



CHAPTER II

THEORETICAL

2.1 Fertilizers

Fertilizer is added to the soil, plant, or other growing medium to supply the essential macronutrients to growing plants. Fertilizer 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 are made from chemical materials. The three major nutrients of fertilizer are nitrogen, phosphorus and potassium.

2.1.1 Types of fertilizers

Fertilizers are made in one of the forms:

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.

Liquid fertilizers

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

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.

Pellet fertilizers

Pellet 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.

2.1.2 Nitrogen fertilizer [9]

The three primary soluble N sources are ammonium sulfate, ammonium nitrate, and urea.

Ammonium Sulfate

Ammonium Sulfate is a white crystalline material containing 20-21% N and 24% S. If produced in the pure crystalline form it is rice-like in appearance, but the pure form is seldom marketed. The marketed product may be grayish in color due to carbon contamination during manufacture.

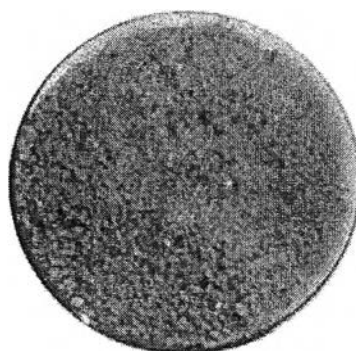


Figure 2.1 Ammonium sulfate [9]

Ammonium Nitrate

Ammonium Nitrate is generally in prilled form containing 33-34% N. It is highly soluble and is also in solution form. Prilled ammonium nitrate may be bright white in color, indicating that the prill has been coated with magnesium chloride, or beige in color, indicating that the product has been coated with a mixture of clays.

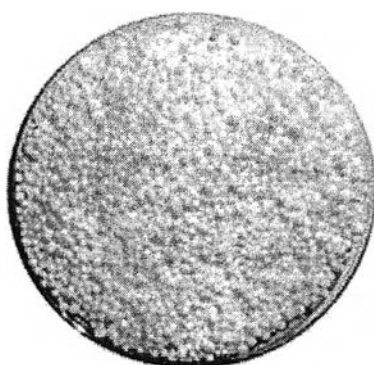


Figure 2.2 Ammonium nitrate [9]

Urea

Urea is a white crystalline solid, generally marketed in prill form, containing 40-46% N. It has physical properties and is not as hygroscopic as ammonium nitrate.

Urea is a low cost nitrogen fertilizer form. This is because of its high nitrogen composition and consequent low transport and storage costs. Urea may be the fertilizer of choice when only nitrogen is needed in a soil fertility program. Urea converts to ammonium bicarbonate within about 48 hours after field application. Nitrogen in this form will tend to volatilize to the air as ammonia gas. This lost fertilizer investment risk can be minimized or eliminated by assuring that the urea gets into the soil and does not merely remain on the surface of the soil or crop foliage. This can be accomplished by irrigating in the urea by plow down soon after surface broadcast application or by banding or injecting the urea directly into the soil.

The three primary plant nutrients: nitrogen, phosphorus and potassium, nitrogen is lost most easily from soil. Generally, nitrogen fertilizer efficiency in

Once in the nitrate form, nitrogen becomes a part of the soil solution. As such it is available to be used by plants. Nitrate can also be tied up by microorganisms, removed through leaching or lost through denitrification. Because of these processes and other, as much as 50 percent of the nitrogen added to soils may never be used by crops.

Leaching

Nitrate nitrogen is the form most subject to leaching losses. Nitrated (NO_3^-) are held only slightly by soil clays and humus (colloids). As a result, they remain in the soil solution and are free to move with the soil water. On the other hand, ammonium (NH_4^+) is attached to soil particles or trapped by soil clays and is not free to move with soil water.

Leaching losses of nitrates during the growing season in the medium and fine-textured soils are estimated to be less than 5 percent. Losses are greater from sandy or gravelly soils (coarse-textured soils)

Erosion

Nitrogen is lost through erosion in association with either water or sediment. Nitrate nitrogen moves primarily in runoff water, whereas ammonium and organic forms of nitrogen move with sediment. Sediment loss from fields can be greatly reduced by using approved soil conservation practices. Runoff can be reduced somewhat.

Denitrification

When soils become saturated with water, air is removed from soil pores. Under anaerobic conditions (absence of oxygen), some bacteria convert significant amounts of nitrate nitrogen to the elemental (N_2) form, which is a gas and is lost back to the atmosphere.

Losses through denitrification are estimated to be 15-30 percent of the total applied nitrogen from an area that has been flooded for three to five days. Fields

flooded for longer periods likely lose even greater amounts. Denitrification losses from well-drained, medium-textured soils that are saturated but not flooded are generally small.

