty acids with three double bonds dry the most rapidly. However, in addition to the number of double bonds, the position of the double bond is important. Conjugated double bonds polymerize and dry more rapidly than isolated double bonds.

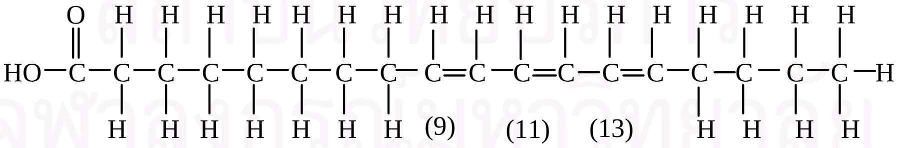
The oils commonly used in coatings today are tung, linseed, soybean, safflower, fish, and castor oils.

2.5.1 Tung oil

Tung oil is obtained from the kernels (oil content about 17.5%) of the fruit of the tung tree, ***Aleurites fordii,*** **Montana**, which has been grown in China for centuries and southern United States since about 1925. The oil is a pale yellow or darker liquid with valuable drying and polymerization properties because of its high content of eleostearic acid. The oil is used mainly in quick-drying enamels and vanishes, and in combination with other drying oils to improve overall properties such as water and alkali resistance.

Figure 2.2 Kernels of tung tree.

The following figure shows the chemical structure of eleostearic acid.



$$\begin{array}{cccccccccccccccccccc} & O & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & \\ & \| & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & | & \\ HO- & C- & C- & C- & C- & C- & C- & C- & C- & C= & C- & C= & C- & C= & C- & C- & C- & C- & C & -H \\ & & | & | & | & | & | & | & | & & & & & & & | & | & | & | & \\ & & H & H & H & H & H & H & H & (9) & & (11) & & (13) & & H & H & H & H & \end{array}$$

Figure 2.3 Structure of eleostearic acid.

Tung oil will dry in the air to form a solid film. This drying is a result of polymerization by the action of atmospheric oxygen (autoxidaton).

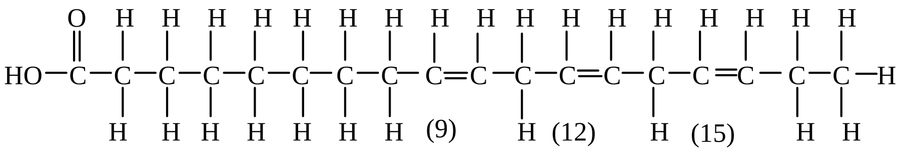
2.5.2 Linseed oil

Linseed oil is obtained from the seeds (oil content, 35-45% dry basis) of the flax plant ***Linum usitatissimum* L.**, grown in many temperate area of the world, notably the United States, Argentina and India. Linseed oil, historically, has been the most important oil in the coating industry.

Figure 2.4 Seed of flax plant.

The crude oil is obtained by pressing or solvent extraction, the latter after a prepressing to remove most of the oil. Crude linseed oil has a dark amber color and stronger characteristic odor. The odor of linseed oil, and of other linolenic acid, appears to be associated to a large extent with highly unsaturated acids of the oil and is inclined to reoccur after the oil has been steam deodorized. The color of linseed oil can be reduced to a pale yellow, similar to that of other refined vegetable oils, by suitable refining and bleaching treatment.

The major component of linseed oil is linolenic acid and the total unsaturated acid content is probably about 85-90%. The quality of linseed oil for technical purposes (or for uses as a drying oil) depends largely on its degree of unsaturation, as indicated by its iodine number. The following figure shows the chemical structure of linolenic acid



$$\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3}$$

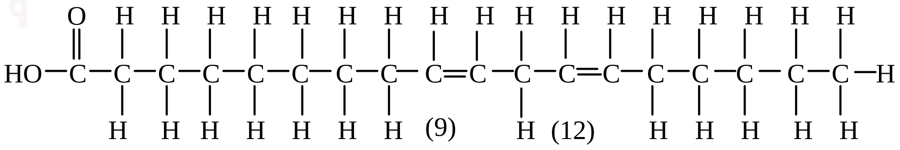
Figure 2.5 Structure of linolenic acid.

Linseed oil has a moderate drying rate because of its high linolenic acid content and its high iodine value the oil is used exclusively as an inedible oil in United State, principally in the manufacture of paints, vanishes, and printing inks, and for other industrial uses.

2.5.3 Soybean Oil

Soybean oil, obtained from the seeds (oil content 20%, average dry basis) of the legume ***Soja max*****,** is the highest volume vegetable oil produced in the world. The crude of oil is obtained by pressing or solvent extraction methods. The main uses of the oil after refining, bleaching and deodorization, and partial hydrogenation are in the manufacture of margarine and shortenings. Soybean oil is also used exclusively in the manufacture of drying oil products.

Crude soybean oil of good quality has a light amber color, which upon alkali refining, is reduced to the light yellow color of most vegetable seed oils. Fatty acid composition of soybean oils usually contains 5-9% of linolenic acid and generally 43-56% of linoleic acid. The following figure shows the chemical structure of linoleic acid.



$$\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_4{-}CH_3}$$

Figure 2.6 Structure of linoleic acid.

Figure 2.7 Seed of legume *Soja max.*

Table 1. Characteristic of vegetable oils.

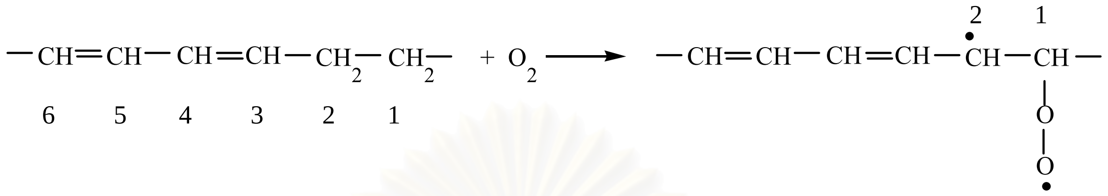
Characteristic	Tung Oil	Linseed Oil	Soybean Oil
Saponification number	189-195	189-195	189-195
Iodine number, Wijs, min.	160-175	177	120-141
Unsaponifiable matter, % max.	Below 1%	1.50	Not over 1.5%
Refractive index at 25^0C	1.516-1.520	1.468	1.470-1.476
Acid number, maximum	0.5	4.0	1.0

2.6 Oxidative polymerization

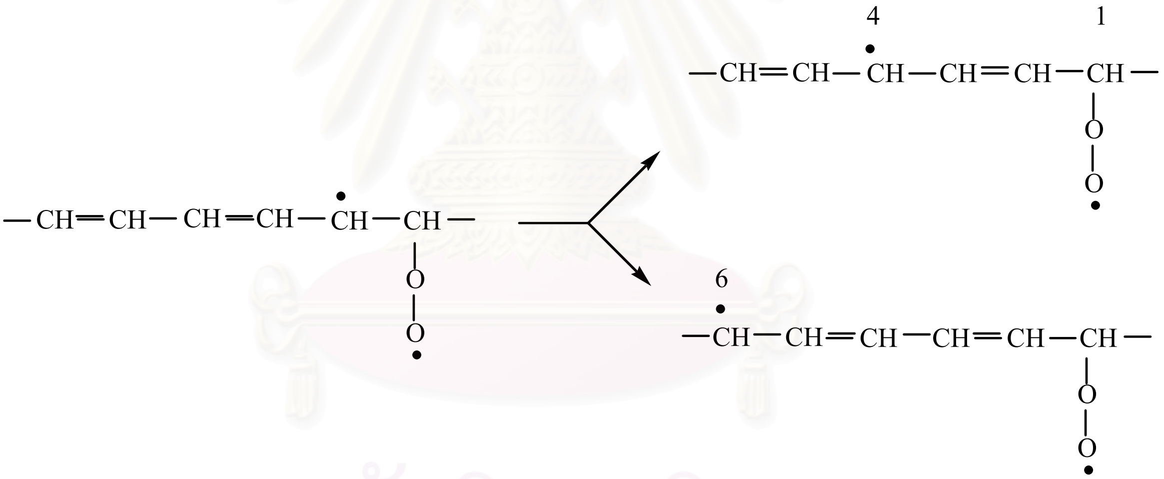
Oxidative polymerization has been the basis reaction of the protective coatings, oilcloth, linoleum and printing ink industries for many years. It was once believed quite generally that fatty chains became linked almost solely by carbon-oxygen linkages in the air-drying of oil films and in the other polymerizations accompanied by oxidation. The drying mechanism must be consistent with the facts. In particular different mechanisms are required for conjugated and non-conjugated oils.

2.6.1 Conjugated oils

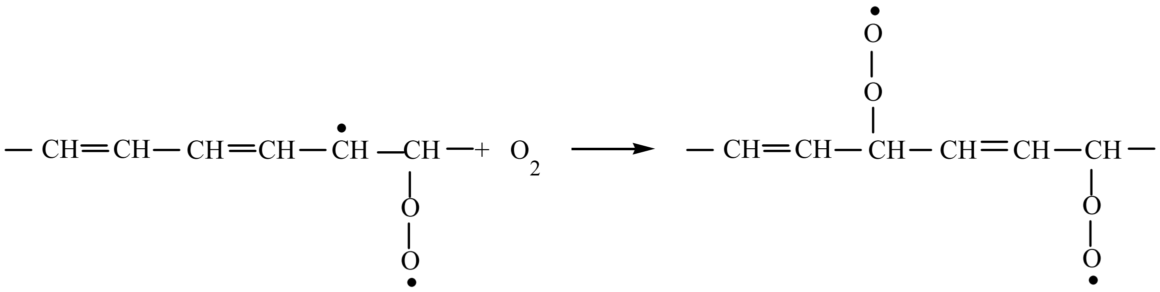
Oxygen attacks conjugated double bonds by direct addition, to form free radicals with two unsatisfied valencies (diradicals).



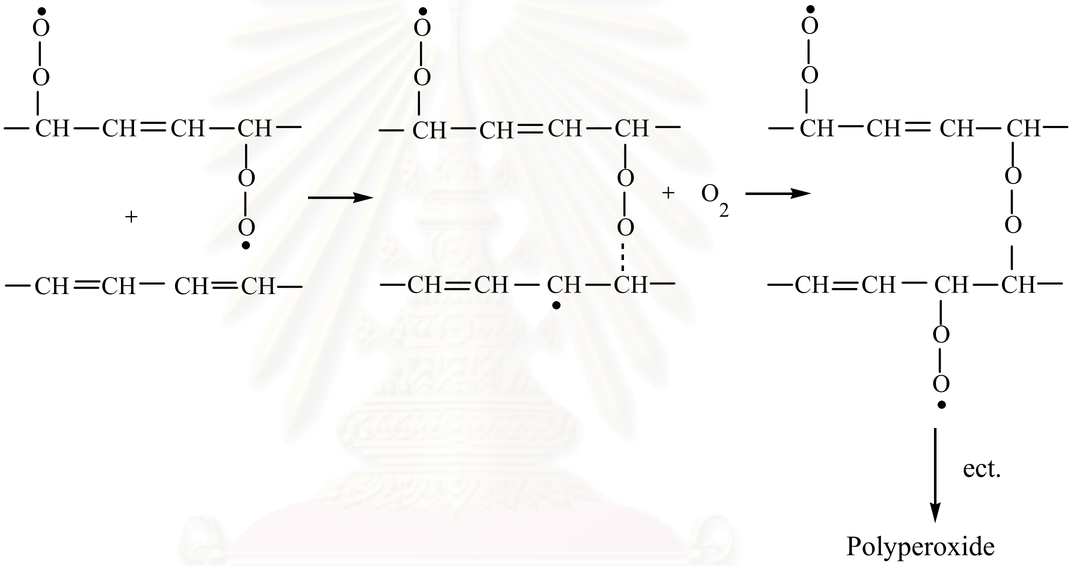
Rearrangement of double bond can take place to give radical sites in the 1, 4 and 1, 6 position as well. Such rearrangements involve only the redistribution of electrons in the molecule and occur.

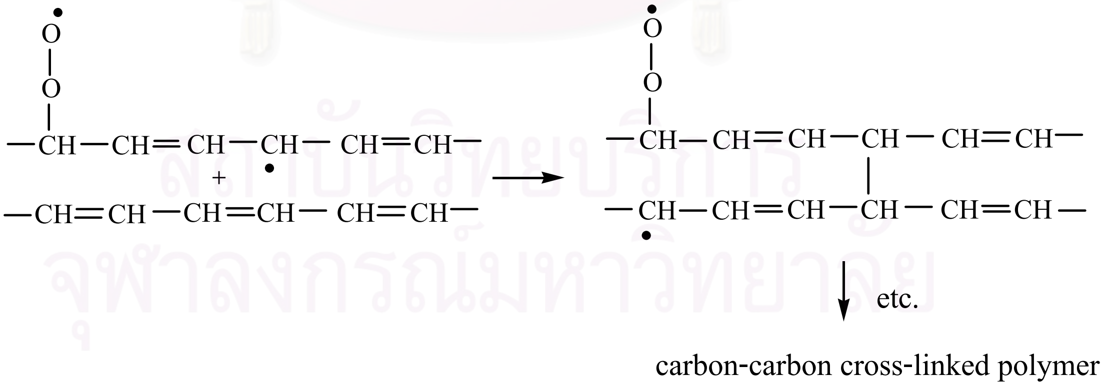


Frequently in unsaturated free radicals, oxygen may react with free carbon valencies to convert them to peroxy radicals.



Cross-linking occurs when the diradicals attack double bonds in other oil molecules. The peroxy radicals produce polyperoxide.

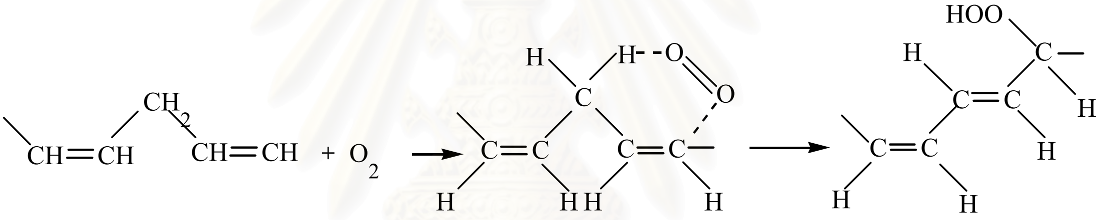




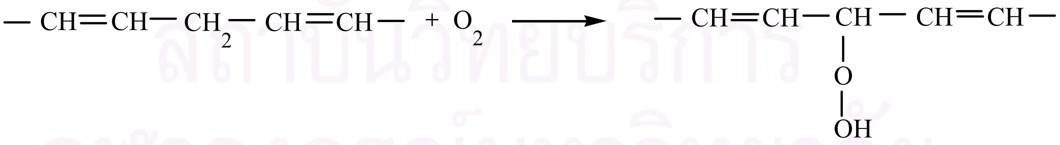
The cross-linking polymerization ceases when the two ends of the growing diradical combine with one another. Polyperoxides are exceptionally stable peroxides, but are decomposed by heat and light to alkoxy radicals, which will in turn react with double bonds to form ether linkages (RC-O-CR).

2.6.2 Non-conjugated oils

The essential difference is that reaction between oxygen (or free radicals) and non-conjugated oils occur without loss of unsaturation. One school of thought states that oxygen does attack the double bond, but that hydroperoxide formation and arrangement of bonds occur simultaneously, so that no unsaturation is lost.



The alternative opinion is that the methylene group between two double bonds is particularly prone to direct oxidation. With oxygen, a hydroperoxide is formed.

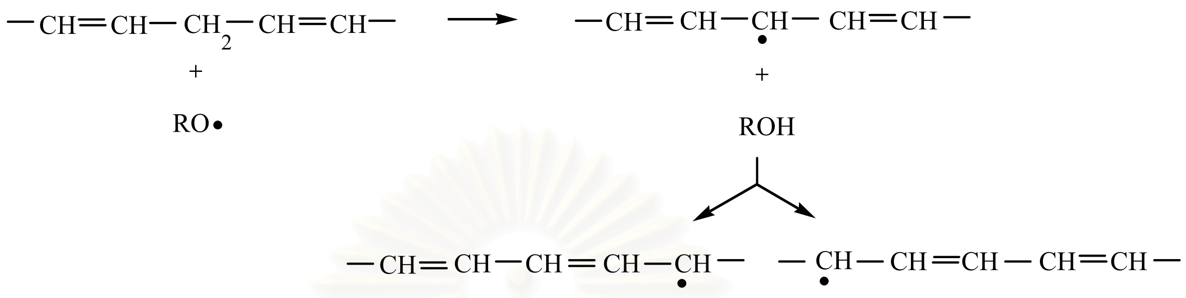


$$-CH{=}CH-CH_2-CH{=}CH- + O_2 \longrightarrow -CH{=}CH-\underset{\substack{|\\ O\\ |\\ OH}}{CH}-CH{=}CH-$$

The decomposition of hydroperoxides by driers is described in the section on driers. Free radicals are also obtained when hydroperoxides are decomposed by heat, light and driers.

$$RC-O-O-H \longrightarrow RC-O\bullet + \bullet O-H$$

A free radical will readily remove a hydrogen atom from the active methylene group between double bonds, transferring its free radical nature to the attacked carbon atom. The new free radical may then rearrange to a conjugated form.



Oxygen can convert these free radicals to peroxy radicals, which in turn may abstract hydrogen from methylene groups to form hydroperoxides. Whichever route is correct, it is generally agreed that hydroperoxide is formed and a substantial amount of isomerization to conjugated forms occurs.

During the initial stages of drying, the chief method of cross-linking is by direct combination of free radical sites on different oil molecules. Peroxy, ether and carbon-carbon links can be formed.

$$\left.\begin{array}{llll} RC{-}O\bullet & + \bullet O{-}CR & \longrightarrow & RC{-}O{-}O{-}CR \\ RC{-}O{-}O\bullet & + \bullet CR & \longrightarrow & RC{-}O{-}O{-}CR \\ RC{-}O{-}O\bullet & + \bullet O{-}O{-}CR & \longrightarrow & RC{-}O{-}O{-}CR + O_2 \end{array}\right\}\ \text{peroxy linkage}$$

$$RC{-}O\bullet \quad + \bullet CR \longrightarrow RC{-}O{-}CR \qquad \text{ether linkage}$$

$$RC\bullet \quad + \bullet CR \longrightarrow RC{-}CR \qquad \text{C-C linkage}$$

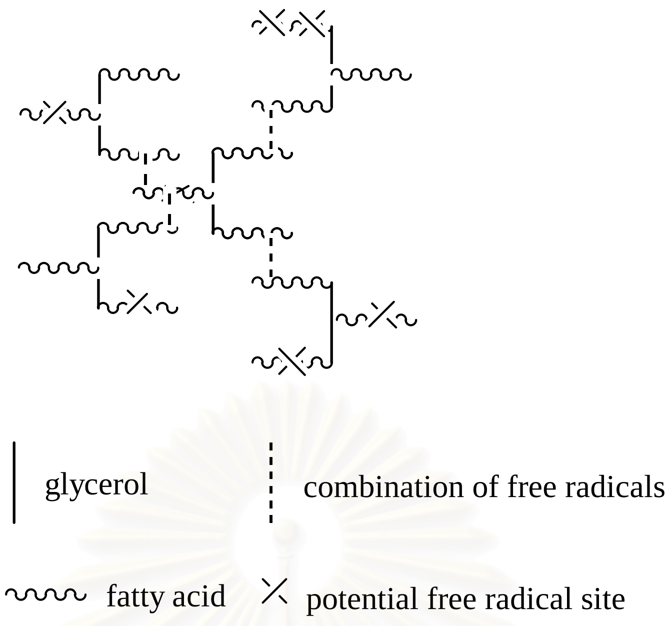


Figure 2.8 The cross-linking of oil molecules.

2.7 Driers (Lundberg, 1961)

A drier is a material, which promotes the drying or hardening process of paints, varnishes, and related oxidizable coatings so as to produce a serviceable film within a reasonable period of time. This definition of driers differentiates them from curing agents, which chemically react or condense with the coating material to become an integral part of the polymer form.

It has also been observed that the active drier metals are capable of having more than one state of valence and that an oxidation-reduction capability exists. The principle commercial products used as driers are a small group of heavy metal soaps of monocarboxylic acids, among which are the cobalt, manganese, and lead soaps of naphthenic acid.

Driers are commonly divided into two main classes according to their catalytic activity. Primary driers, which all possess some catalytic activity and secondary driers, which have no catalytic effect, when used on their own.

Primary driers can initiate and accelerate the oxidative drying process on their own, at least under certain conditions, but the strength of the catalytic activity varies within the group of conventional primary driers. At ambient conditions Co driers are the most active. As the secondary driers possess no catalytic effect, they will have no influence on the drying process if they are used on their own in air-drying systems, but combined with primary driers they become active enhancing the drying, especially the through-drying, and contribute to improved film properties as for instance gloss and film hardness.