Volatilization

Volatilization occurs when urea is converted to ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) when applied to warm moist soils. Ammonium carbonate, in turn, breaks down to form ammonia gas (NH_3). If the reaction takes place on the soil's surface, nitrogen is lost into the atmosphere. Although ammonium losses are usually less than 10 percent, they can be greater when urea is topdressed on warm, moist soils followed by three or more days of good drying conditions. Incorporating with equipment or injecting urea directly into the soil usually eliminates volatilization. Urea can be incorporated with enough water to wet the top two to three inches of soil.

2.3 Slow-release fertilizers and their development [9]

Slow-release fertilizer in which a physical barrier is used to reduce their dissolution rate were commonly prepared by encapsulation (coating or matrix formation) of water soluble granular plant nutrients with low permeability hydrophobic membranes [11]. This fertilizer is an alternative for uniform supply of nutrients to plants, and minimizing potential leaching which lead to a fertilizer burn and environmental toxicities.

They also have an advantage of reducing labor cost during farm application. Several groups of slow-release fertilizer are classified based on the process by which the nutrients are released. 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.

2.3.1 Sulfur-coated urea (SCU)

Sulfur-coated urea has been developed in recent years as a product with the characteristics of slow nitrogen release. This material is basically urea with a coating of elemental sulfur including binding agent and a sealant. Elemental sulfur was

chosen as a coating agent because of its relatively low cost and ease of handling. The mechanism of N release from SCF is by water penetration through micropores or imperfections in the coating. Nitrogen release rates can be varied by controlling the thickness of the sulfur coating. The nitrogen content of SCU ranges from about 10-37% depending on the thickness of sulfur coating.

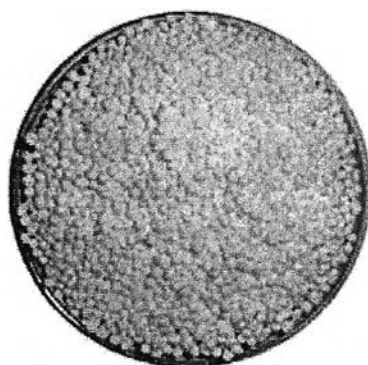


Figure 2.4 Sulfur coated urea [9]

2.3.2 Urea formaldehyde (UF)

Urea reacts with formaldehyde in the presence of a catalyst to form a mixture of compounds that are classified under the general name of urea-form. These materials are white, odorless compounds that contain varying amounts of nitrogen but averaging around 38%. A basic component of urea-forms is methylene-urea polymers varying in chain length and in degree of cross-linking between chains. The mechanism of N release from UF is involve dissolution and microbial decomposition.

Although the urea-forms have been examined agronomically in the United States, they have not received wide attention except as nitrogen sources for very high value crops, turf, and ornamentals. More attention has been given to these compounds in Europe and in Japan.

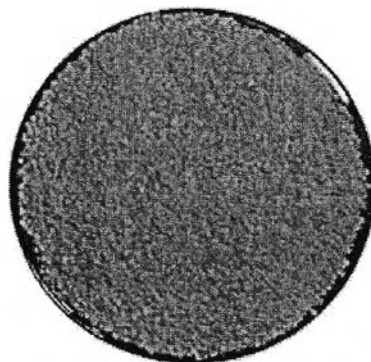


Figure 2.5 Ureaformaldehyde reaction products; Nitroform [9]

2.3.3 Isobutylidene diurea (IBDU)

Isobutylidene diurea is a reaction product of urea and isobutyraldehyde. The compound will be hydrolyzed to urea and isobutyraldehyde. The hydrolysis rate depends on acidity and high temperature. The reaction has been utilized to produce a compound containing approximately 32% nitrogen and having low water solubility. This compound also has the ability to be granulated with soluble nutrient sources of phosphorus and potassium to supply mixed fertilizer formulations with slow nitrogen release.

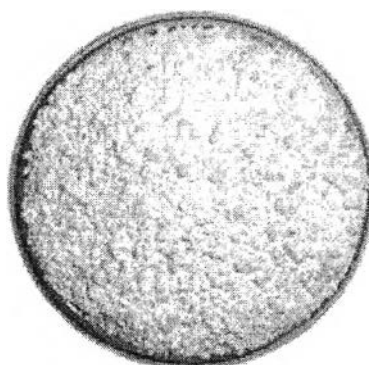


Figure 2.6 Isobutylidene diurea (IBDU) [9]

2.3.4 Polymer-coated

Polymer-coated fertilizer is the most advanced slow-release technology. Most of polymer-coated fertilizer release by diffusion through a semipermeable membrane, the releasing rate can be classified as thermoset or thermoplastic resins. Because of the high costs of process on polymer-coated products, their uses have been limited to high-value applications.