How driers catalyze oxygen uptake is uncertain, but the decomposition of hydroperoxide by primary driers occurs as follows:

Oxidation of cobalt

$$\mathrm{Co^{2+} + ROOH \longrightarrow Co^{3+} + RO^{\bullet} + OH^{-}}$$

Reduction of cobalt

$$\mathrm{Co^{3+} + ROOH \longrightarrow Co^{2+} + RO_2^{\bullet} + H^{+}}$$

$$\mathrm{Co^{3+} + OH^{-} \longrightarrow Co^{2+} + {\bullet}OH}$$

$$\mathrm{Co^{3+} + RO^{-} \longrightarrow Co^{2+} + RO\,\bullet}$$

The cobalt is oxidized and reduced over and over again.

2.8 Drier Metals

2.8.1 Cobalt

Cobalt is far the most active of the five primary metal driers and therefore still the most important and widely used drier in air-drying coatings, solvent-borne as well as waterborne, despite the environmental and health drawbacks.

Cobalt driers give a rapid surface drying. Used alone or in relatively large amounts it may cause surface wrinkling. To avoid a too rapid surface drying and to provide uniform drying cobalt is commonly used in combination with other metal driers, such as manganese, zirconium, rare earth metals and calcium. Cobalt driers can be used on its own in the waterborne system, but are most often combined with a drying accelerator.

Cobalt needs only to be added in very small amounts and does therefore tend to minimise discoloration compared to other drier metals. Cobalt does furthermore not discolour white coatings to the same extent as other driers since the deep blue colour of cobalt counteract the yellow of the oils and alkyd binders and thereby enhances the whiteness of the paint.

2.8.2 Manganese

Manganese driers are some of the most important metal driers next to cobalt driers. Traditional manganese driers are medium in activity having both oxidising and polymerising properties, for which reason they promote both surface and through-drying. Manganese is, in its traditional carboxylate form, used extensively in air-drying products, most commonly in combination with Co driers to enhance the through drying of a coating. Used alone manganese driers have a tendency to produce hard brittle films.

Manganese has a relatively dark color, which makes it most suitable for pigmented coatings, as it tends to discolor light-colored or clear coatings. Light-colored manganese driers are though commercially available today. High atmospheric humidity may severely inhibit the efficiency of manganese.

A new generation of manganese driers has become available which possess more catalytic effect than the traditional type making them more suitable alternatives to Co driers.

2.8.3 Lead

Lead was among the first metals to be used and formulated specifically as a drier. While it is capable of producing a satisfactory dry of an oil film when used alone, it is slow in comparison to cobalt and, therefore, is rarely used without a more active drier being present. Lead is commonly used in combination with cobalt or manganese, and such a combination produces the best results in most air-dried finishes. Lead is used at higher concentrations than most of the other metals with the usual range being from 0.5 to 1 percent of metal by weight based upon the oxidizable vehicle.

2.9 Equipments for coating process

Equipment use in film coating can be classified into two general categories; coating pan and fluidized bed processors. Their systems are used to contain the materials being coated and provide an environment for the coating to dry. They should also provide a means to ensure that an equal amount of coating material is applied evenly to each substrate.

2.9.1 Fluidized bed

Fluidized bed equipment is the preferred choice of equipment for aqueous coating system. Aqueous film coating can be applied to the fluidized material by variety of techniques, including spraying from the top, from bottom or tangentially.

Particles within the diameter of 0.1-1.5 mm can be obtained by operation of the fluidized bed granulation apparatus. Properties such as particle diameter, bulk density of the particle and fluidity can be adjusted to a certain extent by changing the following operating conditions:

1. Inlet temperature
2. Position of spray nozzle
3. Pressure of spraying air
4. Overall quantity of spraying liquid and its flow velocity
5. Orifice diameter of the nozzle
6. Physical properties of spraying liquid (density, viscosity, temperature)
7. Hot air flow rate

The important point of operation is how to optimize these conditions by setting proper values for the experiment.

Figure 2.9 Fluidized bed.

2.9.2 Coating pan

Coating pan is used almost exclusively for the application of polymer films to tablets. The pan is well matched to tablet coating due to the gentle rolling action of the rotating bed and its ability to coat large batches.

In a standard coating pan, add the pieces to be glazed and start tumbling. The best results will be obtained when the coating pan is filled to its maximum capacity. Coverage will depend on the size and type of confection being coated. The volume of glaze to be added depends on the individual preference and the LB cut being used. After the glaze has been added and mixed through the product, cool dry air should be forced into the pan until the coating is dry and a shiny gloss is obtained. An exhaust fan should be used in the pan to vent the fumes.

This procedure will take time depending on what types of materials are used for coating. Once it is completed, remove the glazed pieces from the pan and store in a temperature and humidity controlled environment until ready for packaging and shipment. The advantage of coating pan is easy to operate, clean, excellent performance and simple maintenance.

Figure 2.10 Pan coating.

2.10 Literature reviews

Hepburn and Arizal (1988, 1989) prepared controlled release chemical fertilizer by coating urea fertilizer with sulfur compound. The fertilizer could be controlled release but it was not very good because there were a lot of porous on the coated surface. The coated fertilizer was brittle. Moreover, production was complicated and high cost.

Salman (1988) prepared encapsulating urea prills with polymeric materials in order to reduce the release rate of urea. Various types of polymers, including polystyrene, polycarbonate, a copolymer of vinyl chloride and vinyl acetate, poly (vinyl acetate), and low-density polyethylene (LDPE) were tested. Except for LDPE-coated urea, very high dissolution was observed (95%), even at a high coating percentage (15%). This was mainly due to the presence of large pinholes and to the nonuniformity of the coating film. LDPE-coated urea had much lower dissolution. For a coating percentage of 6, the dissolution was 25-30%.

Valkanas (1992) prepared controlled release potassium fertilizer, which was coated by using mixtures of paraffin waxes and wood rosin. It was found that the release rate of nutrient was decreased. The release rate mechanism of potassium sulfate was explained by square root of time under the diffusion controlled release mechanism. Release rate of potassium sulfate increased while the amount of potassium sulfate was increased.

Hudson (1995) prepared the sulfur coated urea fertilizer and improves the coated surface to be none porous and made the fertilizer to have abrasion resistant by sealant. The sealant was a mixture of different waxes such as petroleum waxes, synthetic waxes, natural waxes, vegetable and mineral waxes with polymer that was soluble in wax. Then, the conditioner such as diatomaceous earth, calcium silicate, clay minerals, and perlite was added. Urea fertilizer that was coated by 13 % sulfur and 1% sealant has a good moisture barrier. If 1.5% sealant was added, the abrasion resistant of fertilizer increased and it was found that conditioner improved release rate.

Hon (1997) prepared controlled release nitrate fertilizer by mixing fertilizer with cellulosic material from newspaper's paper and thermoplastic resin such as polyethylene. They found that nitrate was released within 24 hours.

Al-Zahrani (2000) prepared controlled release fertilizer which was coated with paraffin and polyethylene waxes. Dissolution test were performed for matrix-type formulations in order to determine the influence of waxes on the fertilizers release rate. The release times were at least doubled for all of the fertilizers while using either paraffin wax or polyethylene wax. The polyethylene wax gave longer release time than the paraffin wax.

Tomaszewska and Jarosiewicz (2002) prepared controlled release fertilizer using polysulfone as a coating material for soluble NPK granular fertilizer. The coating was formed by the phase inversion technique (wet method). It was experimentally confirmed that the use of polysulfone as a coating material for a soluble fertilizer decreases the release rate of components. In addition, coating of fertilizers leads to improvement of handing properties, and the crushing strength of all coated fertilizers was an average of 40% higher than that of uncoated NPK fertilizer.

Barh (1927) provided an inexpensive water proofing composition containing a vegetable drying oil, such as tung oil, linseed oil, or poppy seed oil; a gum or resin, such as colophony; and one more mixture of members of the paraffin series. This product when applied to the material will spread over all surface irregularities in a thin protective film which is impervious to moisture.

Kiatkanarat (2003) prepared prepolymer film for coating NPK fertilizer by two methods: reaction of epoxidized vegetable oils with amine compounds, and cross-linking of vegetable oils using metallic salt as catalyst. The result showed that among 3 vegetable oils studied, the most suitable oils for preparing the prepolymer film were tung oil and 1:1 tung oil/soybean oil mixture in the presence of 0.5 percent cobalt naphthenate as a catalyst. It gave a smooth and dry film. Slow release fertilizer were prepared using tung oil as composition in prepolymer film gave the slowest releasing rate, following by a mixture of tung oil and soybean oil, tung oil coated on wax, epoxidized palm oil which was reacted with amine compounds coated on wax, and one layer of wax.

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. NPK fertilizer 8-24-24 : Kemira growhow Co., Ltd.
2. Urea fertilizer 46-0-0 : Rojpanakitt Co., Ltd.
3. Commercial tung oil : Bank of Thailand
4. Commercial linseed oil : Union Chemical 1986 Co., Ltd.
5. Commercial soybean oil : Industries PLC
6. Cobalt naphthenate : Fluka
7. Sodium hydroxide : Merck
8. *p*- dimethylaminobenzaldehyde : B D H Chemicals., Ltd
9. Ethanol : Merck
10. Hydrochloric acid : Merck
11. Cesium chloride : Merck

3.2 Equipments

1. Scanning Electron Microscope (SEM); JSM- 5800LV
2. Atomic Absorption Spectrophotometer (AAS); AA-300
3. Fluidized Bed; Model GA-22 Yamato Scientific Co., Ltd.
4. UV Visible Spectrophotometry; UV-160 Shimadzu Co., Ltd.
5. Pan Coater; Faculty of Pharmaceutical, Chulalongkorn University

6. pH meter; Mettler Toledo Co., Ltd.
7. Water Bath Tempette; TE-16 D, Techne (Cambridge) Limited.

The quality of the coating depends on a number of process variables. Therefore, preliminary experiments were conducted to examine these variables and to find the optimum coating conditions. The main process variables include (1) type of catalyst, (2) amount of catalyst, (3) amount of drying oil, (4) type of drying oil, (5) coating process.

3.3 Effect of the amount of catalyst

In this study, catalyst for film drying was cobalt naphthenate. The amount of catalyst was varied from 0.01, 0.05, 0.1, 0.5, 1.0, and 2.0 percent by weight.

3.4 Effect of amount of drying oil

In this study, the amount of drying oil were varied from 5, 10, 15, and 20 part per hundred.

3.5 Preparation of fertilizer

The fertilizer used in this study was a commercial water-soluble granular fertilizer, NPK 8-24-24 and urea fertilizer. The diameter of granules used was in the range from 2 to 5 mm. Fertilizers were dried in oven at 80°C for 24 hours to remove moisture and kept in desiccator until use.

3.6 Fertilizer coating process

In this study, coated fertilizers were prepared by fluidized bed and pan coating method. Procedure of coating fertilizers method is described below.

3.6.1 Fluidized bed

- Approximately 100 grams of fertilizer was filled in fluidized bed chamber and then inserted into the apparatus and sealed pneumatically.
- When the aspirator switch is turned on, then the aspirator adjusting dial was rotated to adjust air flow rate and to start the fluidization of the sample.
- Turn on the heater switch, and turn the inlet temperature adjusting dial to display set-temperature on the inlet-temperature display.
- Since the outlet temperature is displayed on the outlet temperature display, open the needle valve after confirmation of temperature rise and heating up of the chamber. Then turn ON the pump switch to deliver drying oil and spray it through nozzle. Control the proper drying oil flow rate by the pump-adjusting dial.
- When fluidity of the sample is not in good condition, increase air flow rate by aspirator adjusting dial or start to rotate the stirring blade by turning on the stirrer switch.
- When desired coated-fertilizer is obtained, turn off the heater and aspirator switch then take out the fluidized bed chamber and collect the coated fertilizer.
- The coated fertilizer was placed in the oven at 80°C for 24 hours period to allow the coated layer to dry.

3.6.2 Pan coating

- Approximately 100 grams of fertilizer was placed into the coating drum of pan coater followed by drying oil and catalyst.
- While fertilizer was coating, hot air was allowed to flow into coating drum in order to dry the granular.
- The coated fertilizer was placed in the oven at 80°C for 24 hours period to allow the coated layer to dry.
- Multiple coatings were prepared by coated single-coated dried fertilizer granules several times with drying oil.

3.7 Morphology

The coating morphology was examined using a scanning electron microscopy (SEM). Before the measurement, the coated fertilizer granule was cut to obtain cross sections, and then coated with a gold layer for SEM observation.

3.8 Release experiments

3.8.1 Preparation solution

- Approximately 0.24 grams of coated fertilizer granules were placed in 30 ml. of deionized water maintained at room temperature.
- At regular time intervals, 5 ml. of solution was withdrawn from the flask and replaced with fresh deionized water.
- The collected solution was analyzed for released amount of nutrients.

3.8.2 Determination of potassium content

In NPK coated fertilizer, the potassium content was determined by flame photometric analysis using an atomic absorption spectrophotometer operating in flame absorption mode in the presence of cesium chloride.

3.8.2.1 Sample preparation for potassium analysis

1. Approximately 1.26 g of cesium chloride was dissolved in 100 ml volumetric flask and dilute to 1000 ml with deionized water.
2. Approximately 3 ml of cesium solution was added into 1 ml of sample solution and analyzed by atomic absorption spectrophotometer.

3.8.2.2 Calibration curve

To determine the potassium release content, a calibration curve was first construct from atomic absorption spectrophotometric measurement of standard potassium. Various concentration of standard potassium was prepare by pipette 5, 10, 20, 50 ml of standard potassium solution (1g/L) into 100 ml volumetric flasks and diluted to volume with distilled water.

3.8.3 Determination of urea content

The urea release from coated fertilizers was determined by using colorimetric method; *p*-Dimethylaminobenzaldehyde (DMAB) was employed as the color producer for spectrophotometric measurement according to analytical protocol described by Potts (Potts, 1963).

3.8.3.1 Reagent

p-Dimethylaminobenzaldehyde (DMAB) solution: DMAB (16.00 g) was dissolved in 95 % ethyl alcohol (1000 ml) and then concentrated HCl (100 ml) was added into the mixture while shaking thoroughly. This solution was stable for 1 month.

3.8.3.2 Calibration curve

To determine the urea release content, a calibration curve was first constructed from UV absorption measurement of standard urea. Various concentration of standard urea were prepared by dissolving 5.00 g urea in 1000 ml distilled water. Then, pipetted 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20 ml of standard urea solution into 100 ml volumetric flasks and diluted to volume with distilled water.

3.8.3.3 Determination of urea concentration

The sample solution (5 ml) was mixed thoroughly with 5 ml of DMAB solution in a test tube. After 10 minutes, the mixture was poured into 1 cm cuvette, and then placed in the sample holder of UV- Visible spectrophotometer and the absorbance was read at 440 nm. (using the reagent blank to set the spectrophotometer to 100 % transmittance).

3.9 Effect of drying oil type

In this study, various drying oil were used to coat fertilizers to evaluate the influence of the type of drying oil coatings. These oil are linseed oil, tung oil, soybean oil, mixture of linseed oil and soybean oil (1:1), mixture of linseed oil and tung oil (1:1).

3.10 Effect of number of drying oil film layer

In this study, the effect of number layer of drying oil film to release rate of nutrient was investigated. Single-coated dried fertilizer granules were coated with drying oil for two layers, four layers, six layers, eight layers.

3.11 Effect of temperature

The influence of temperature on the release rate of nutrients through the polymer coating was also determined. The test was performed at temperature of 20, 25, 30, 35, and 40^0C in aqueous medium.

Samples under temperature controlled, were collected every 30 minutes. The solution was collected and analyzed for the amount of urea.

3.12 Effect of pH

The influence of pH on the release rate of nutrient through the polymer coating was also determined. The test was performed at pH 5, 6, 7, 8, 9, and 10 in aqueous medium.

Sample was collected every hour. The solution was collected and analyzed for the amount of urea.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Solubility of uncoated fertilizers

Fertilizers used in this study were uncoated fertilizers available in market. Figures 4.1 and 4.2 show the photograph of uncoated NPK fertilizer and urea fertilizer respectively. In this study, both fertilizers were used for solubility test. It was found that both fertilizers were easily dissolved in deionized water.

Figure 4.1 NPK fertilizer 8-24-24 before coating.

Figure 4.2 Urea fertilizer 46-0-0 before coating.

Figures 4.3 and 4.4 show the amount of potassium and urea solubilized in water at 30^{o}C as the function of time for the first period of the test. The curves of both series showed analogous trends over the time. Urea was released completely in 3 minutes and the NPK fertilizer, potassium was released completely in 80 minutes. Urea fertilizer is white crystalline solid containing only 46% nitrogen. On the other hand NPK fertilizer composes of many components including filler, thus it dissolves slower than urea fertilizer.

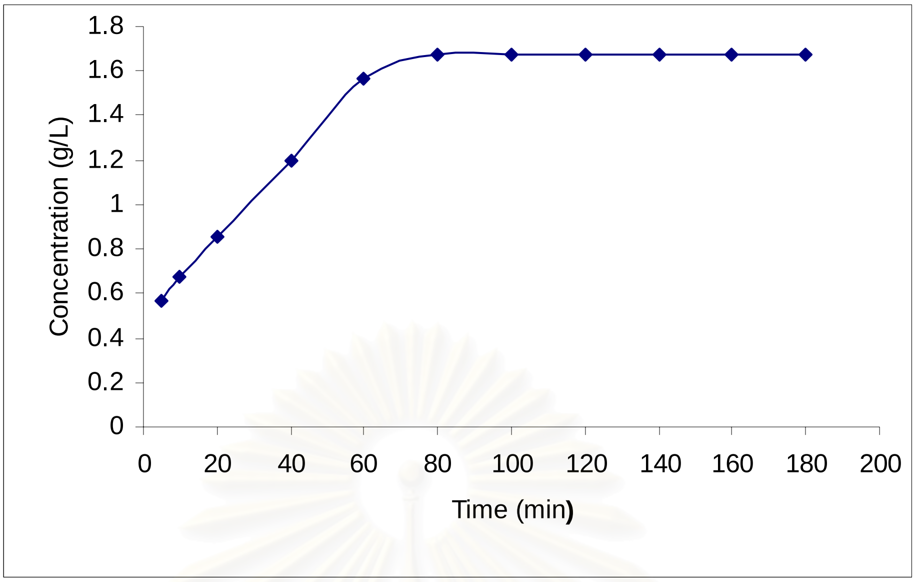


Figure 4.3 Dissolution profile of potassium in uncoated NPK fertilizer.

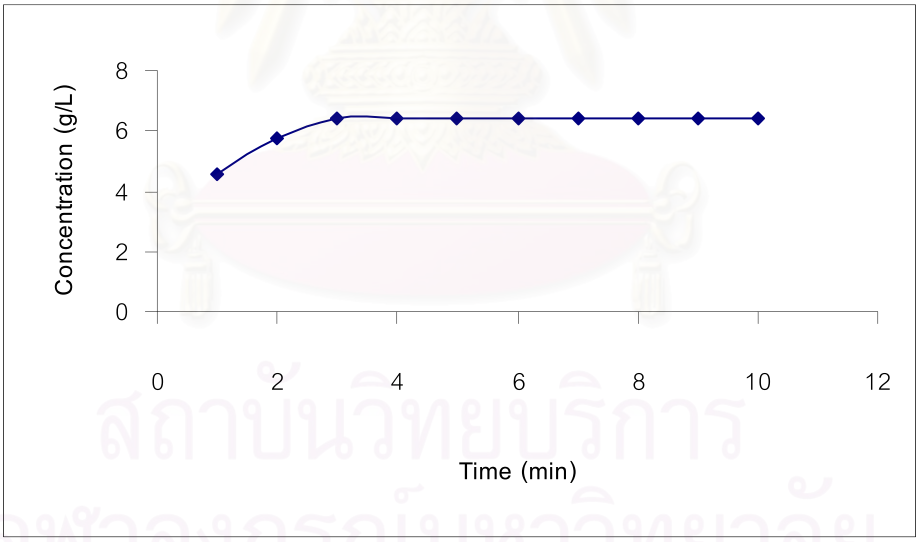
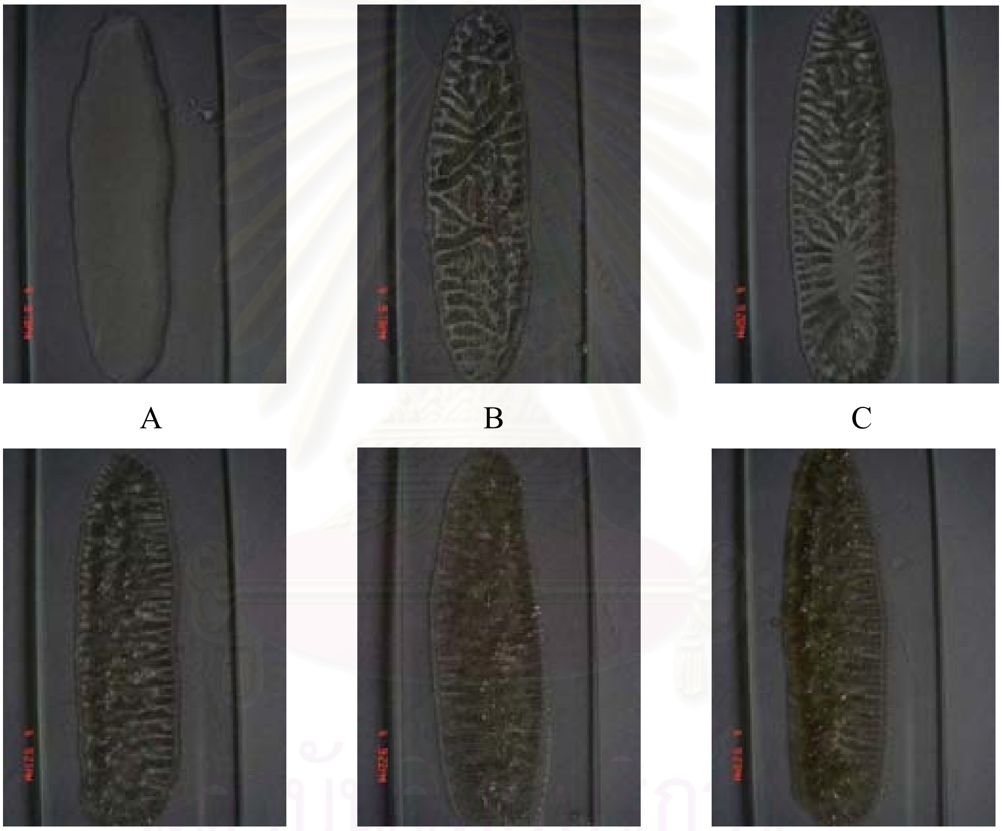


Figure 4.4 Dissolution profile of urea in uncoated urea fertilizer.

4.2 Effect of the amount of catalyst

It is known that the concentration of catalyst affects the drying property of polymer film. Concentrations that are too low or too high cause the polymer films coating granules to be incomplete or damage. In this study, cobalt naphthenate was used as catalyst and it was varied from 0.01, 0.05, 0.1, 0.5, 1.0, and 2.0 percent by weight. The effect of concentration of catalyst on film drying was demonstrated in Figure 4.5.



A B C

D E F

Figure 4.5 Characteristic of polymer film when using different amount of catalyst at 30^{0}C for 120 minute.

A. 0.01 % Cobalt naphthenate B. 0.05% Cobaltnaphthenate

C. 0.1% Cobalt naphthenate D. 0.5% Cobalt naphthenate

E. 1 % Cobalt naphthenate F. 2% Cobalt naphthenate

Figure 4.5 indicated that the high concentration of catalyst gave a rapid surface drying which may cause surface wrinkling. If the surface dries too rapidly the oxygen uptake is prohibited to go beneath the surface of the coating film. This leaves the coating film mobile and soft right under the surface due to a low degree of cross-linking. Movements of the coating beneath the dry surface result in wrinkles in the film. Therefore, cobalt naphthenate at 1 percent by weight was selected for coating process.

4.3 Preparation of controlled release fertilizers

There are three types of controlled-release fertilizers: slightly soluble materials, such as urea formaldehyde; materials for deep placement, such as urea super granules; and coated fertilizers. This experiment deals with the last approach, particularly with drying oil coated fertilizers.

The equipment chosen for coating process will be important because many processing factors are equipment-dependent. There are many types of equipment to be used in the preparation of controlled-release fertilizers. In this study, fluidized bed and pan coating method were selected for the preparation of coated fertilizer because they were simple methods and can be easily incorporated in any existing fertilizer plant. In addition, the optimum condition of each method on fertilizer coating will be investigated.

4.3.1 Fluidized bed

The first method for the preparation of controlled-release fertilizer was fluidized bed method. Fertilizer used in this experiment was NPK fertilizer, linseed oil was used as a coating material and 1% cobalt naphthenate was used as catalyst. The fluidized bed conditions were varied as shown in table 4.1.

Table 4.1 Fluidized bed conditions.

Temperature (C^o)	50, 60, 70, 80, 90
Drying air (m^3/ min)	0.5, 0.6, 0.7, 0.8, 0.9
Pressure of spraying air (Kgf/m^2)	0.5,1.0,1.5,2.0,2.5
Time (minutes)	5, 10, 15, 20, 25, 30

The amount of fertilizer coated is limited by the capacity of ventilator. If the weight of the fertilizer particles exceeds 500 grams, they cannot be fluidized. Furthermore, film formation was not completed. In this experiment, 20 grams of fertilizer was appropriate for coating. The optimum coating conditions was temperature at 80^0C, pressure of spraying air at 2.0 Kgf / m^2, drying air at 0.6 m^3/ min, and time for processing at 20 minutes. Values higher than the upper limit cause particle attrition, which gives rise to high porosity and an increase in the dissolution rate. Values below the lower limit will prevent fluidization and proper atomization of the coating solution.

As a result, coated fertilizers agglomerated and showed uniform coating. The coated fertilizers were placed in an oven at 80^oC for 24 hours to allow the coated layer to dry.

Figure 4.6 Coated fertilizer by fluidized bed method.

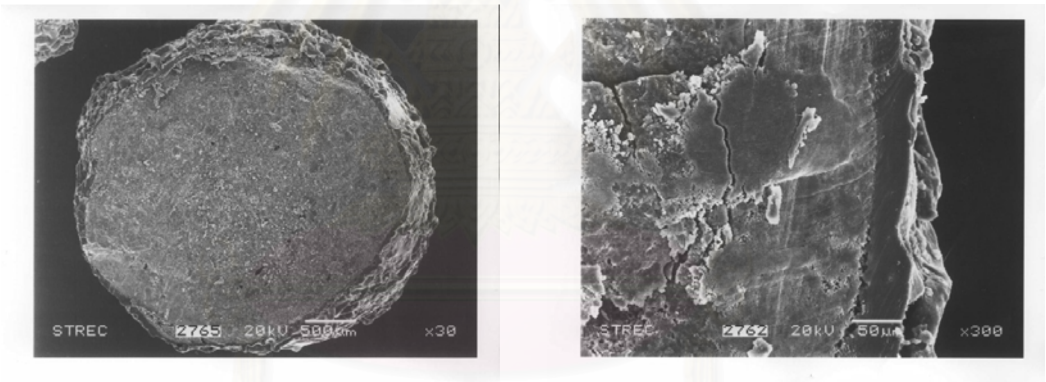


Figure 4.7 SEM of coated fertilizer with linseed oil by fluidized bed method.

After the coated fertilizer was dried, the color of exterior surface of coated NPK fertilizer was yellow instead of green, blue, and pink which were the original colors of fertilizer. Figures 4.6 and 4.7 show that surface of coated fertilizer was not smooth and film formation was not completed. Since the thickness of polymer film had influence on releasing rate, therefore this coated fertilizer was not practical. Furthermore, drying oil was not appropriate to coat fertilizer by fluidized bed because it had tendency to block the spray nozzle. However, fluidized bed was used to coating fertilizer when used other coating materials i.e. polystyrene, polycarbonate, and low-density polyethylene (LDPE).

4.3.2 Pan coating

Pan coating is used almost exclusively for the application of polymer films to tablets. The pan is well matched to tablet coating due to the gentle rolling action of the rotating bed and its ability to coat large batches. In addition, pan coating is a simple and not expensive method. In this experiment, the diameter of coating drum is 35 centimeter. Fertilizer used in this experiment was NPK fertilizer, in which the weight was varied from 20, 50, 100, 200, 500, and 1,000 gram. Linseed oil (10 pph) was used as a coating material and 1% cobalt naphthenate as catalyst. Two of the most important parameters affecting the quality of coating are the size and physical characteristics of the fertilizer. Fertilizer must be spherical, smooth, hard, and has narrow size distribution. Figure 4.8 shows the good characteristic of coated fertilizer by pan coating method.

Figure 4.8 Coated fertilizers with pan coating method.

From this experiment, it was found that 100 grams of NPK fertilizer was suitable to be coated with 35 cm. diameter of pan coating. The SEM of coated fertilizer (Figure 4.10) shows that pan coating method gave better product than those obtained by fluidized bed method. The surface appears smooth, compact, homogeneous, and film forming was complete. Thus in this research, pan coating method was used to coat fertilizer.

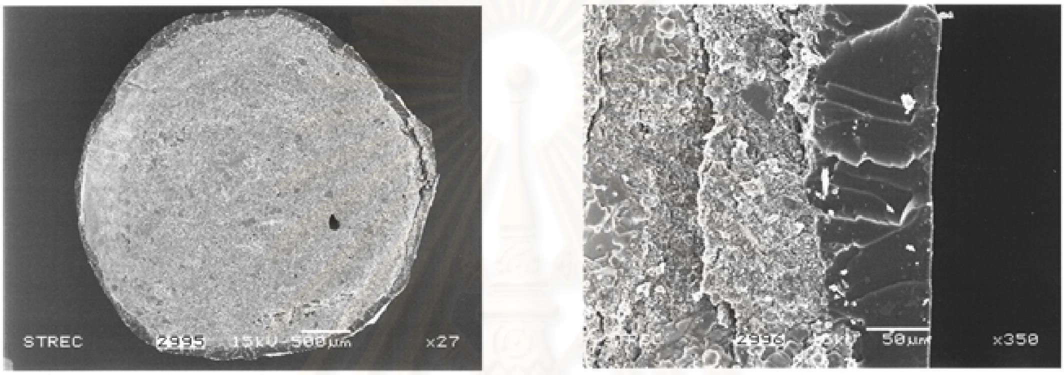


Figure 4.9 SEM of coated fertilizer with linseed oil by pan coating method.

4.4 Effect of amount of drying oil

Amount of drying oil is one of the factors which influence the coating process by pan coating. The amount of drying oil was varied from 5, 10, 15, and 20 pph. Fertilizer used in this experiment was NPK fertilizer, linseed oil was used as coating material, and 1 % cobalt naphthenate as catalyst. The influence of amount of drying oil coating is shown in Figure 4.10

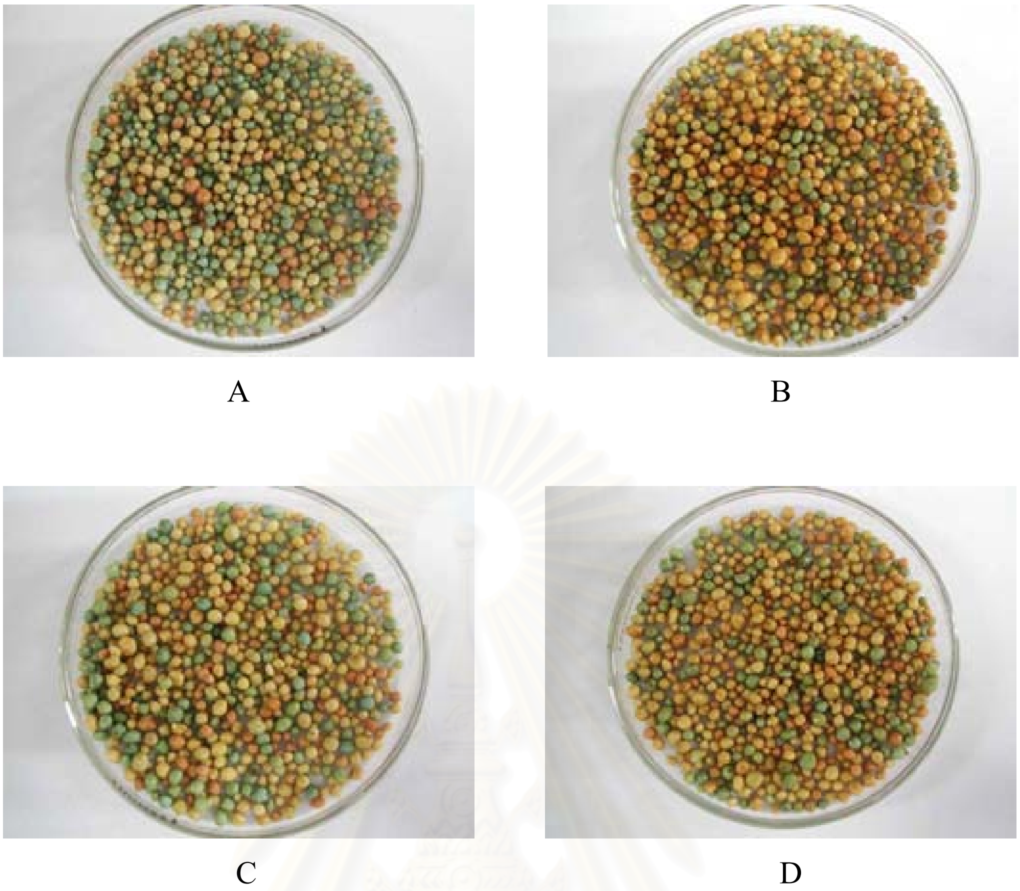


Figure 4.10 Comparison of the effect of amount of linseed oil.

A. 5 pph linseed oil coated fertilizer.

B. 10 pph linseed oil coated fertilizer.

C. 15 pph linseed oil coated fertilizer.

D. 20 pph linseed oil coated fertilizer.

From Figure 4.10 it was found that fertilizer can be coated with 5 pph linseed oil and it can increase amount of linseed oil to 10 pph. The higher amount of linseed oil was not appropriate to coat fertilizer by pan coating method because excess drying oil may cause polymerization on surface of coating pan instead of on fertilizer surface. Thus in this research 10 pph linseed oil was used to coat fertilizer.

4.5 Effect of drying oil type

The suitable coating material for fertilizer coating must be nonreactive, essentially immiscible with the material being encapsulated and capable of being rapidly hardened to form a film. Various materials have been used as coatings, including organic polymers, paraffin waxes, and vegetable oils. In this experiment, vegetable oils were selected as coating materials i.e. linseed oil, tung oil, soybean oil, a mixture of tung and linseed oil, and a mixture of linseed oil and soybean oil because drying oils will form biodegradable film which was degraded by microorganism in soil and without ecologically damaging effect to the environment. Furthermore, vegetable oil is not expensive compared to other coating material such as organic polymer and waxes.

4.5.1 Tung oil coated fertilizer

Tung oil is conjugated drying oil. The principal component in tung oil is eleostearic acid. This oil is converted by the oxygen of air to dry, hard, and insoluble film. From this reason, tung oil was selected to coat fertilizer for controlled release nutrients. Fertilizer used in this experiment was NPK fertilizer, 10 pph tung oil was used as coating material by pan coating method and 1% cobalt naphthenate as catalyst. The photograph of tung oil coated fertilizer is shown in Figure 4.11

Figure 4.11 Fertilizer coated with 10 pph tung oil by pan coating method.

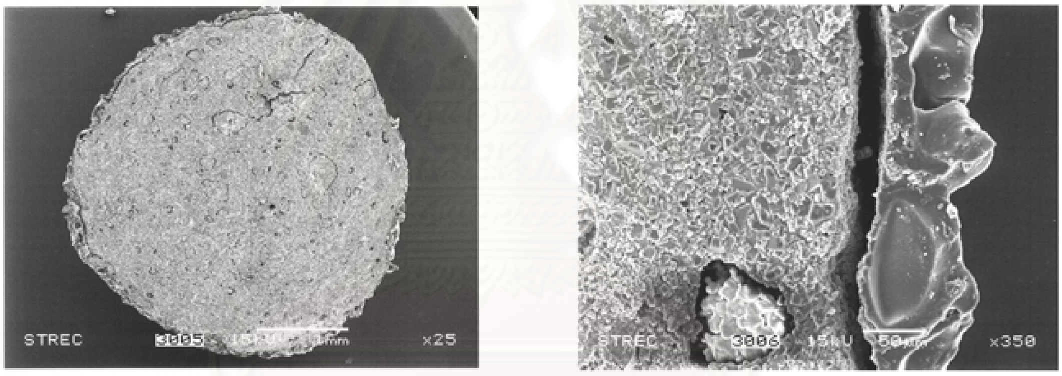


Figure 4.12 SEM of coated fertilizer with 10 pph tung oil.

The preparation of coated fertilizer with tung oil took 15 minutes for coating process. The product from this method shows unacceptable characteristics of coated fertilizer such as roughness of surface and the coating film was not adhearing to the fertilizer surface as shown in Figures 4.11 and 4.12. It can be explain that tung oil contains about 80 % eleostearic acid which is a conjugated fatty acid therefore this oil is very reactive to uptake oxygen to polymerization. Rapid polymerization had effect on film forming by pan coating method because one part of tung oil will polymerize on surface of coating pan. The remaining will be polymerized and formed film on surface of fertilizer, thus film forming of tung oil was not complete. Furthermore, product from this coating has much porosity, which influences to release mechanism.

Even though tung oil was useful in paint and vanish industry but it is not appropriate for preparation of controlled-release fertilizers by pan coating. The method for improving properties of tung oil is carried out by addition other oil to reduce drying property which will be mentioned in section 4.5.4.

4.5.2 Linseed oil coated fertilizer

Linseed oil is a non-conjugated drying oil. The principal component in linseed oil is linolenic acid. This oil can be polymerized to film forming similar to tung oil. Fertilizer used in this experiment was NPK fertilizer, 10 pph linseed oil was used as coating material by pan coating method and 1% cobalt naphthenate as catalyst. The photograph of linseed oil coated fertilizer is shown in Figure 4.13.

Figure 4.13 Fertilizer coated with 10 pph linseed oil.

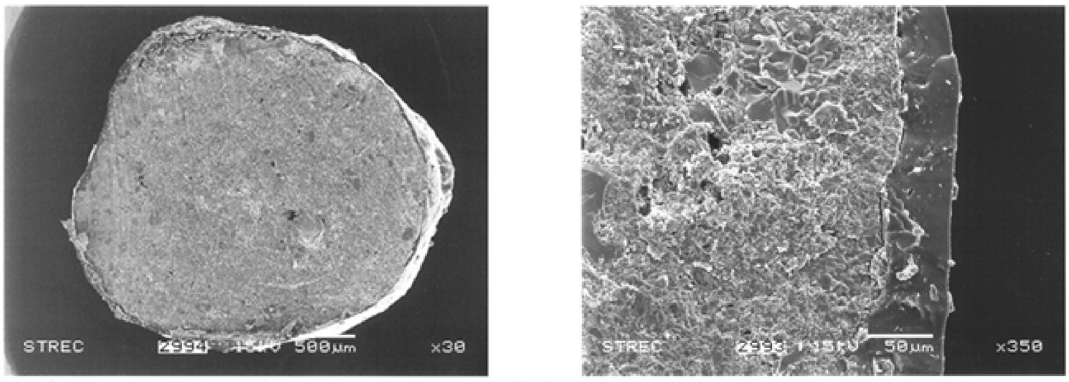


Figure 4.14 SEM of coated fertilizer with 10 pph linseed oil.

From Figures 4.13 and 4.14, the fertilizer coated with linseed oil gave good characteristic of coated fertilizer i.e. smooth, compact, sparkle, non-aggregation, complete film- forming and water resistant. These coated fertilizers took 45 minutes for drying. Coated fertilizers with linseed oil have longer drying time than tung oil because the major component of fatty acid in linseed oil is linolenic acid, which is a non-conjugated fatty acid. Conjugated oils like tung oil favor polymerization and oxidation and dry more rapidly than non-conjugated oils (like linseed oil). It can be explained with oxidative polymerization, when oxygen attack at non-conjugated molecule produces hydroperoxides are the primary products then free radicals are released by hydroperoxides decomposition. Although, linseed oil had longer drying time than tung oil but product from coating gave better characteristic and film forming was more complete.

4.5.3 Soybean oil coated fertilizer

The principal component of soybean oil is linoleic acid. The main use of the oil is in cooking manufacture of margarine and shortening. In addition, soybean oil was used in coating industrial because soybean oil is semi-drying oil, it can be polymerized to form film. Fertilizer used in this experiment was NPK fertilizer, 10 pph soybean oil was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. The photograph of soybean oil coated fertilizer is shown in Figure 4.15.

Figure 4.15 Fertilizer coated with 10 pph of soybean oil.

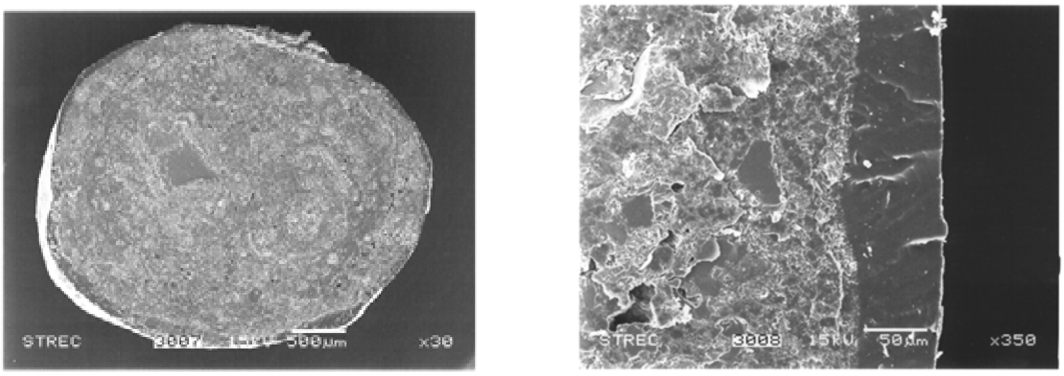


Figure 4.16 SEM of coated fertilizer with 10 pph soybean oil.

The photograph and SEM of soybean oil coated fertilizer are shown in Figures 4.15 and 4.16. They indicated good characteristic of coated fertilizer i.e. spherical, smooth, sparkle, hardness, and complete film-forming. These coated fertilizers took 120 minutes for drying. Linoleic acid has two double bonds, which is reactive site for oxidative polymerization thus it is less active than eleostrearic acid in tung oil and linolenic acid in linseed oil. Therefore, when used soybean oil for coating fertilizer it had longer drying time than tung oil and linseed oil. This disadvantage could be improved by addition of other drying oils which had better drying properties which will be mentioned in section 4.6.5.