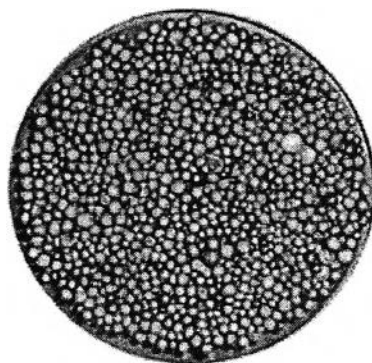


Figure 2.7 Polymer coated fertilizer; dicyclopentadiene polymers (Osmocot™) [9]

2.4 Model of releasing [12]

2.4.1 Solution/diffusion through continuous plasticized polymer phase

The polymer and other additives are dispersed homogeneously in continuous phase. The polymer film has molecular sized openings between the cross-linked polymer chains. The openings must be wetted for nutrients to diffuse.

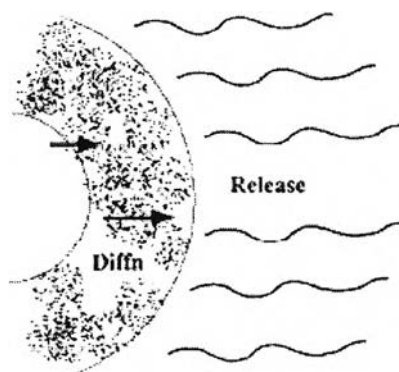


Figure 2.8 Solution/diffusion through continuous plasticized polymer phase [12].

2.4.2 Solution/diffusion through plasticizer channels

When the solubility of the nutrients in the plasticizer is higher than in water, it is possible that the nutrients would be preferentially transported through such plasticizer channels.

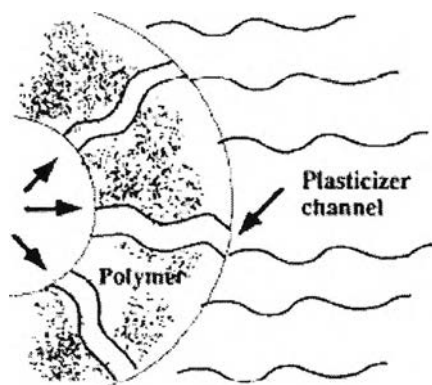


Figure 2.9 Solution/diffusion through plasticizer channels [12].

2.4.3 Diffusion through aqueous pores

This model described a non-homogeneous and discontinuous coating but punctuated with pores. These pores filled with solution when the dosage form comes in contact with an aqueous mechanism in these pores can range from pure molecular diffusion to convection, depending on the pore size.

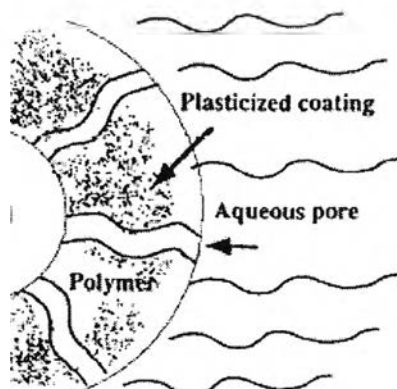


Figure 2.10 Diffusion through aqueous pores [12].

2.4.4 Osmotically driven release

The osmotically driven release is a well known model for porous membranes. When the sufficient osmotic pressure is generated by the core material, the water molecule penetrated to high osmotic pressure location and dissolved nutrients out.

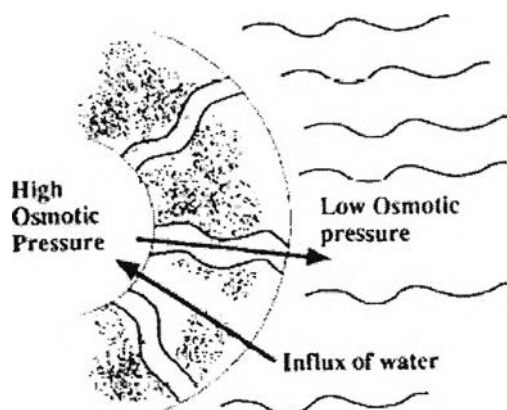


Figure 2.11 Osmotically driven release [12].

2.5 Nutrient releasing mechanism

When applied the fertilizer in a soil, the releasing of nutrients of nutrients are occurred with a combination of mechanism outside those of the coating materials.

Microbial action

Microorganisms in soil and/or environment act to breakdown the fertilizer elements into more basic compounds. The activity levels of micro-organisms depend on a soil temperature. Cold temperatures affect less activity and less breakdown, while warmer temperatures increase activity and breakdown.

Osmosis

Nutrients will move from a place of higher concentration to that of lower concentration. For example, the higher concentrations of nitrogen in the fertilizer granule will slowly migrate to the soil where is a less nutrient-rich.

Hydrolysis

Hydrolysis is an interaction of water with the fertilizer or coatings will break down the compounds and release the nutrients into the soil. The hydrolyzed rate of fertilizer or coating is depends on a types of functional groups, materials, moisture and temperature.

Physical Breakdown

The fertilizer handle can make a cracking and breaking on fertilizer due to nutrient released rapid rate.

2.6 Cashew Nut Shell Liquid (CNSL)

The cashew nut is attached to the cashew apple and is grey colored, kidney shaped and 2.5–4.0 cm in length. The shell is about 0.3 cm thick, having a soft leathery outer skin and a thin hard inner skin. Between these skins is the honeycomb structure containing the phenolic material popularly called CNSL. Inside the shell is

the kernel wrapped in a thin brown skin, known as the testa. The nut thus consists of the kernel (20–25%), the shell liquid (20–25%), and the testa (2%), the rest being the shell.

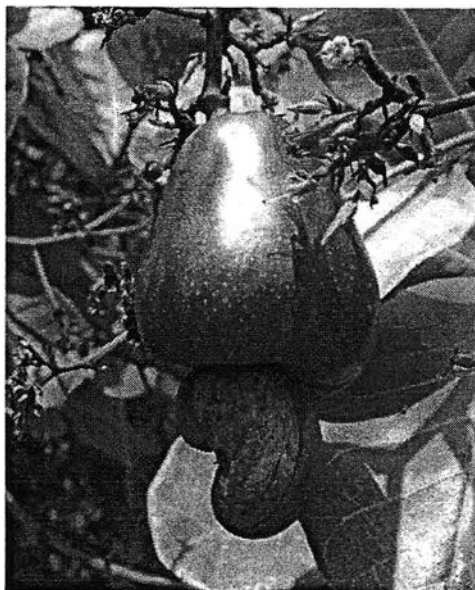


Figure 2.12 Cashew apple [13]

Cashew nut shell liquid (CNSL) is obtained as a by-product from mechanical processing for edible use of cashew kernel (*Anacardium occidentale* L.) and is a mixture of anacardic acid **1**, cardanol **2** and smaller amounts of cardol **3** and 2-methylcardol **4** [14]. Due to the easy thermal decarboxylation of anacardic acid **1**, the main component of distilled CNSL is cardanol **2** (yield up to 70–80% and purity up to 90%) as a mixture of saturated (3-*n*-pentadecylphenol), monoolefinic [3-(*n*-pentadeca-8-enyl)phenol], diolefinic [3-(*n*-pentadeca-8,11-dienyl)phenol], and triolefinic [3-(*n*-pentadeca-8,11,14-trienyl)phenol] long-chain phenols, with an average value of two double bonds per molecule. Cardol **3** and methylcardol **4** are present in smaller percentages (Figure 2.13).

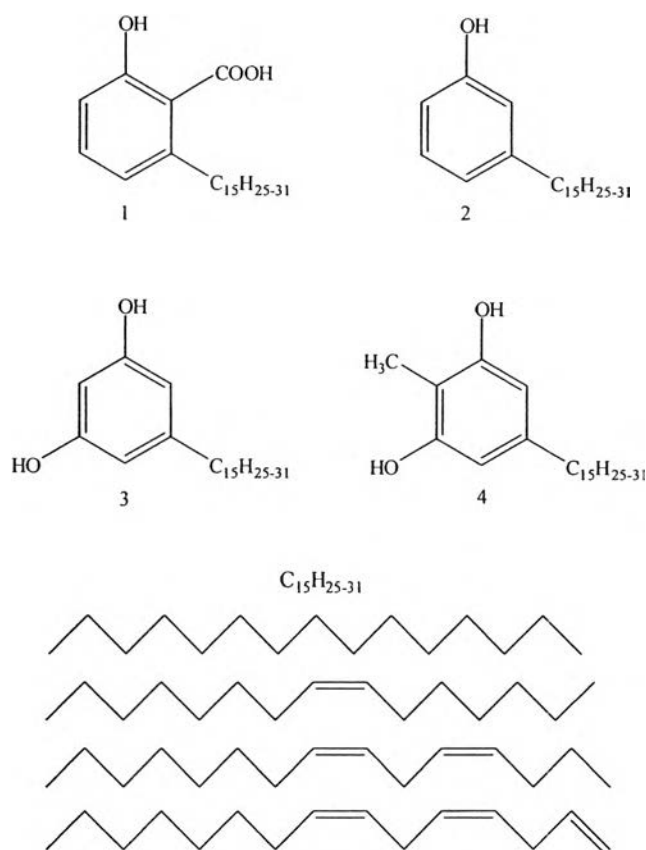


Figure 2.13 Components of CNSL

World-wide cashew nut production is presently estimated to be 1,200,000 tons per annum and the availability of CNSL is 300,000–360,000 tons per annum. As the production of cashew nuts is rising every year the availability of up to 600,000 tons per annum of CNSL should be reached in the near future.