4.5.4 Tung oil and linseed oil coated fertilizer

From previous section (4.5.1), the tung oil was not appropriate to coat fertilizers because film forming was too fast and film forming was not complete. The main goal for this section is to improve the properties of tung oil for coating by addition of other drying oils which had longer drying time. Fertilizer used in this experiment was NPK fertilizer, 10 pph a mixture of tung oil and linseed oil (1:1) was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. The photograph of coated fertilizer is shown in Figure 4.17.

Figure 4.17 Fertilizer coated with 10 pph tung oil and linseed oil (1:1).

From Figure 4.17 it was found that when a mixture of tung oil and linseed oil (1:1) was used to coat fertilizer, product from coating had good characteristics but it did not show the sparkle of film. Although, the sparkle of film was not a factor that influences releasing rate of nutrient but commercial fertilizer should have attractive appearance. These coated fertilizers took 60 minutes for drying which is a suitable time for drying.

As mentioned above, addition of linseed oil to tung oil (1:1) can improve characteristic of tung oil for coating fertilizer but coated fertilizer was not sparkle. Thus a mixture of tung oil and linseed oil (1:1) was not appropriate to be used for fertilizer coating.

4.5.5 Soybean oil and linseed oil coated fertilizer

From section 4.5.3 it was found that soybean oil coated fertilizer gave good characteristic of coated fertilizer but it had longer time for drying. This section will overcome this problem by the addition of linseed oil. Furthermore, this process will reduce cost of drying oil because soybean oil is non expensive. Fertilizer used in this experiment was NPK fertilizer, 10 pph mixture of soybean oil and linseed oil 1:1 was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. The photograph of coated fertilizer is shown in Figure 4.18.

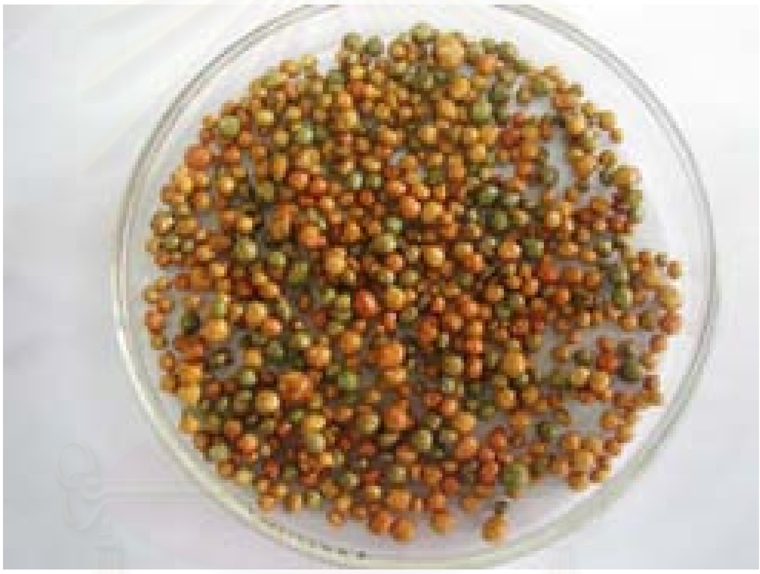


Figure 4.18 Fertilizer coated with 10 pph soybean oil and linseed oil (1:1).

From figure 4.18, it was observed that coated fertilizer gave good characteristics i.e. smooth surface, compact, sparkle, and water resistance. These results were compared with linseed oil coated fertilizer and it was found that there is no difference between the two types of coating materials except drying time. Mixed soybean oil and linseed oil coated fertilizers took 90 minutes for drying. Thus, addition of linseed oil reduced drying time of soybean oil. However it took longer time for drying process. Thus, linseed oil was more appropriate to coat fertilizer than mixed soybean oil and linseed oil (1:1).

Table 4.2 The potassium releasing in gram per litre with various drying oils.

Type of drying oil	1 weeks	2 weeks	3 weeks	4 weeks	5 weeks	6 weeks	7 weeks	8 weeks	9 weeks	10 weeks
Linseed oil	0.6796	0.8441	0.8821	0.9074	1.0360	1.1425	1.3392	1.4448	1.5836	1.6684
Soybean oil	1.2096	1.4652	1.6062	1.6062	1.6062	1.6062	1.6062	1.6062	1.6062	1.6062
Linseed oil+ soybean oil	0.9644	1.2091	1.3531	1.4111	1.5156	1.6210	1.6210	1.6210	1.6210	1.6210

The effect of drying oil type used for coating preparation on the release of potassium after 10 weeks is shown in Figure 4.19. A comparison was made between drying oil coatings, which exhibit the most favorable properties, i.e., those which released the smallest quantity of nutrient.

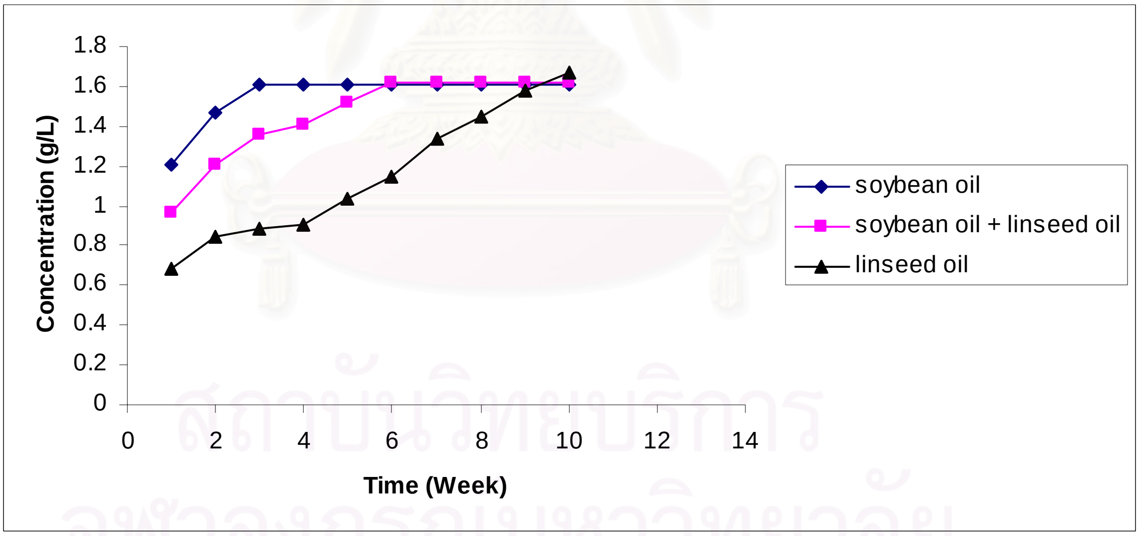


Figure 4.19 The influence of drying oil type used for coating formation on the release of potassium from NPK coated fertilizer.

The experimental results indicated that, the curves of three series showed analogous trends. There is a comparatively rapid release during the first few weeks, then a decreasing rate of release during the following two weeks and finally a constant rate of release at a reasonably high level. The release rate of potassium from the fertilizer coated with soybean oil was the highest. In the case of coating prepared from linseed oil, the release rate of nutrients was much slower. Because the main fatty acid of linseed oil is linolenic acid which has three double bonds so it shows higher cross-linking structure than soybean oil film. Higher cross-linking structures reduce porosity of polymer film thus potassium was released at the slowest rate in linseed oil coated fertilizer.

It is interesting to compare drying coated NPK fertilizer with the commercially available NPK fertilizer (Osmocote). The releasing rate of potassium for linseed oil coated fertilizer (228 micron) and osmocote are shown in Figure 4.20. It was found that releasing rate of linseed oil coated fertilizer had analogous trend with osmocote.

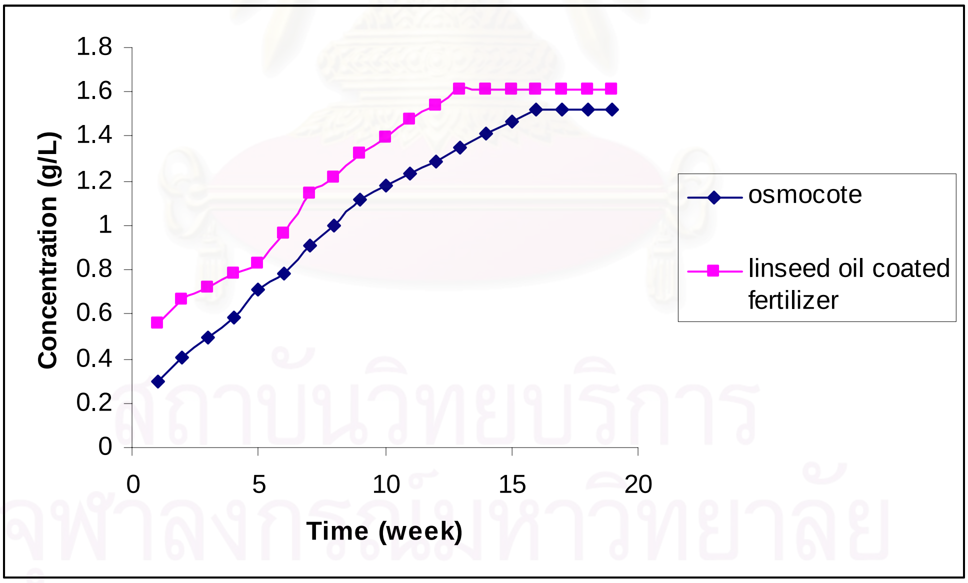


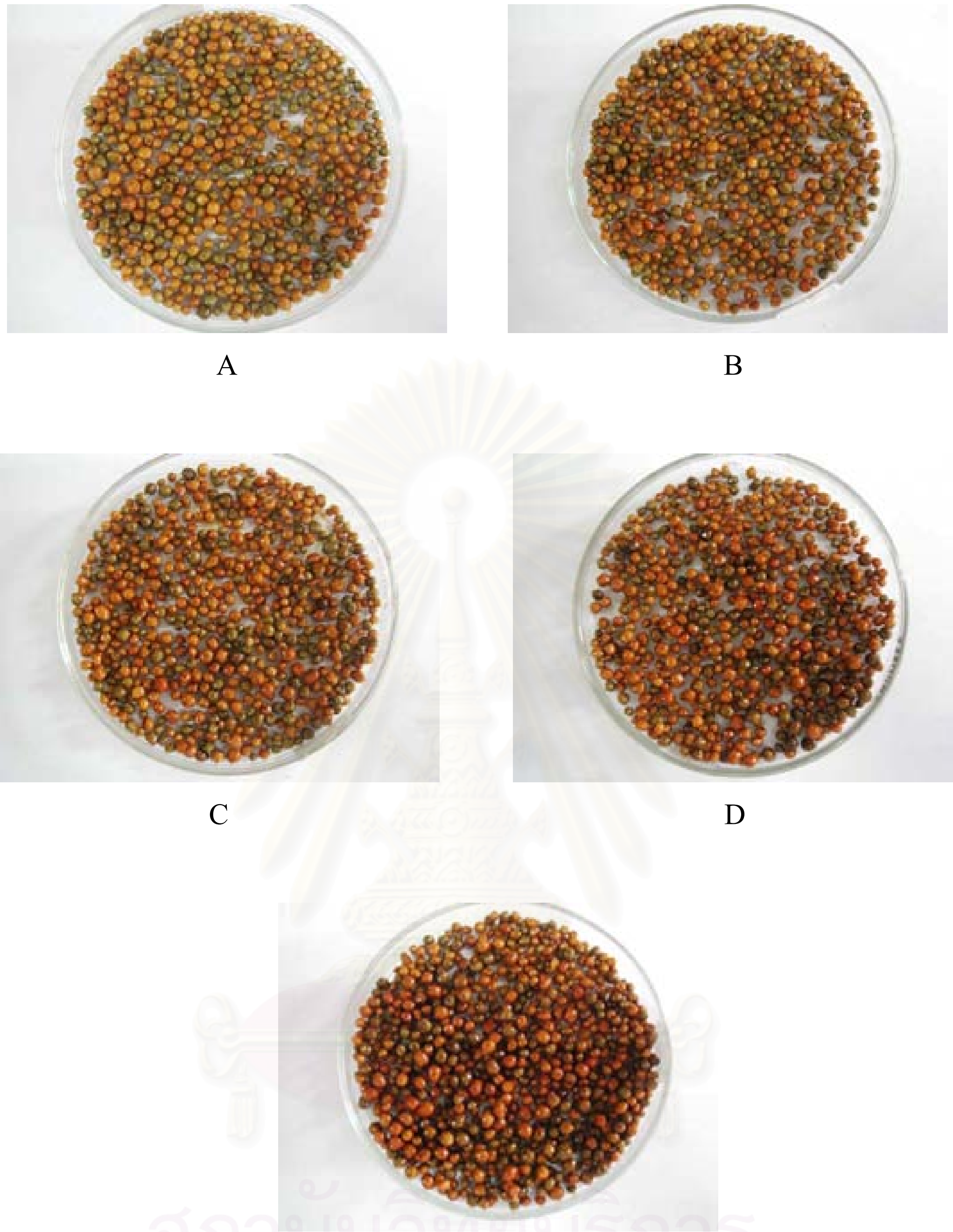
Figure 4.20 Comparison of the releasing rate of linseed oil coated fertilizer (228 micron) and osmocote.

4.6 Effect of number of drying oil layer

Multiple layers of coating on the nutrient particles may be applied to control degree of releasing rate. The releasing rate can be adjusted to any thickness of film desired, by applying more coating layers.

4.6.1 Effect of number of linseed oil layer

From section 4.5.2, it was shown that linseed oil was appropriate for coating fertilizer. Thus in this section, the effect of thickness of linseed oil film to releasing rate was investigated. Fertilizer used in this experiment was NPK fertilizer, 10 pph linseed oil was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. In this experiment, two layers, four layers, six layers, eight layers, and ten layers coated on fertilizer were prepared. Their potassium releasing rates were compared. The photographs of coated fertilizers are shown in Figure 4.21.



A B

C D

E

Figure 4.21 Comparison of number of linseed oil layer.

A. Two layers coated fertilizer. B. Four layers coated fertilizer.

C. Six layers coated fertilizer. D. Eight layers coated fertilizer.

E. Ten layers coated fertilizer.

From Figure 4.21 it was observed that the yellow color of linseed oil film was darker when the number of linseed oil layers were increased. In addition, drying time was decreased when the number of linseed oil layers were increased. Furthermore, product from coating showed good characteristics of coated fertilizer.

The average thickness of fertilizer coated with linseed oil is presented in Table 4.3, the results demonstrate that the thickness of coatings is influenced by number of layer coated.

Table 4.3 The average thickness of linseed oil film on coated NPK fertilizer.

Number of layer coated	Thickness of coating (micron)
2	53±6
4	96±4
6	131±4
8	185±3
10	228±3

The SEM images revealed that for multiplayer there is no border between the first and second layers. Moreover, the subsequent coating repairs any defects of the first coated layer. These results demonstrated that the increase number of layer of coating led to a proportional increase in thickness.

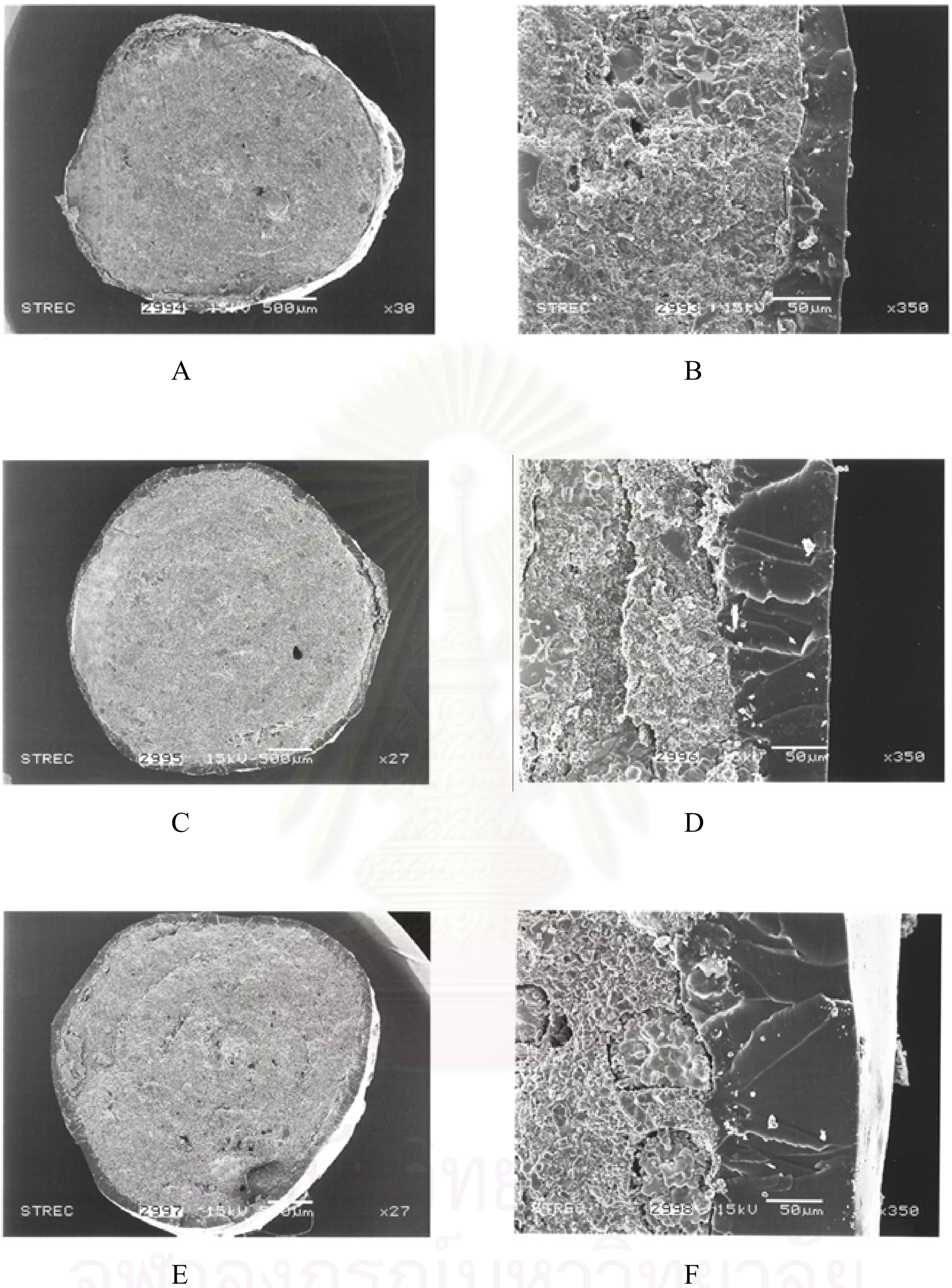
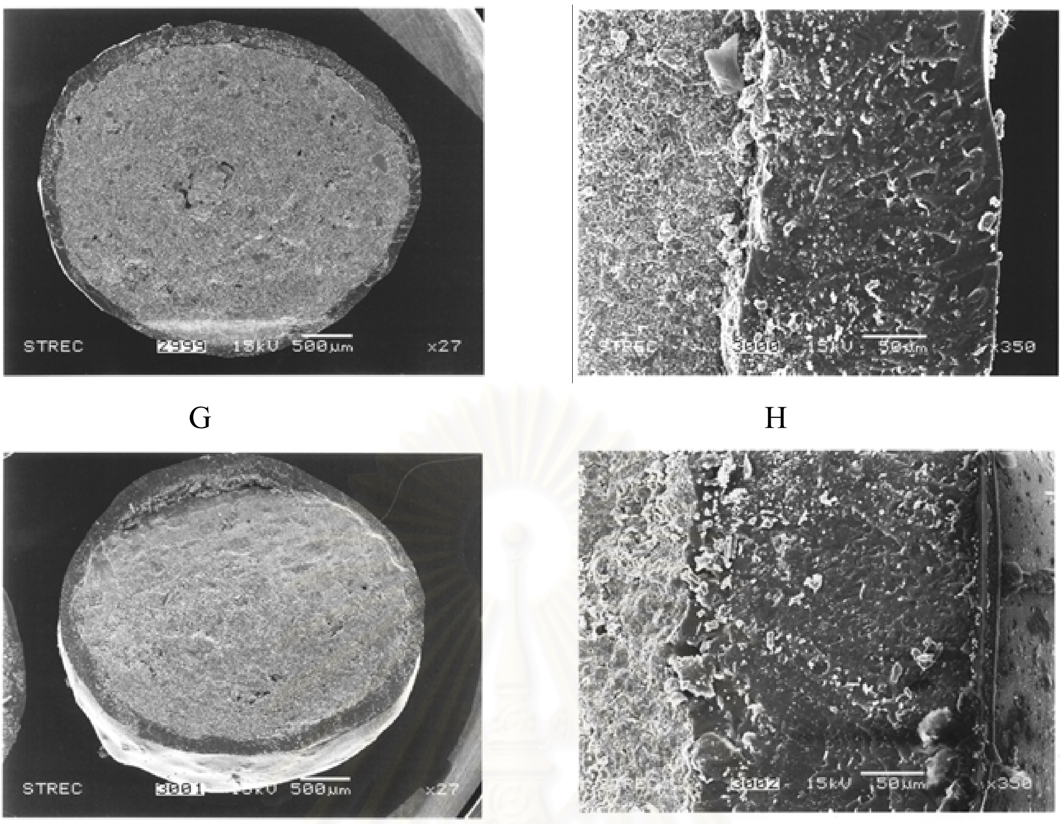


Figure 4.22 SEM of NPK coated fertilizer with 10 pph linseed oil.