2.6.1 Chemical composition

Thermally treated CNSL, whose main component is cardanol, a phenol derivative having a *meta*-substituent of a C15 unsaturated hydrocarbon chain mainly with 1-3 double, has various potential industrial utilizations such as resins, friction lining materials, and surface coatings [7]. Cardanol is easily available, and it has a low cost. The special properties of cardanol are high thermal stability and mechanical strength.

2.6.2 Application

CNSL is a source of a long chain *m*-substituted phenol, which promises to be an excellent monomer [15]. This monomer can be polymerized to get various polymeric products and/or can be suitably modified to chemical intermediates for industrial use.

PolyCNSL or polycardanol was prepared by oxidative polymerization method. The polymerization catalyzed by the Fe-salen catalyst (iron-*N, N'*-ethylene-bis(salicylideneamine)), a model of peroxidase, showed high catalytic activity for oxidative polymerization of various phenols was performed using hydrogenperoxide as oxidizing agent [16, 17, 18].

Furthermore, the polymer from CNSL and cardanol has been prepared either by condensation with electrophilic agents such as formaldehyde or by chain polymerization at the unsaturated sites chain using acid catalysts.

2.7 Drying oil

2.7.1 Composition of natural oils [19, 20]

Naturally occurring oils are triglycerides, triesters of glycerol and fatty acids. Some triglycerides are drying oils, but many are not. The reactivity of drying oils with oxygen results from the presence of diallylic groups or conjugated double bonds. Esters of many different fatty acids occur in nature.

The oils are mixtures of mixed triglycerides with different fatty acids distributed among the triglyceride molecules.

2.7.2 Fatty acids

The nature of the fatty acid present in oil determines its characteristics. Fatty acids with 18 carbon atoms are most common; those found in oils that are most important in coatings follow.

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 unsaturated, 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.

Table 2.1 Common fatty acids found in drying oils [19]

Common names	Structure
Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$
Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Linoleic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Linolenic acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Pinolenic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$
Ricinoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
α -Eleostearic acid	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$

2.7.3 Modified drying oils [21]

Both nonconjugated and conjugated drying oils can be thermally polymerized by heating under an inert atmosphere to form *bodied oils*. Bodied oils have higher viscosities and are used in oil paints to improve application and performance characteristics. Process temperatures may be as high 300-320 °C for

nonconjugated oils and 225-240 °C for conjugated oils, although the reactions occur at an appreciable rate at somewhat lower temperatures. At least in part, bodying may result from thermal decomposition of hydroperoxides, always present in natural oils, to yield free radicals, resulting in a limited degree of cross-linking. It has also been shown that thermal rearrangement to conjugated systems occurs followed by Diels-Alder reactions, which lead to formation of dimers. Since tung oil has a high concentration of conjugated double bond, it undergoes thermal polymerization more rapidly than nonconjugated oils (e.g., linseed oil). One must be careful to control the heating of tung oil or the polymerization will lead gelation.

Viscosity of drying oils can also be increased by passing air through oil at relatively moderate temperatures, 140-150 °C, to produce *blown oil*. Presumably, reactions similar to those involved in cross-linking cause autoxidative oligomerization of the oil.

2.7.4 Vegetable oil

2.7.4.1 Tung oil [19]

Tung oil obtained from the fruits of two species of the family Aleurites, *Aleurites fordii* Hemmley and *Aleurites montana* Wilson. Tung oil is also known as “China wood” oil or simply as “wood” oil. 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.

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 (autoxidation).

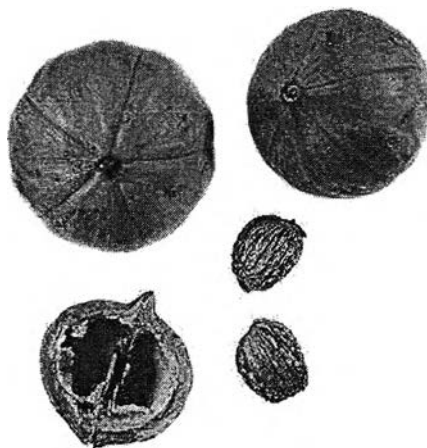


Figure 2.14 Tung seeds [22]

2.7.4.2 Linseed oil [19, 23]

Linseed oil (*Linum usitatissimum*) is also called flaxseed oil. Linseed oil is a tried and trusted servant of the surface coatings industry. Originally linseed was cultivated for the stalk of the flax plant which yielded the linen fibre, the earliest of vegetable fibers used by humans. Oil content of the seed varies between 30-37%.