A, B. 53 micron

C, D. 96 micron

E, F. 131 micron



G H

I J

Figure 4.23 SEM of NPK coated fertilizer with 10 pph linseed oil.

G, H. 185 micron

I, J. 228 micron

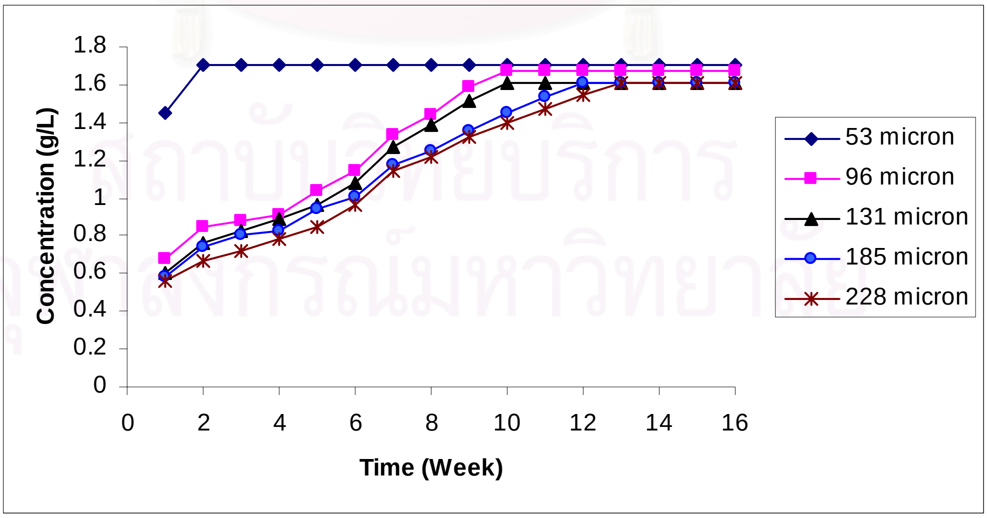


Figure 4.24 Comparison of release rate of potassium between different thickness of linseed oil coated fertilizer.

The release rate is a function of the coating structure, and it can be controlled by the thickness and porosity of the coating. The thickness of the film depends upon the desired degree of water protection. The thicker of film, the more likely that water penetration would be slowed down.

As can be seen in Figure 4.24, the release rate was estimated from the amount of potassium (in g/L) released with time in relation to the initial concentration of this component in the fertilizer. It was shown that the release rate of nutrients from coated granules decreased when number of linseed oil layer in the coating fertilizer was increased. This effect could be described that the increase number of linseed oil layer increased the thickness of linseed oil film on the granule surface, which resulted in less chance of water to penetrate into the fertilizer granular. The ingredients from two-layers linseed oil coated fertilizer were released most rapidly. Thus 84.81 % of potassium was released after 1 week of test. It was influenced by the high porosity of the coating and the thin skin layer. The ingredients from ten-layer coated fertilizer were released more slowly.

The ten-layers coated fertilizer (228 micron) is possible to control the releasing rate of fertilizer so that the nutrient release starts preferably after 7 days and released completely in 91 days.

4.6.2 Effect of number of soybean oil layer

From section 4.5.3, product from coating fertilizer with soybean oil gave good characteristics of coated fertilizer although it took longer time to dry. Thus this section, the effect of thickness of soybean oil film to releasing rate was investigated. Fertilizer used in this experiment was NPK fertilizer, 10 pph soybean oil was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. In this experiment, two layers, four layers, six layers, and eight layers coated on fertilizer were prepared. The photographs of coated fertilizer are shown in Figure 4.25.

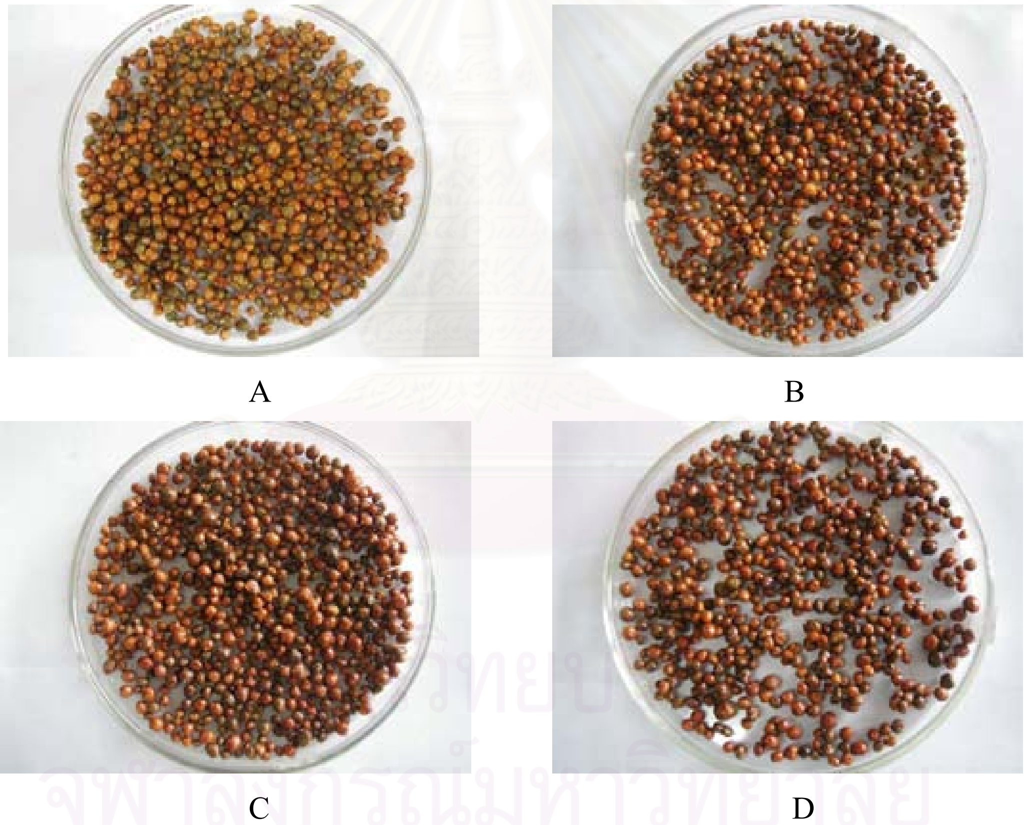


Figure 4.25 Comparison of number of soybean oil layer.

A. Two layers coated fertilizer.

B. Four layers coated fertilizer.

C. Six layers coated fertilizer.

D. Eight layers coated fertilizer

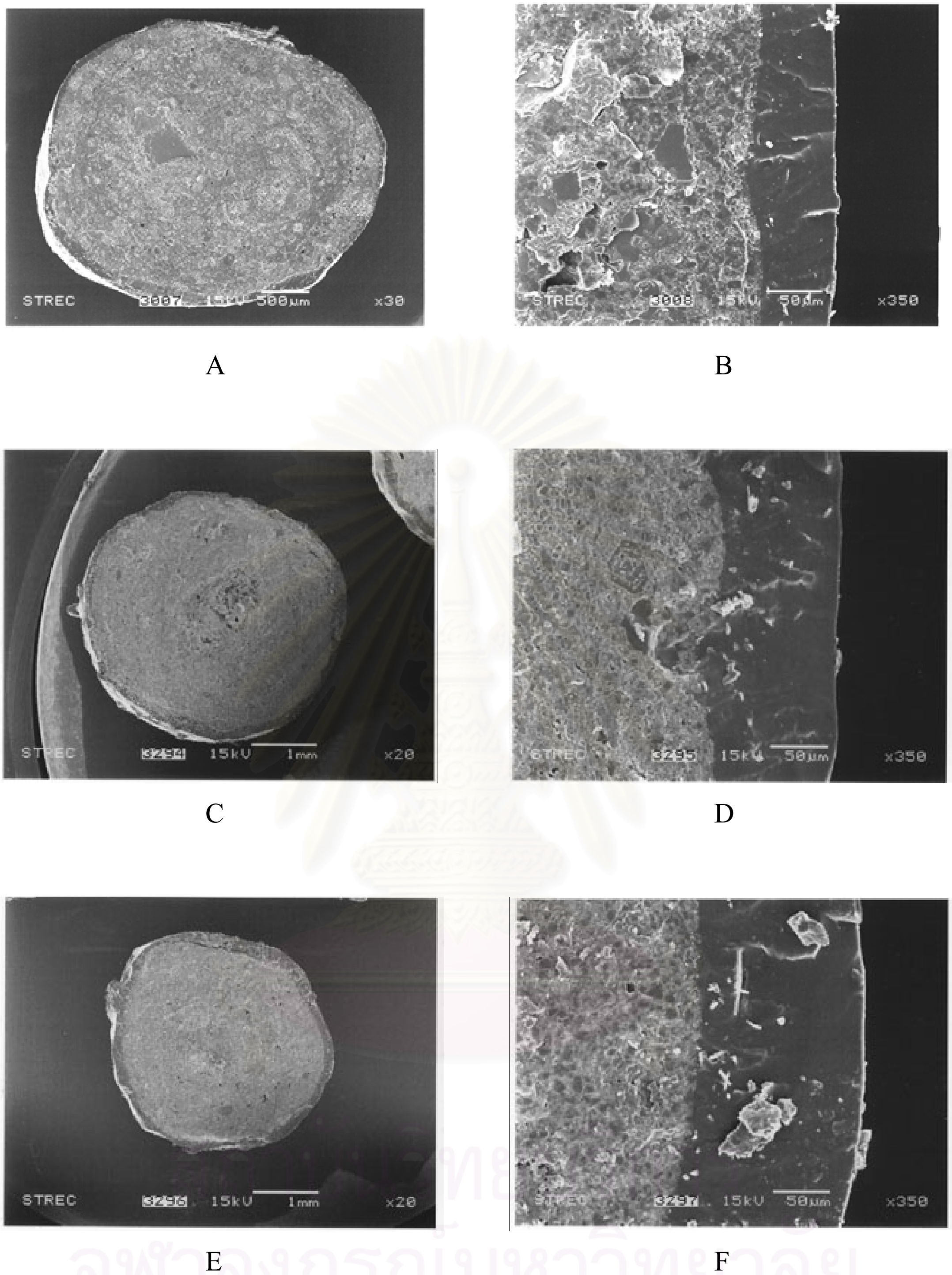
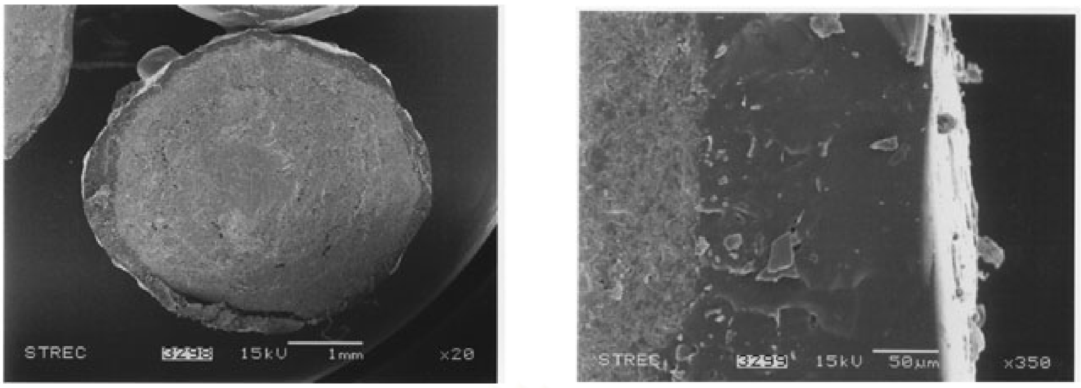


Figure 4.26 SEM of NPK coated fertilizer with 10 pph soybean oil.

A, B. Two layers coated fertilizer.

C, D. Four layers coated fertilizer.

E, F. Six layers coated fertilizer.



G H

Figure 4.27 SEM of NPK coated fertilizer with 10 pph soybean oil.

G, H. Eight layers coated fertilizer.

Table 4.4 The average thickness of soybean oil film on coated NPK fertilizer.

Number of layer coated	Thickness of coating (micron)
2	64±3
4	106±5
6	143±3
8	197±5

From Table 4.4 it was observed that the thickness of soybean oil film increased when the number of soybean oil layer was increased. The thickness of soybean oil was similar to those coated with linseed oil.

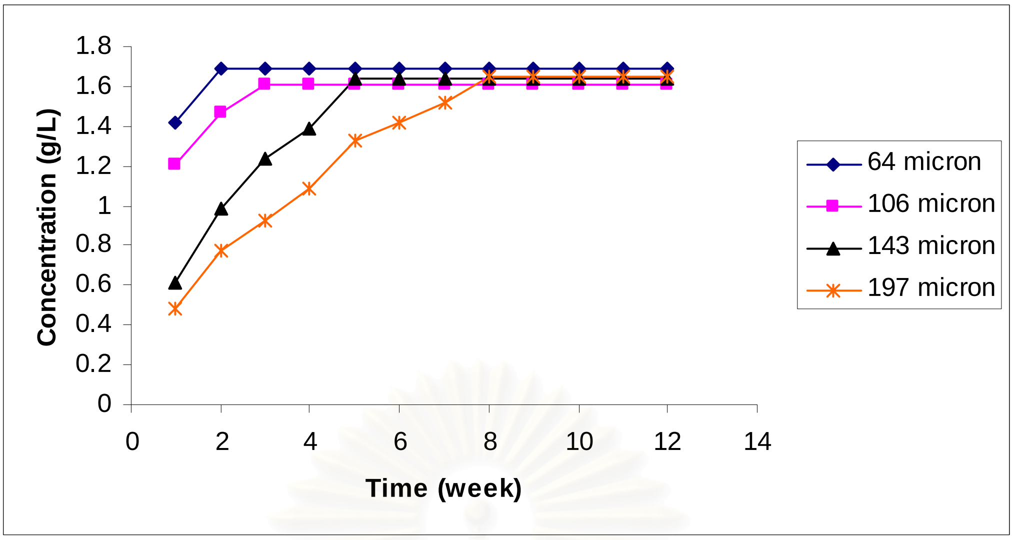


Figure 4.28 Comparison of release rate of potassium release between different thickness of soybean oil layer.

From Figure 4.28, it was observed that the releasing rate of potassium is analogous trend with linseed oil coated fertilizer. The most rapid release was 64 micron thickness film in which potassium was released completely within two weeks. The 197 micron coated-fertilizer gave the longest period of potassium release.

4.6.3 Effect of number layer of a mixture of linseed oil and soybean oil coated fertilizer.

In this experiment, a mixture of linseed oil and soybean oil was used as coating material and the releasing rate from different film thickness of coated fertilizer was compared. Fertilizer used in this experiment was NPK fertilizer, 10 pph mixture of linseed oil and soybean oil was used as coating material by pan coating method and 1 % cobalt naphthenate as catalyst. The photographs of product are shown in Figure 4.29.

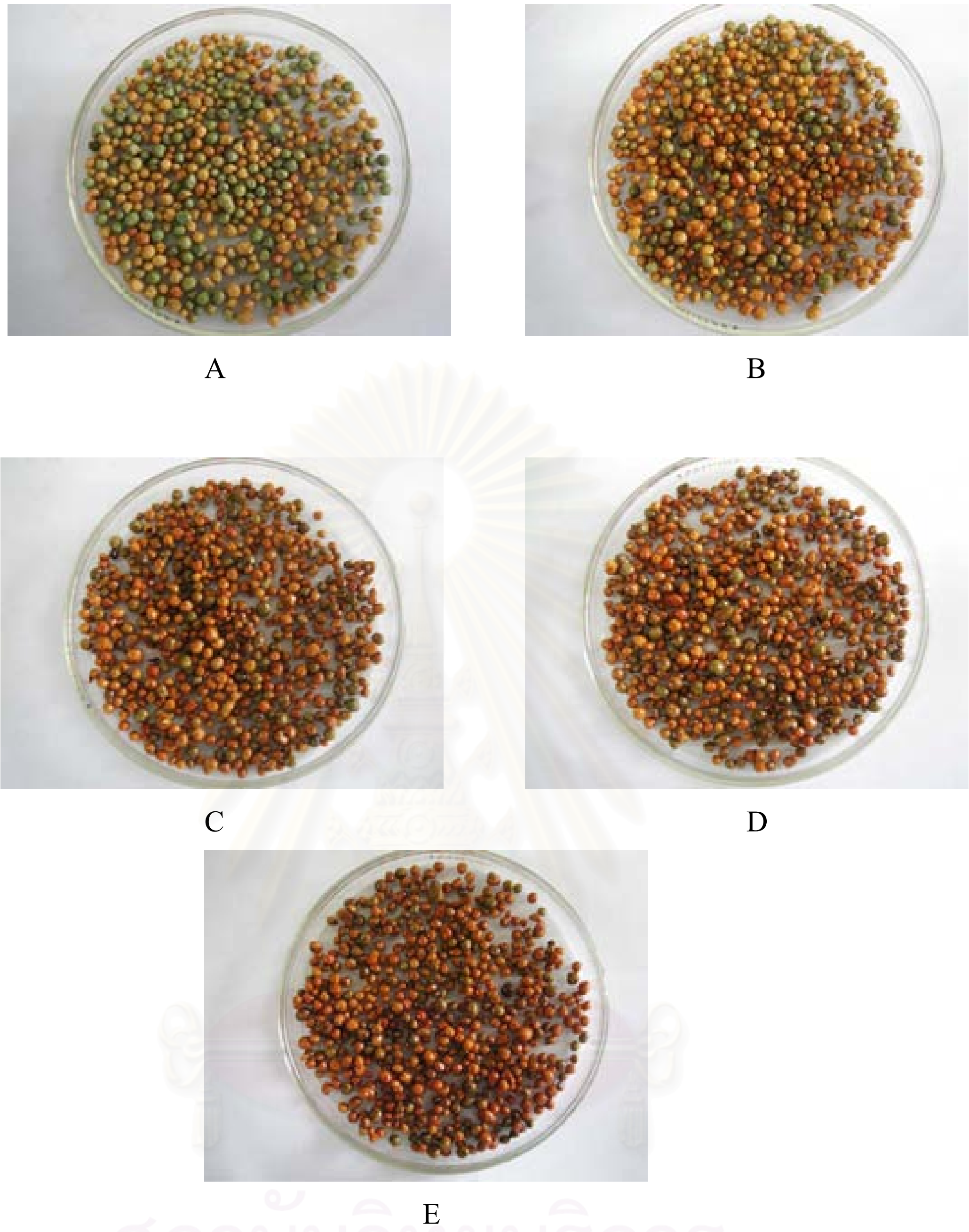


Figure 4.29 Comparison of number layer of mixture of linseed oil and soybean oil.

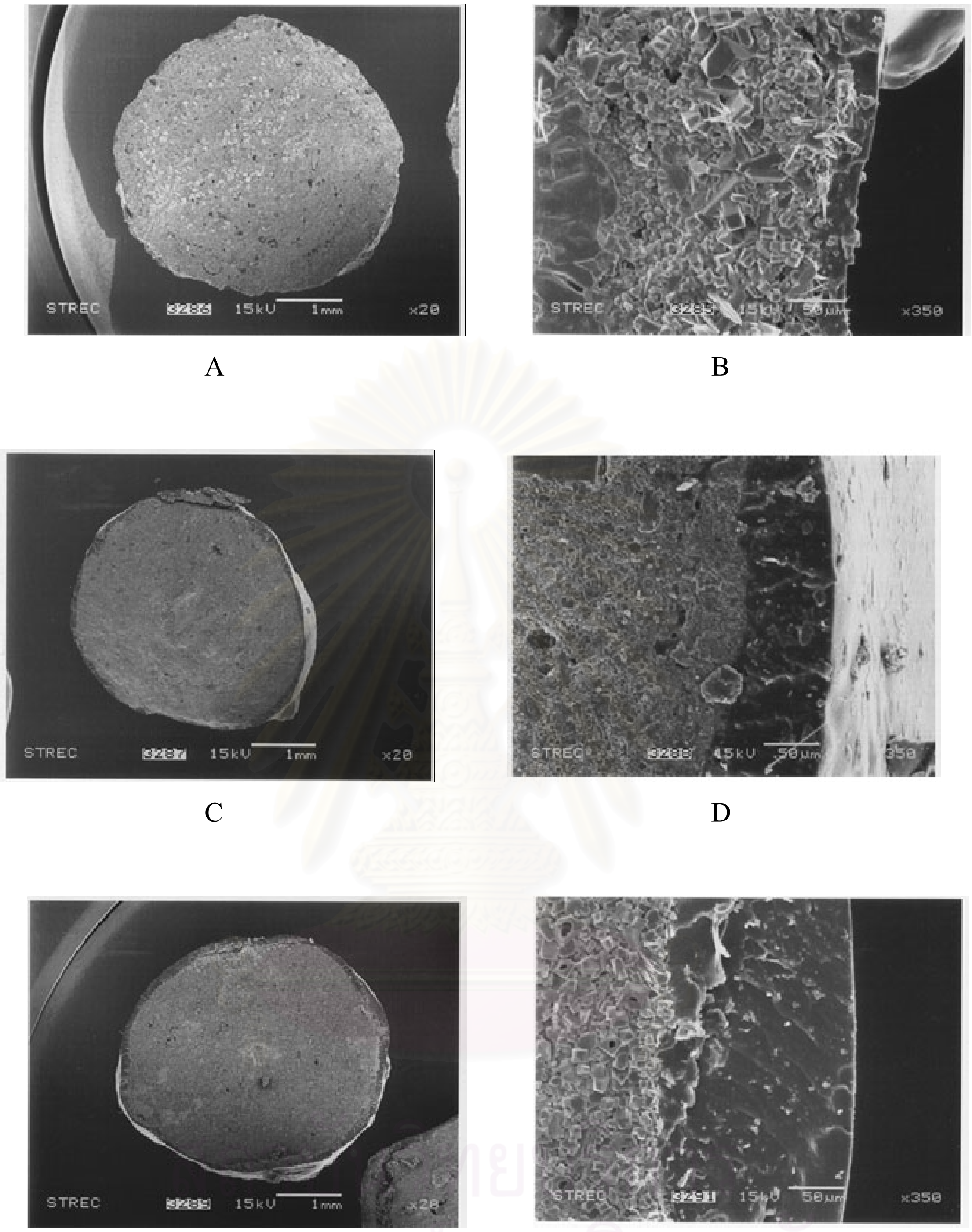
A. One layers coated fertilizer.

B. Two layers coated fertilizer.

C. Four layers coated fertilizer.

D. Six layers coated fertilizer.

E. Eight layers coated fertilizer.



A B

C D

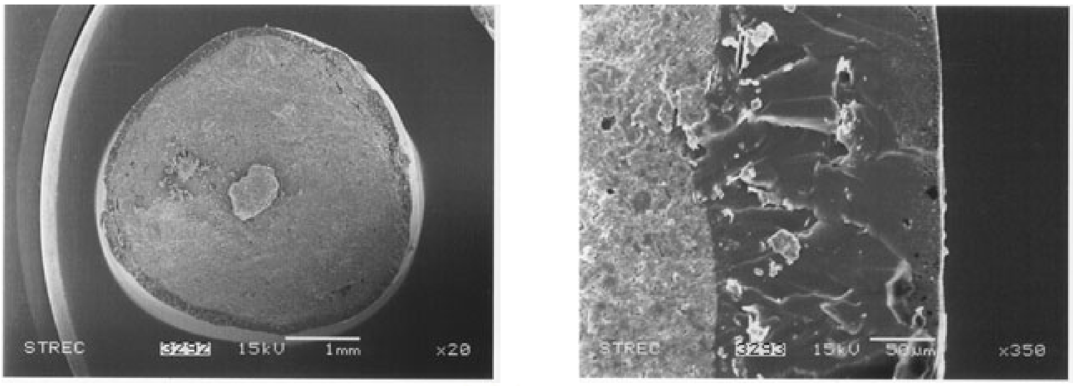
E F

Figure 4.30 SEM of coated fertilizer with 10 pph linseed Oil: soybean Oil (1:1).

A, B. Two layers coated fertilizer.

C, D. Four layers coated fertilizer.

E, F. Six layers coated fertilizer.



G H

Figure 4.31 SEM of coated fertilizer with 10 pph linseed Oil: soybean Oil (1:1).

G, H. Eight layers coated fertilizer.

Table 4.5 The average thickness of a mixture of linseed oil and soybean oil film on coated NPK fertilizer.

Number of layer coated	Thickness of coating (micron)
2	53±5
4	93±6
6	164±6
8	185±6

From Figures 4.30 and 4.31 it was observed that thickness of coating is influenced by the number of coating layer.

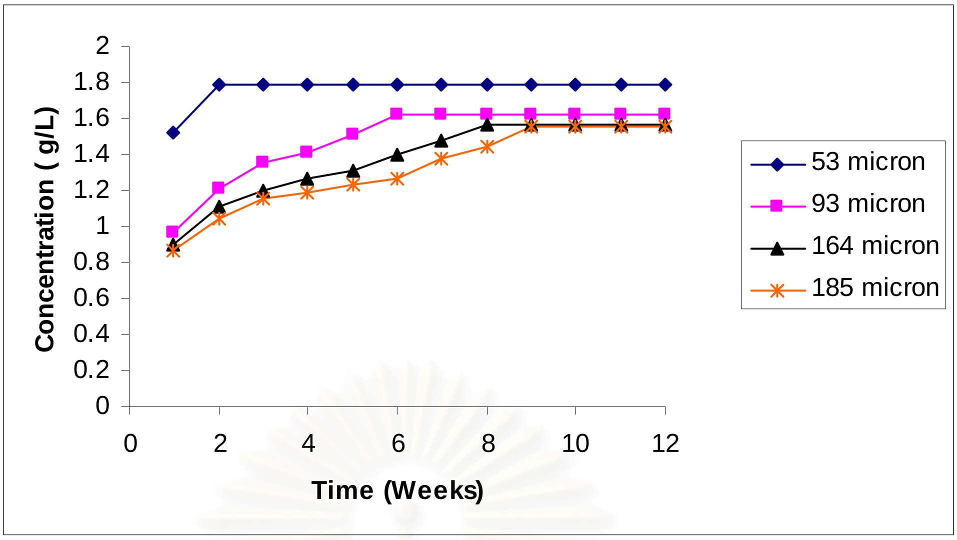


Figure 4.32 Comparison of release rate of potassium between different thickness of film on fertilizer coated with a mixture of linseed oil and soybean oil.

Figure 4.32 shows that when increase the thickness of coating, releasing rate of potassium was decreased.

4.7 Coated urea fertilizer

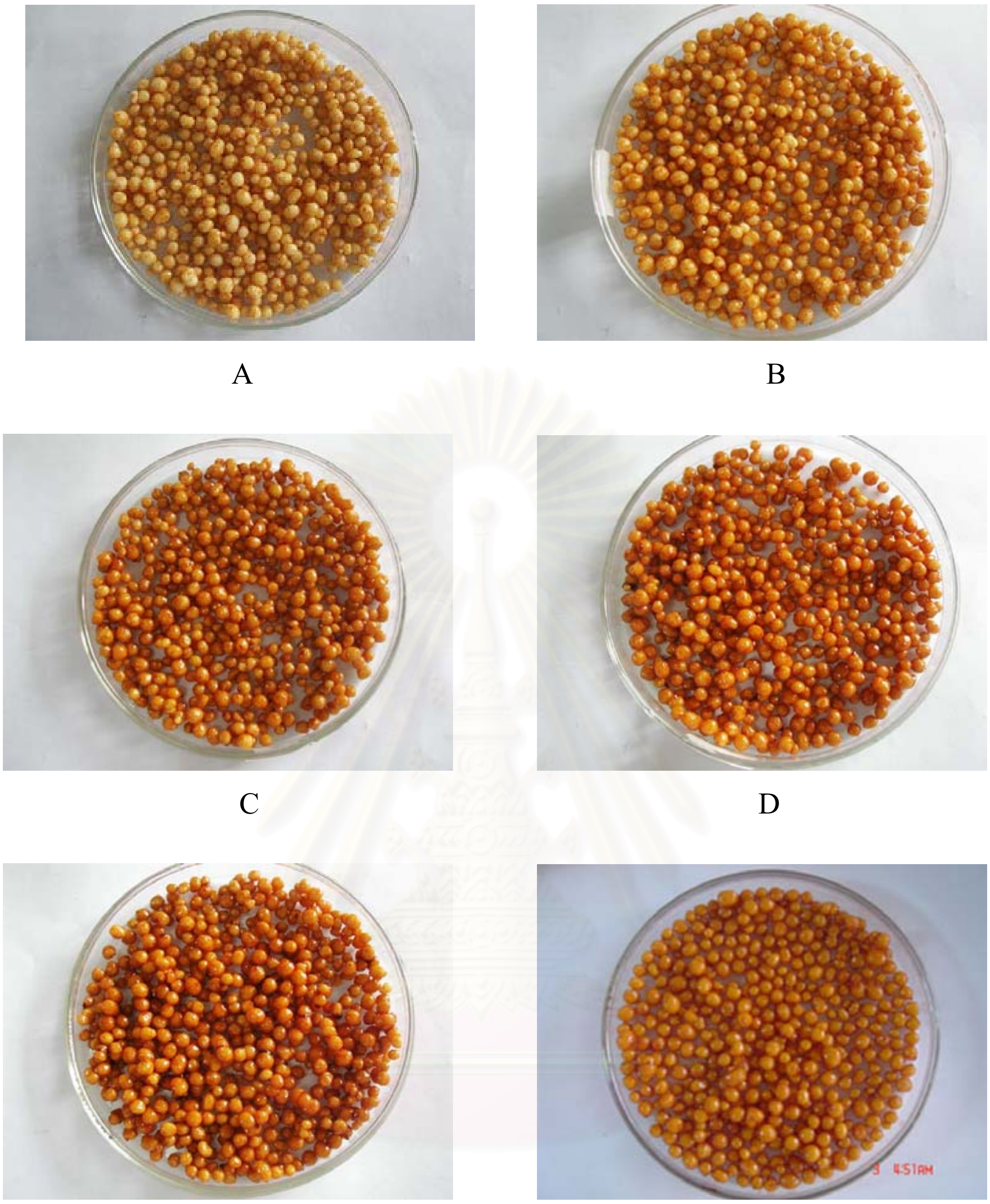
Urea fertilizer is considered one of the world's leading nitrogen fertilizers due to its high nitrogen content (46%), low cost, and commercial availability. It has, however, the major limitation of easy dissolution in water and rapid hydrolysis. This causes high nitrogen loss through ammonium volatilization. Coated urea fertilizer was used to control nitrogen loss. In this experiment, urea coated fertilizer was prepared by coating urea fertilizer with 10 pph linseed oil by pan coating method and 1% cobalt naphthenate as catalyst.

Figure 4.33 Urea fertilizer coated with 10 pph linseed oil.

Figure 4.33 shows photograph of urea coated fertilizer by pan coating method. It was observed that urea fertilizer before coating by linseed oil had white color and after coating it had yellow color. Coated urea fertilizer had good characteristic of coating i.e. smooth, compact, sparkle, complete film- forming, and water resistance.

4.8 Effect of number linseed oil layer on urea fertilizer

The coating film acts as a barrier for mass transfer and hence reduces the rate of water diffusion into the granules and the diffusion of ingredients outside the granule. Thus the thickness of coating influenced releasing rate of urea. In this experiment, the thickness of film was compared. Urea fertilizer was used as fertilizer in this experiment, 10 pph linseed oil was used as coating material by pan coating method, and 1% cobalt naphthenate as catalyst. The photographs of linseed oil coated urea fertilizer are shown in Figures 4.34 and 4.35.



A B C D E F

Figure 4.34 Comparison of the number of linseed oil layer on coated urea fertilizer.

A. One layer coated Fertilizer.

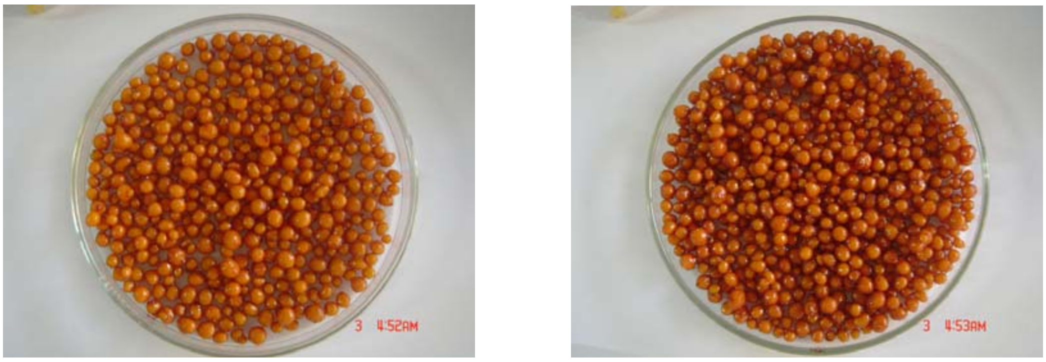
B. Two layers coated Fertilizer.

C. Four layers coated Fertilizer.

D. Six layers coated Fertilizer.

E. Eight layers coated Fertilizer.

F. Ten layers coated Fertilizer.

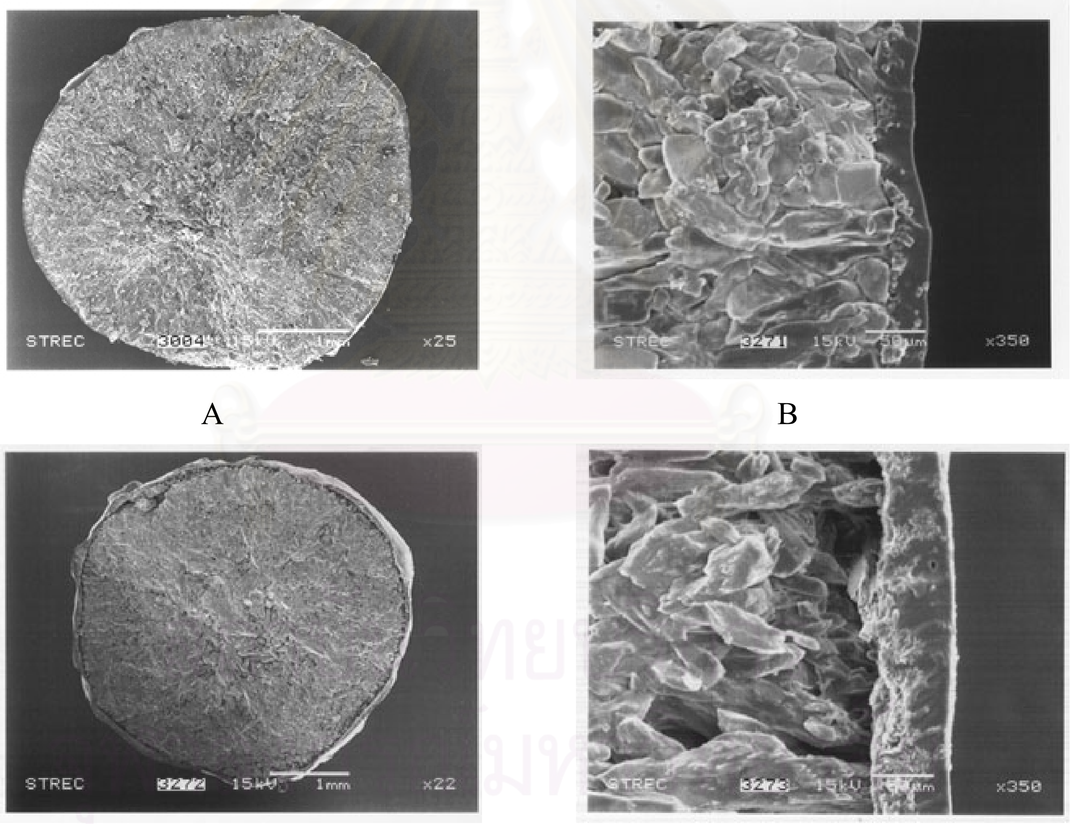


G H

Figure 4.35 Comparison of the number of linseed oil layer on coated urea fertilizer.

G. Twelve layers coated Fertilizer.

H. Fourteen layers coated Fertilizer.



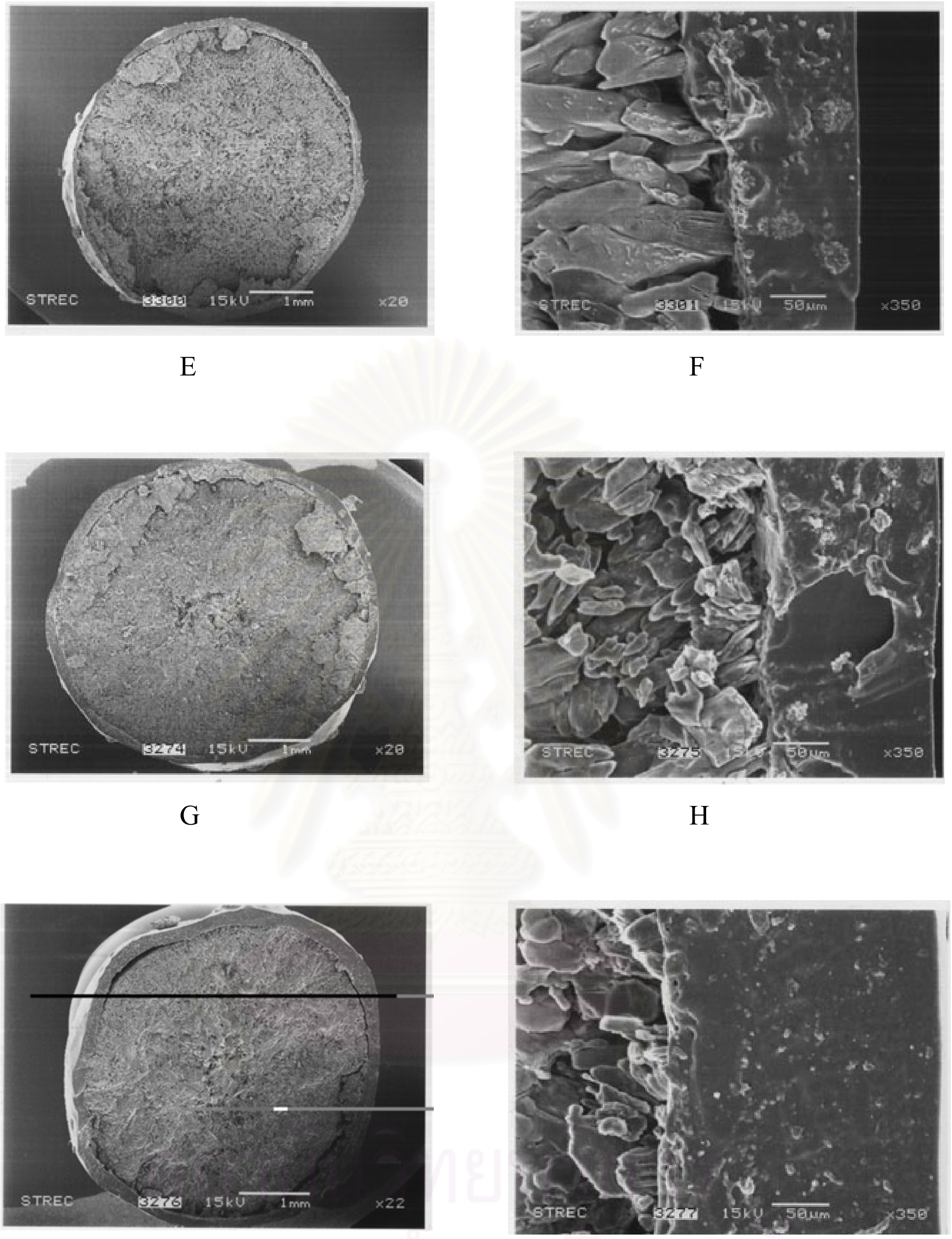
A B

C D

Figure 4.36 SEM of linseed oil coated urea fertilizer.

A, B. One layer coated fertilizer.

C, D. Two layers coated fertilizer.