Linseed oil consists of a mixture of triglycerides of mainly palmitic, stearic, oleic, linoleic and linolenic acids. The drying of linseed oil is an oxidation and polymerization process, during which the triglycerides undergo cross-linking. Linseed oil, historically, has been the most important oil in the coatings industry. Although its use has decreased because of other material, linseed oil still leads in volume in the coating industry. Linseed oil has a moderate drying rate. Because of its high linolenic acid content, linseed oil yellow on aging. It is used as the principal vehicle in house paints and also as the drying oil in some alkyds.

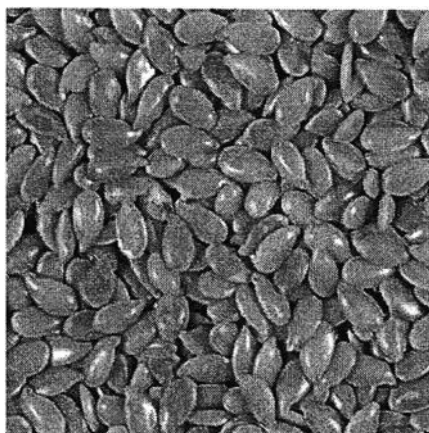


Figure 2.15 Flax seeds [24]

Table 2.2 Typical fatty acid compositions [23]

Oil	Percentage of fatty acids					
	Saturated	Oleic	Linoleic	Linolenic	eleostearic	Iodine value
Tung	5	8	4	3	80	165
Linseed	11	21	18	50	-	180

2.8 Autoxidation

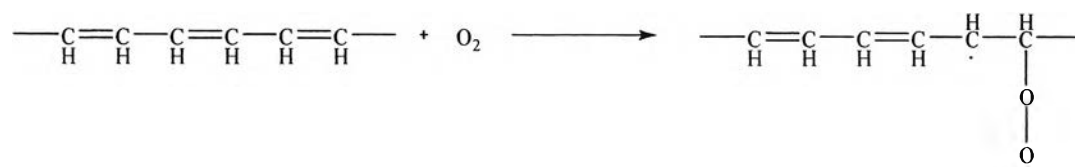
The autoxidation must be consistent with the facts. In particular different mechanisms are required for conjugated and non-conjugated hydrocarbon.

2.8.1 Conjugated oil

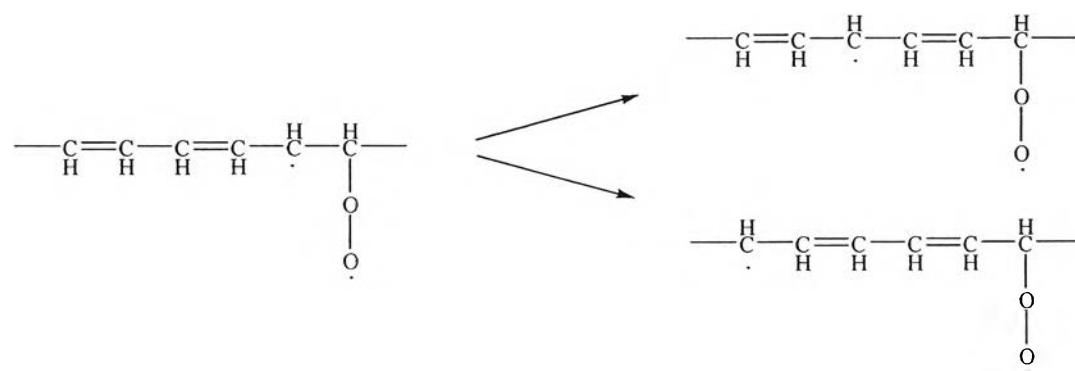
Oils containing conjugated double bonds, such as tung oil, dry more rapidly than any nonconjugated drying oil. Free radical polymerization of the conjugated diene systems can lead to chain-growth polymerization, rather than just a combination of free radicals to form cross-links. High degrees of polymerization, rather than just a combination of free radicals formed by chain transfer also yield cross-links. In general, the water and alkali resistance of films derived from conjugated oils are superior, presumably because more of the cross-links are stable carbon-carbon bonds.

However, since the α -eleostearic acid in tung oil has three double bonds, discoloration on baking and aging is severe.