E F

G H

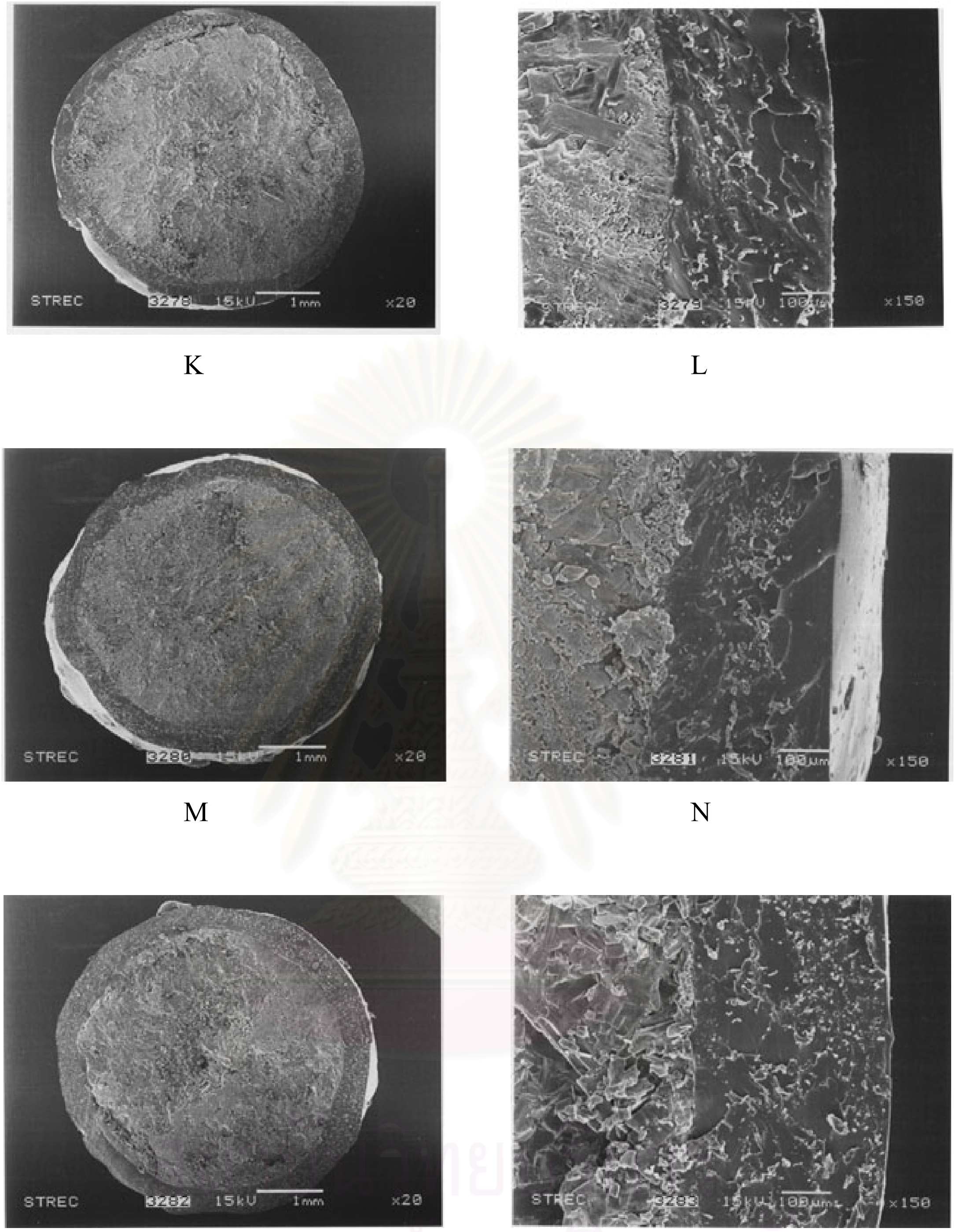
I J

Figure 4.37 SEM of linseed oil coated urea fertilizer

E, F. Four layers coated fertilizer.

G, H. Six layers coated fertilizer.

I, J. Eight layers coated fertilizer.



K L

M N

O P

Figure 4.38 SEM of linseed oil coated urea fertilizer.

G, H. Six layers coated fertilizer. I, J. Eight layers coated fertilizer.

K, L. Ten layers coated fertilizer. M, N. Twelve layers coated fertilizer.

O, P. Fourteen layers coated fertilizer.

From Figures 4.34 and 4.35 it was observed that the yellow color of linseed oil film was intense when the number of linseed oil layers were increased. The microscopic structures of the fertilizer coatings, obtained by using scanning electron microscopy, are shown in Figures 4.36, 4.37, and 4.38. As can be observed, the thickness is increased gradually when the number layer of coating was increased. Characteristic of coated fertilizer is smooth, dry film, and complete film forming. Coated urea fertilizer has advantages for controlled urea release.

Table 4.6 The average thickness of linseed oil film on coated urea fertilizer.

Number of layer coated	Thickness of coating (micron)
1	30±1
2	55±4
4	114±1
6	147±1
8	224±3
10	269±2
12	306±2
14	378±7

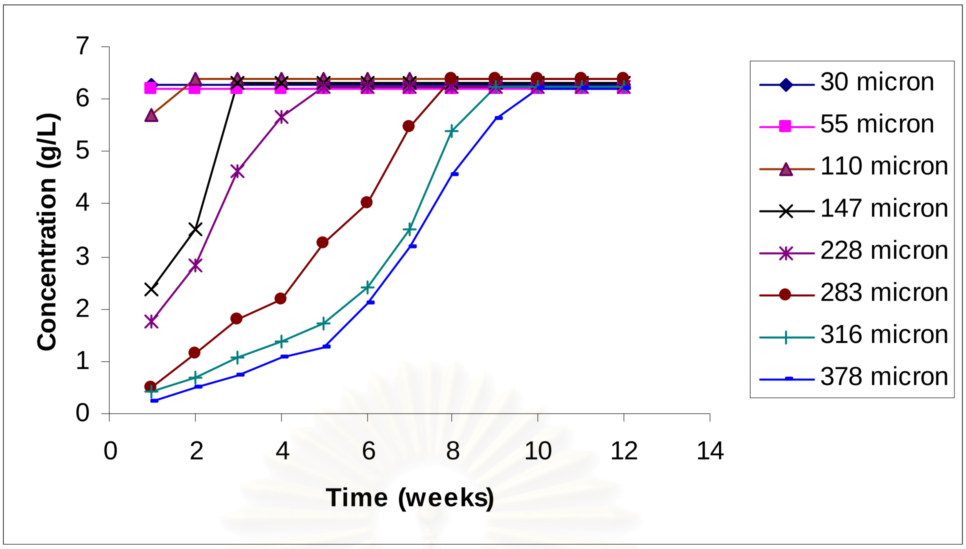


Figure 4.39 Comparison of releasing rate of urea between different thickness of linseed oil coated urea fertilizer.

The releasing time for some individual pellets having different coating thickness are shown in Figure 4.39. For urea particle having a coating thickness of 30 micron, immediate and relatively rapid release of urea occurs, while for a coating thickness of 378 micron, there is an extended period of time on release rate. A high rate of urea release in the case of these fertilizers suggests the presence of large pinholes and imperfections in the coating film. On the other hand, the increasing of the film thickness gave lower porosity of the coating and denser skin layer decreased the rate of urea release. It can be concluded that when the thickness of coating was increased, releasing rate of urea was decreased.

4.9 Effect of temperature on releasing rate

The influence of temperature on the releasing rate of urea through the drying oil coating is present in Figure 4.40. The test was performed using 114 micron coated urea fertilizer. The temperatures were varied from 20, 25, 30, 35, and 40^{0}C. The results indicated that the temperature has a significant influence on the release of urea from coated urea. The dependence of the dissolution rate of the encapsulated material on the temperature is mainly due to the increase solubility of base fertilizer and a higher diffusion rate as the temperature increases. When the test was finished (after 240 minutes) 0.0808 g/L of urea at 20^{0}C were released. In the case of the test performed at 40^{0}C, after 240 min 0.3329 g/L of urea was released.

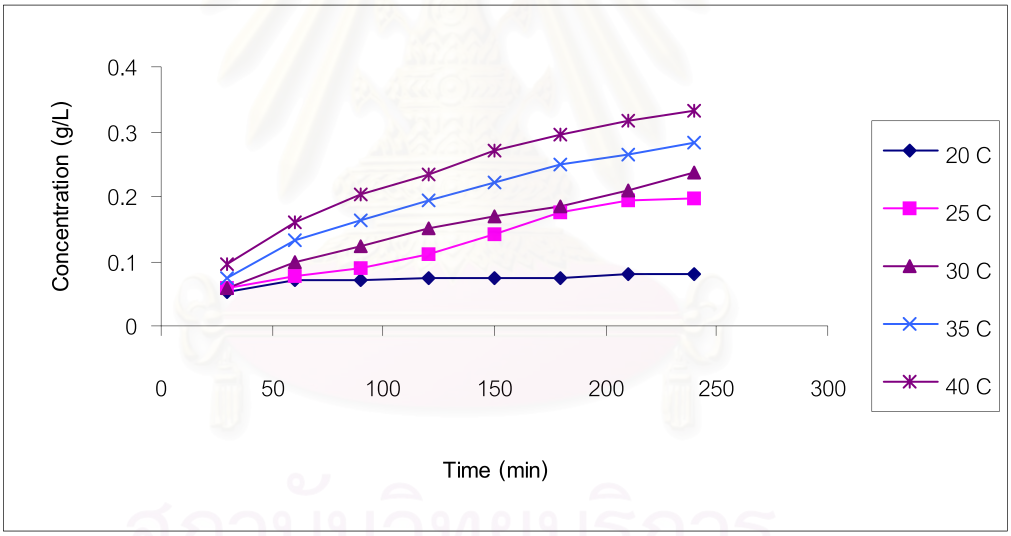


Figure 4.40 Influence of temperature on the releasing rate of urea using 114 micron coated urea fertilizer.

4.10 Effect of pH on releasing rate

Acid–base condition is one of the factor influencing releasing rate of fertilizer. In this experiment, the test was performed using 114 micron coated urea fertilizer. The pHs were 5, 6, 7, 8, 9, and 10. Samples were collected at 60, 120, 280, and 240 minutes. The influence of pH on the releasing rate of urea through the drying oil coating is present in Figure 4.35.

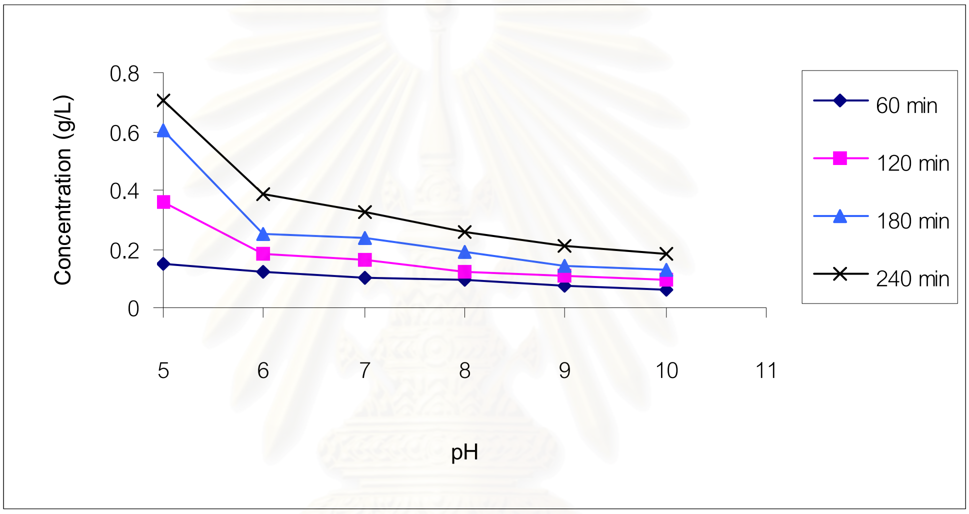


Figure 4.41 Influence of pH on the releasing rate of urea using 114 micron coated urea fertilizer.

From Figure 4.41, the concentration of urea that dissolves in water was plotted as a function of pH. It was observed that at low pH, releasing rate of urea is higher than those at high pH. It can be described that when water penetrated into core urea particle, it created osmotic pressure to release nutrient to the outside of layer. Under acidic condition, the coating film is more effectively hydrolyzed than that of the basic condition. Thus, it created more porosity for water to penetrate into core urea particle.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusion can be drawn from this study:

1. Comparison of the coating process shows that the pan coating was more appropriate for coating fertilizer than fluidized bed. The coated fertilizers had good characteristics, i.e. smoothness, dry film, good surface hardness. Furthermore, this method of fertilizer coating is inexpensive to produce economical controlled release fertilizers and having all of the characteristic and features desired by the industry.

2. Investigation on the effect of amount of drying oil (linseed oil) indicated that 10 part of linseed oil per hundred part of fertilizer was suitable for pan coating method.

3. Investigation on the amount of catalyst for coating process indicated that 1.0 percent cobalt naphthenate is appropriate to be used in this coating process.

4. The release rate of coated fertilizer with linseed oil was slower than those of other drying oils. Tung oil is not suitable for coating because it is very fast drying thus film forming is incomplete and difficult to control. Thus, linseed oil is more appropriate for use as coating material.

5. The increase of the film thickness on coating causes a decrease of the release rate of microelements, due to a denser structure. The urea coated fertilizer having film thickness at 378 micron can be released completely in 70 days and NPK coated fertilizer 228 micron can be released completely in 91 days.

6. The increase of temperature caused an increase in releasing rate of urea.

7. The increase of pH caused decrease releasing rate of urea.

5.2 Recommendations for future work

1. Preparation of controlled-release fertilizer should be performed by other method such as phase inversion technique.

2. The drying oil coated fertilizers should be tested in the field.

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APPENDICES

APPENDIX A

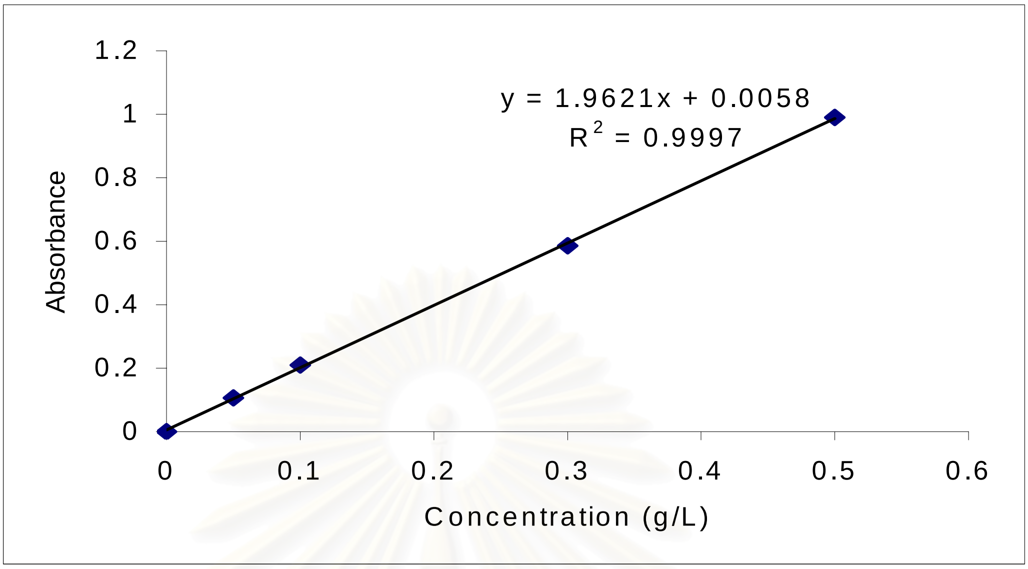

Figure A1. Calibration curve of standard potassium solution.

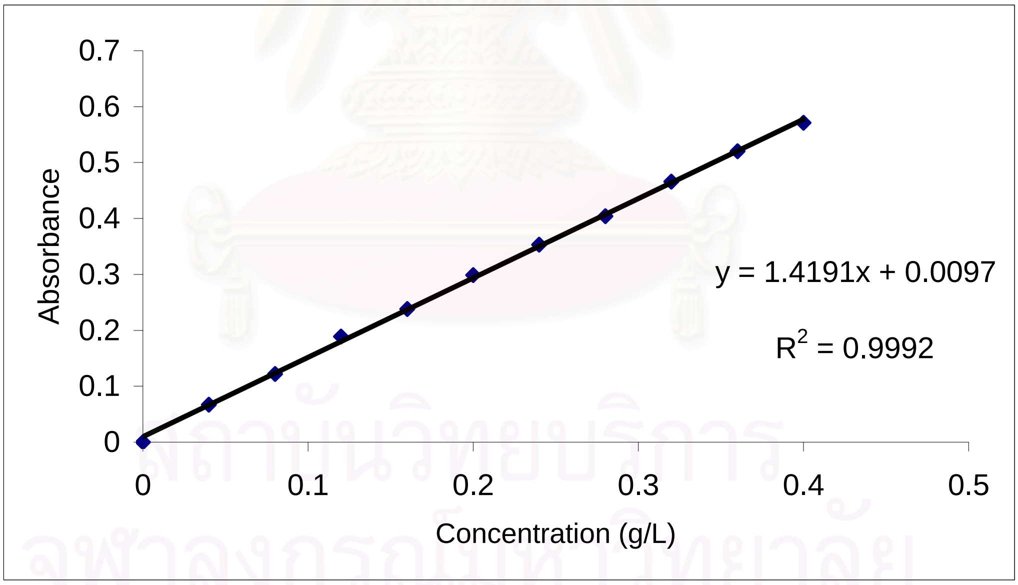

Figure A2. Calibration curve of standard urea solution.

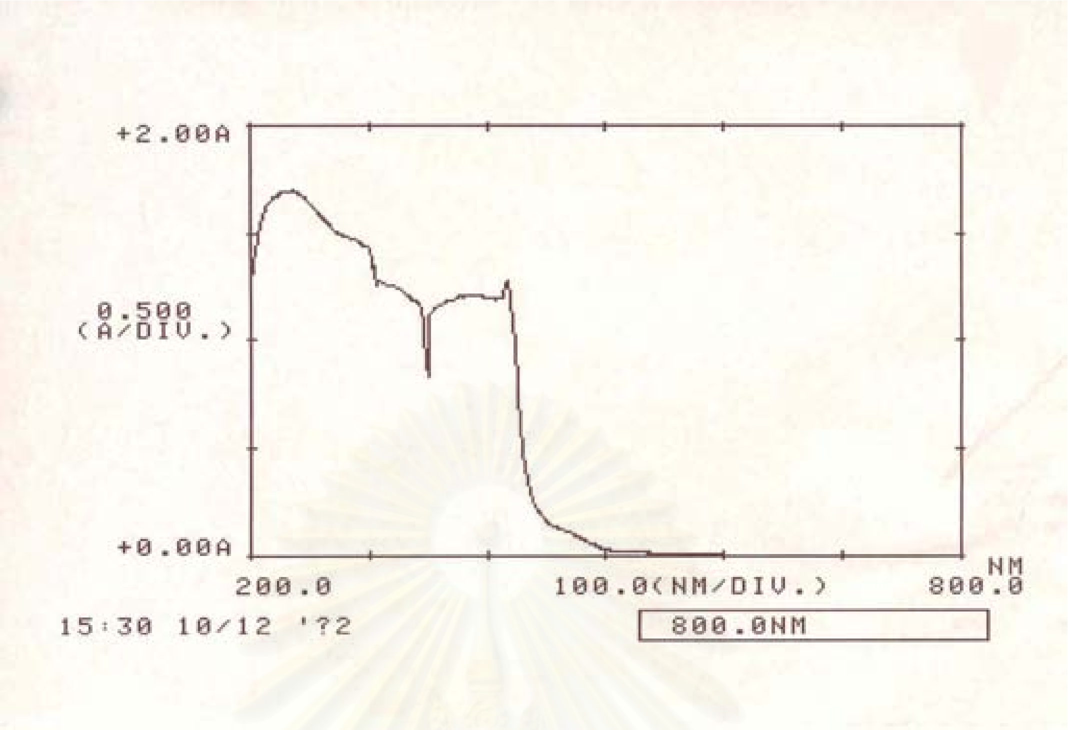

Figure A3. UV-Visible spectrum of *p*-dimethylaminobenzaldehyde.

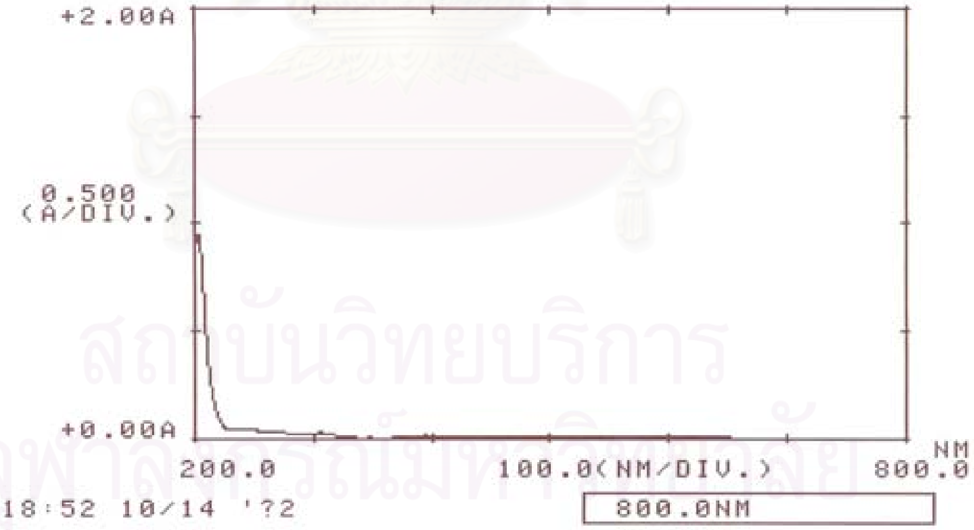

Figure A4. UV-Visible spectrum of standard urea solution.

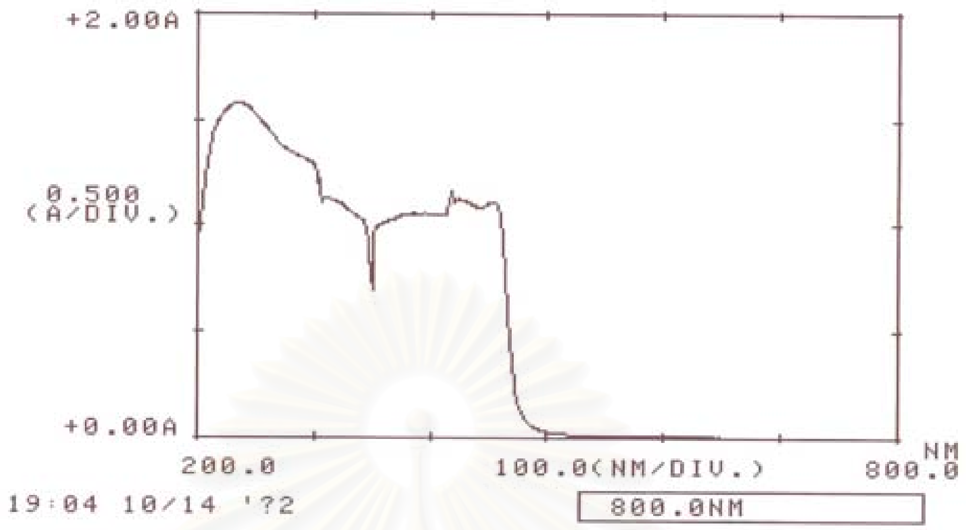

Figure A5. UV-Visible spectrum of urea solution and *p*-dimethylaminobenzaldehyde.

APPENDIX B

Table B1. Calibration curve of standard potassium solution for determined concentration of potassium. (Atomic Absorption Spectrophotometry)

Amount of 1 g/L Potassium Solution (ml)	Concentration (g/L)	Absorbance
0	0	0.000
5	50	0.107
10	100	0.210
20	300	0.586
50	500	0.990

Table B2. Calibration curve of standard urea solution for determined concentration of urea. (UV-VIS Spectrophotometry)

Amount of 5 g/L Urea Solution (ml)	Concentration (g/L)	Absorbance
0	0.00	0.000
2	0.04	0.067
4	0.08	0.122
6	0.12	0.189
8	0.16	0.238
10	0.20	0.299
12	0.24	0.353
14	0.28	0.404

Table B3. Calibration curve of standard urea solution for determined concentration of urea. (UV-VIS Spectrophotometry)

Amount of 5 g/L Urea Solution (ml)	Concentration (g/L)	Absorbance
16	0.32	0.466
18	0.36	0.520
20	0.40	0.582
22	0.44	0.648
24	0.48	0.699
26	0.52	0.748

Table B4. Solubility of uncoated NPK fertilizer.

Time (min)	Absorbance	Potassium release (g/L)	Potassium concentration (g/L)
5	0.276	0.5660	0.5660
10	0.284	0.1111	0.6771
20	0.349	0.0729	0.8508
40	0.507	0.3426	1.1934
60	0.656	0.3714	1.5648
80	0.709	0.1104	1.6752
120	0.709	0.0000	1.6752
160	0.709	0.0000	1.6752
180	0.709	0.0000	1.6752

Table B5. Solubility of uncoated urea fertilizer.

Time (min)	Absorbance	Urea Release (g/L)	Urea Concentration (g/L)
1	0.471	4.5686	4.5686
2	0.517	1.2025	5.7711
3	0.565	0.6598	6.4309
4	0.565	0.0000	6.4309
5	0.565	0.0000	6.4309
10	0.565	0.0000	6.4309
30	0.565	0.0000	6.4309
60	0.565	0.0000	6.4309
90	0.565	0.0000	6.4309
120	0.565	0.0000	6.4309
150	0.565	0.0000	6.4309
180	0.565	0.0000	6.4309

Table B6. The average thickness of coating film on NPK fertilizer coated with linseed oil.

Number of layer	Thickness of linseed oil film (micron)			Average (micron)	S.D.
	1	2	3		
Two layers	46	53	59	53	6.24
Four layers	96	100	91	96	4.43
Six layers	136	128	129	131	4.62
Eight layers	181	187	186	185	3.08
Ten layer	228	231	225	228	3.12

Table B7. The average thickness of coating film on NPK fertilizer coated with soybean oil.

Number of layer	Thickness of soybean oil film (micron)			Average (micron)	S.D.
	1	2	3		
Two layers	62	68	62	64	3.24
Four layers	103	103	112	106	5.41
Six layers	140	143	146	143	3.12
Eight layers	191	198	203	197	5.95

Table B8. The average thickness of coating film on NPK fertilizer coated with a mixture of linseed oil and soybean oil (1:1).

Number of layer	Thickness of linseed oil+ soybean oil film (micron)			Average (micron)	S.D.
	1	2	3		
Two layers	50	50	59	53	5.26
Four layers	87	90	100	93	6.51
Six layers	162	171	159	164	6.50
Eight layers	190	187	178	185	6.50

Table B9. The average thickness of linseed oil coated urea fertilizer.

Number of layer	Thickness of linseed oil film (micron)			Average (micron)	S.D.
	1	2	3		
One layers	31	28	31	30	1.80
Two layers	50	56	59	55	4.77
Four layers	114	115	111	114	1.97
Six layers	146	150	146	147	1.64
Eight layers	224	228	221	224	3.14
Ten layers	268	267	271	269	2.07
Twelve layers	307	304	308	306	2.18
Fourteen layers	378	371	385	378	7.14

Table B10. Releasing rate of coated NPK fertilizer with linseed oil (14 weeks).

Thickness(µm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
1Week			
53	0.694	1.4460	1.4460
96	0.330	0.6796	0.6796
131	0.296	0.6084	0.6084
185	0.283	0.5816	0.5816
228	0.273	0.5604	0.5604
2 Week			
53	0.701	0.2590	1.7050
96	0.354	0.1645	0.8441
131	0.319	0.1506	0.7590
185	0.312	0.1562	0.7378
228	0.278	0.1042	0.6646
3 Week			
53	0.701	0.0000	1.7050
96	0.359	0.0386	0.8821
131	0.338	0.0643	0.8233
185	0.329	0.0644	0.8022
228	0.295	0.0518	0.7164
4 Week			
53	0.701	0.0000	1.7050
96	0.368	0.0253	0.9074
131	0.363	0.0639	0.8872

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration (g/L)
185	0.338	0.0283	0.8305
228	0.323	0.0674	0.7838
5 Week			
53	0.701	0.0000	1.7050
96	0.427	0.1286	1.0360
131	0.395	0.0783	0.9655
185	0.389	0.1135	0.9440
228	0.383	0.1396	0.8520
6 Week			
53	0.701	0.0000	1.7050
96	0.534	0.1065	1.1425
131	0.504	0.1123	1.0778
185	0.470	0.0625	1.0067
228	0.452	0.0438	0.9672
7 Week			
53	0.701	0.0000	1.7050
96	0.553	0.1967	1.3392
131	0.522	0.1875	1.2653
185	0.492	0.1727	1.1794
228	0.472	0.1728	1.1400
8 Week			
53	0.701	0.0000	1.7050
96	0.587	0.1056	1.4448

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
131	0.567	0.1244	1.3897
185	0.506	0.0672	1.2466
228	0.495	0.0784	1.2184
9 Week			
53	0.701	0.0000	1.7050
96	0.645	0.1388	1.5836
131	0.617	0.1275	1.5172
185	0.549	0.1036	1.3502
228	0.539	0.1043	1.3227
10 Week			
53	0.701	0.0000	1.7050
96	0.674	0.0848	1.6684
131	0.652	0.0921	1.6093
185	0.586	0.0953	1.4455
228	0.567	0.0762	1.3989
11 Week			
53	0.701	0.0000	1.7050
96	0.674	0.0000	1.6684
131	0.661	0.0370	1.6463
185	0.624	0.0943	1.5398
228	0.596	0.0750	1.4739

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
12 Week			
53	0.701	0.0000	1.7050
96	0.674	0.0000	1.6684
131	0.661	0.0000	1.6463
185	0.649	0.0681	1.6079
228	0.623	0.0694	1.5433
13Week			
53	0.701	0.0000	1.7050
96	0.674	0.0000	1.6684
131	0.661	0.0000	1.6463
185	0.649	0.0000	1.6079
228	0.651	0.0695	1.6128
14 Week			
53	0.701	0.0000	1.7050
96	0.674	0.0000	1.6684
131	0.661	0.0000	1.6463
185	0.649	0.0000	1.6079
228	0.651	0.0000	1.6128

Table B11. Releasing rate of coated NPK fertilizer with soybean oil (10 weeks).

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
1Week			
64	0.682	1.4204	1.4204
106	0.582	1.2096	1.2096
143	0.296	0.6088	0.6088
197	0.237	0.4844	0.4844
2 Week			
64	0.698	0.2707	1.6911
106	0.607	0.2556	1.4652
143	0.426	0.3755	0.9843
197	0.339	0.2939	0.7783
3 Week			
64	0.698	0.0000	1.6911
106	0.654	0.1410	1.6062
143	0.518	0.2549	1.2392
197	0.383	0.1426	0.9209
4 Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.568	0.1482	1.3874
197	0.449	0.1642	1.0851

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
5Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.676	0.2522	1.6396
197	0.553	0.2445	1.3296
6 Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.676	0.0000	1.6396
197	0.576	0.0900	1.4196
7 Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.676	0.0000	1.6396
197	0.614	0.0946	1.5142
8 Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.676	0.0000	1.6396
197	0.655	0.1030	1.6442
9Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
143	0.676	0.0000	1.6396
197	0.655	0.0000	1.6442
10 Week			
64	0.698	0.0000	1.6911
106	0.745	0.0000	1.6062
143	0.676	0.0000	1.6396
197	0.655	0.0000	1.6442

Table B12. Releasing rate of coated NPK fertilizer with mixture of linseed and soybean

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
1Week			
53	0.729	1.5204	1.5204
93	0.465	0.9644	0.9644
164	0.433	0.8964	0.8964
185	0.419	0.8676	0.8676
2 Week			
53	0.737	0.2706	1.7910
93	0.505	0.2447	1.2091
164	0.466	0.2186	1.1150
185	0.434	0.1758	1.0434
3 Week			
53	0.737	0.0000	1.7910
93	0.554	0.1440	1.3531
164	0.490	0.0876	1.2026
185	0.471	0.1073	1.1507
4 Week			
53	0.737	0.0000	1.7910
93	0.570	0.0580	1.4111
164	0.514	0.0650	1.2676
185	0.483	0.0419	1.1926
5Week			
53	0.737	0.0000	1.7910

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
93	0.615	0.1045	1.5156
164	0.530	0.0449	1.3125
185	0.496	0.0358	1.2284
6 Week			
53	0.737	0.0000	1.7910
93	0.657	0.1054	1.6210
164	0.568	0.0862	1.3987
185	0.509	0.0343	1.2627
7 Week			
53	0.737	0.0000	1.7910
93	0.657	0.0000	1.6210
164	0.598	0.0800	1.4787
185	0.574	0.1405	1.3754
8 Week			
53	0.737	0.0000	1.7910
93	0.657	0.0000	1.6210
164	0.636	0.0933	1.5720
185	0.573	0.0375	1.4407
9Week			
53	0.737	0.0000	1.7910
93	0.657	0.0000	1.6210

Thickness(μm)	Absorbance	Potassium release (g/L)	Total potassium concentration(g/L)
164	0.636	0.0000	1.5720
185	0.632	0.1158	1.5565
10 Week			
53	0.737	0.0000	1.7910
93	0.657	0.0000	1.6210
164	0.636	0.0000	1.5720
185	0.632	0.0000	1.5565

Table B13. Releasing rate of coated urea fertilizer (seven days).

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
1 Day			
30*	0.571	5.5274	5.5274
55*	0.539	5.2206	5.2206
114	0.082	0.2512	0.2512
147	0.069	0.2138	0.2138
224	0.048	0.1536	0.1536
269	0.012	0.0502	0.0502
306	0.004	0.0272	0.0272
378	0.000	0.0000	0.0000
2 Day			
30*	0.576	0.9690	6.4964
55*	0.540	0.9091	6.1297
114*	0.190	1.6651	1.9163
147*	0.092	0.7566	0.9704
224	0.078	0.1117	0.2653
269	0.030	0.0600	0.1102
306	0.024	0.0619	0.0891
378	0.019	0.0704	0.0704
3 Day			
30	0.576	0.0000	6.4964
55*	0.565	0.3530	6.4827
114*	0.311	1.4377	3.3540

*3.33 times dilution

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
147*	0.113	0.3275	1.2979
224*	0.095	0.7425	1.0078
269	0.080	0.1536	0.2638
306	0.030	0.0277	0.1162
378	0.026	0.0162	0.0866
4 Day			
30	0.576	0.0000	6.4964
55	0.565	0.0000	6.4827
114*	0.324	0.3642	3.7182
147*	0.167	0.5723	1.8702
224*	0.119	0.1118	1.1196
269*	0.124	0.1101	0.3739
306	0.069	0.1166	0.2334
378	0.034	0.0412	0.1278
5 Day			
30	0.576	0.0000	6.4964
55	0.565	0.0000	6.4827
114*	0.366	0.4634	4.1816
147*	0.174	0.1625	2.0327
224*	0.151	0.5675	1.6871
269	0.135	0.0917	0.4656
306	0.083	0.0596	0.2930
378	0.048	0.0471	0.1749

*3.33 times dilution

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
6 Day			
30	0.576	0.0000	6.4964
55	0.565	0.0000	6.4827
114*	0.482	1.1893	5.3709
147*	0.189	0.1709	2.2036
224*	0.162	0.2000	1.8871
269	0.146	0.0470	0.5126
306	0.104	0.0701	0.3631
378	0.061	0.0451	0.2200
7 Day			
30	0.576	0.0000	6.4964
55	0.565	0.0000	6.4827
114*	0.560	0.9462	6.3171
147*	0.236	0.4792	2.6828
224*	0.184	0.2443	2.1314
269	0.162	0.0536	0.5662
306	0.140	0.1151	0.4782
378	0.074	0.0449	0.2699

*3.33 times dilution

Table B14. Releasing rate of coated urea fertilizer (11 weeks).

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
<u>1 Week</u>			
30*	0.648	6.2657	6.2657
55*	0.639	6.1794	6.1794
114*	0.587	5.6808	5.6808
147*	0.240	2.3538	2.3538
224*	0.179	1.7689	1.7689
269	0.165	0.4894	0.4894
306	0.137	0.4091	0.4091
378	0.069	0.2139	0.2139
<u>2 Week</u>			
30*	0.648	0.0000	6.2657
55*	0.639	0.0000	6.1794
114*	0.562	0.7071	6.3879
147*	0.319	1.1498	3.5036
224*	0.260	1.0714	2.8403
269	0.372	0.6758	1.1652
306	0.217	0.2978	0.7069
378	0.156	0.2853	0.4992
<u>3 Week</u>			
30	0.648	0.0000	6.2657
55	0.639	0.0000	6.1794

*3.33 times dilution

Thickness(µm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
114*	0.562	0.0000	6.3879
147*	0.592	2.8091	6.3126
224*	0.428	1.7895	4.6298
269	0.161	0.6255	1.7907
306	0.471	0.3518	1.0587
378	0.213	0.2112	0.7104
4 Week			
30	0.648	0.0000	6.2657
55	0.639	0.0000	6.1794
114	0.562	0.0000	6.3879
147*	0.592	0.0000	6.3126
224*	0.428	1.0126	5.6424
269*	0.161	0.3727	2.1634
306	0.325	0.3319	1.3906
378	0.213	0.3524	1.0628
5 Week			
30	0.648	0.0000	6.2657
55	0.639	0.0000	6.1794
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224*	0.547	0.5954	6.2378
269*	0.211	0.2730	3.2428

*3.33 times dilution

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
306*	0.151	0.3417	1.7323
378*	0.109	0.2122	1.2750
6 Week			
30	0.648	0.0000	6.4964
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224*	0.547	0.0000	6.2378
269*	0.359	1.0585	4.0353
306*	0.247	0.6885	2.4208
378*	0.212	0.8108	2.0855
7 Week			
30	0.648	0.0000	6.4964
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224	0.547	0.0000	6.2378
269*	0.414	1.4263	5.4616
306*	0.310	1.0884	3.5092
378*	0.284	1.1071	3.1926
8Week			
30	0.648	0.0000	6.4964

*3.33 times dilution

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224	0.547	0.0000	6.2378
269*	0.564	0.9090	6.3706
306*	0.482	1.8666	5.3758
378*	0.401	1.3434	4.5359
9 Week			
30	0.648	0.0000	6.4964
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224	0.547	0.0000	6.2378
269*	0.564	0.0000	6.3706
306*	0.551	0.8558	6.2316
378*	0.504	1.1051	5.6410
10 Week			
30	0.648	0.0000	6.4964
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224	0.547	0.0000	6.2378

*3.33 times dilution

Thickness(μm)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
269	0.564	0.0000	6.3706
306*	0.551	0.0000	6.2316
378*	0.542	0.5484	6.1894
11 Week			
30	0.648	0.0000	6.4964
55	0.639	0.0000	6.4827
114	0.562	0.0000	6.3879
147	0.592	0.0000	6.3126
224	0.547	0.0000	6.2378
269	0.564	0.0000	6.3706
306	0.551	0.0000	6.2316
378*	0.542	0.0000	6.1894

*3.33 times dilution

Table B15. Releasing rate of osmocote fertilizer (16 weeks).

Time (week)	Absorbance	Urea release (g/L)	Total urea concentration(g/L)
1	0.149	0.0000	0.3004
2	0.193	0.1008	0.4008
3	0.238	0.0986	0.4994
4	0.277	0.0896	0.5863
5	0.333	0.1205	0.7068
6	0.367	0.0756	0.7824
7	0.424	0.1229	0.9053
8	0.467	0.0945	0.9998
9	0.523	0.1200	1.1198
10	0.549	0.0592	1.1790
11	0.573	0.0527	1.2317
12	0.597	0.0514	1.2831
13	0.629	0.0693	1.3524
14	0.656	0.0599	1.4123
15	0.691	0.0544	1.4667
16	0.701	0.0570	1.5237

Table B16. Effected of temperature on releasing rate of urea.

Time(min)	Absorbance	Urea release (g/L)	Urea concentration (g/L)
<u>20°C</u>			
30 min	0.013	0.0531	0.0531
60 min	0.015	0.0166	0.0697
90 min	0.015	0.0007	0.0704
120 min	0.016	0.0031	0.0735
150 min	0.016	0.0004	0.0739
180 min	0.016	0.0001	0.0740
210 min	0.018	0.0058	0.0798
240 min	0.018	0.0010	0.0808
<u>25°C</u>			
30 min	0.015	0.0589	0.0589
60 min	0.018	0.0184	0.0773
90 min	0.021	0.0117	0.0890
120 min	0.029	0.0248	0.1138
150 min	0.033	0.0157	0.1295
180 min	0.040	0.0227	0.1522
210 min	0.046	0.0210	0.1732
240 min	0.050	0.0150	0.1882
<u>30°C</u>			
30 min	0.015	0.0589	0.0589
60 min	0.025	0.0384	0.0973
90 min	0.032	0.0265	0.1238

Time (min)	Absorbance	Urea release (g/L)	Urea concentration(g/L)
120 min	0.040	0.0274	0.1512
150 min	0.045	0.0189	0.1701
180 min	0.049	0.0147	0.1848
210 min	0.057	0.0254	0.2102
240 min	0.065	0.0272	0.2374
35°C			
0.020 min	0.0366	0.0732	0.0732
0.036 min	0.0596	0.0581	0.1313
0.044 min	0.0711	0.0328	0.1641
0.052 min	0.0825	0.0283	0.1924
0.060 min	0.0940	0.0277	0.2201
0.068 min	0.1055	0.0276	0.2477
0.072 min	0.1112	0.0161	0.2638
0.078 min	0.1198	0.0199	0.2837
40°C			
30 min	0.028	0.0962	0.0962
60 min	0.045	0.0802	0.1609
90 min	0.056	0.1341	0.2034
120 min	0.064	0.1695	0.2334
150 min	0.075	0.1945	0.2700
180 min	0.082	0.2250	0.2962
210 min	0.088	0.2468	0.3178
240 min	0.092	0.2648	0.3329

Table B17. Effect of pH on releasing rate of urea.

Time (min)	Absorbance	Urea release (g/L)	Urea concentration (g/L)
pH 5			
60 min	0.046	0.1478	0.1478
120 min	0.110	0.2084	0.3562
180 min	0.184	0.2472	0.6034
240 min	0.206	0.1043	0.7077
pH 6			
60 min	0.037	0.1220	0.1220
120 min	0.054	0.1026	0.1844
180 min	0.072	0.0688	0.2532
240 min	0.115	0.1349	0.3881
pH7			
60 min	0.030	0.1018	0.1018
120 min	0.046	0.0630	0.1648
180 min	0.068	0.0736	0.2384
240 min	0.095	0.0898	0.3282
pH 8			
60 min	0.028	0.0962	0.0962
120 min	0.032	0.0275	0.1238
180 min	0.054	0.0677	0.1915
240 min	0.072	0.0629	0.2554

Time (min)	Absorbance	Urea release (g/L)	Urea concentration (g/L)
pH 9			
60 min	0.021	0.0761	0.0761
120 min	0.029	0.0356	0.1117
180 min	0.038	0.0318	0.1435
240 min	0.050	0.0656	0.2090
pH 10			
60 min	0.015	0.0589	0.0589
120 min	0.025	0.0386	0.0975
180 min	0.034	0.0321	0.1296
240 min	0.050	0.0513	0.1809

VITA

Miss.Waristha Saengrith was born on September 29, 1982 in Kalasin, Thailand. She receives the Bachelor's degree in Chemistry from Faculty of Science, Chulalongkorn University in March 2003. She attended the Master's Degree Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and graduated in April 2005.