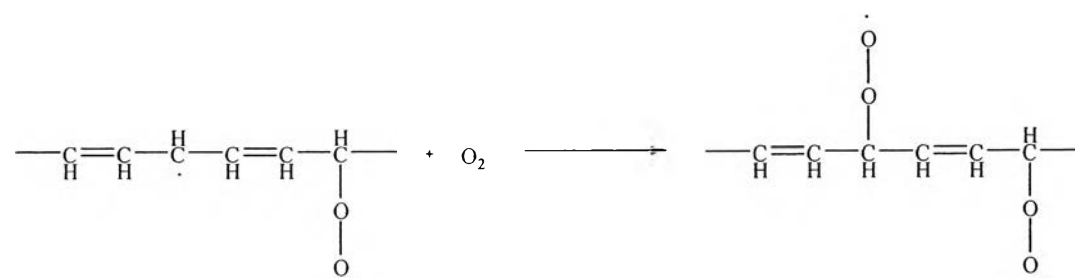
Oxygen attacks conjugated double bonds by direct addition, to form free radicals with two unsatisfied valencies (diradicals).



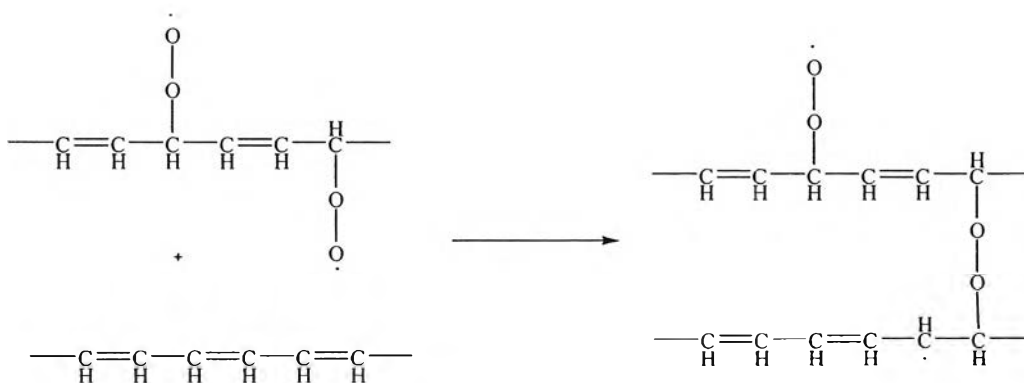
Rearrangement of double bonds can take place to give radical sites in the 1, 4 and 1, 6 positions as well.



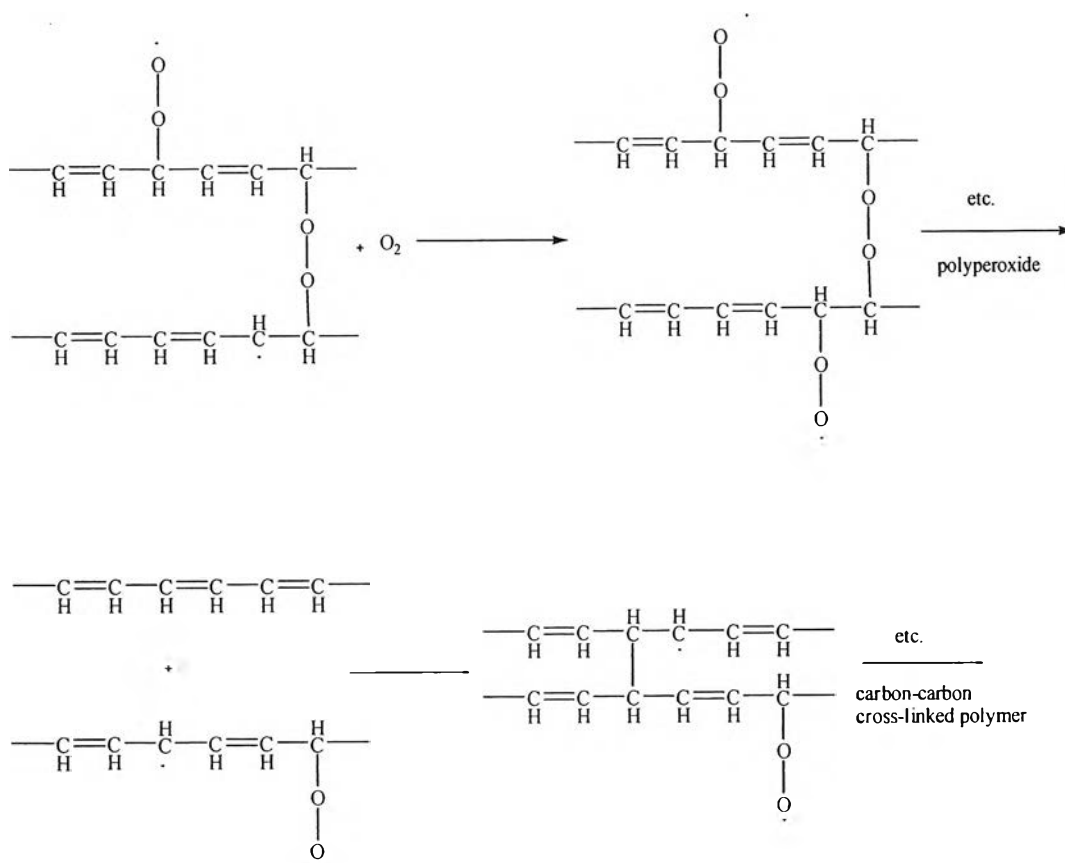
Such rearrangements involve only the redistribution of electrons in the molecule and occur frequently in unsaturated free radicals. Oxygen may react with free carbon valencies to convert them to peroxy radicals.



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



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 (RC-O.), which will in turn react with double bonds to form ether linkages (RC-O-CR).

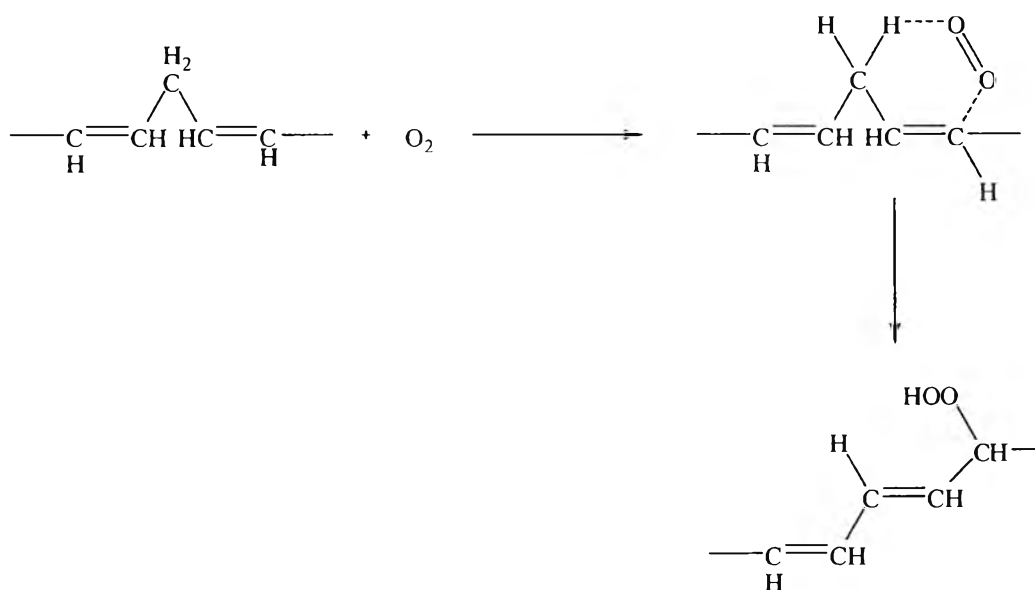


If 1, 4 diradicals are formed from triple unsaturation, the remaining double bonds are non-conjugated and hydroperoxide formation can occur in the manner shown in the next section.

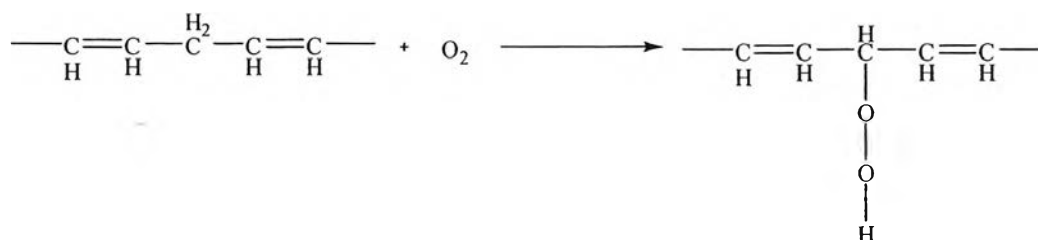
If 1, 2 Or 1, 6 diradicals are formed, the remaining double bonds are conjugated and one will react with oxygen. Since each reaction produces two free valencies, the maximum functionality of eleostearic acid is four and that of the triglyceride twelve.

2.8.2 Non-conjugated oils

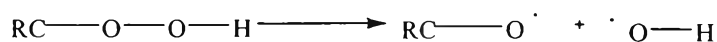
The essential difference is that reactions between oxygen (or free radicals) and non-conjugated oils occur without loss of unsaturation. One school of thought states that oxygen does attack the double bond, but that hydroperoxide formation and rearrangement of bonds occur simultaneously, so that no unsaturation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



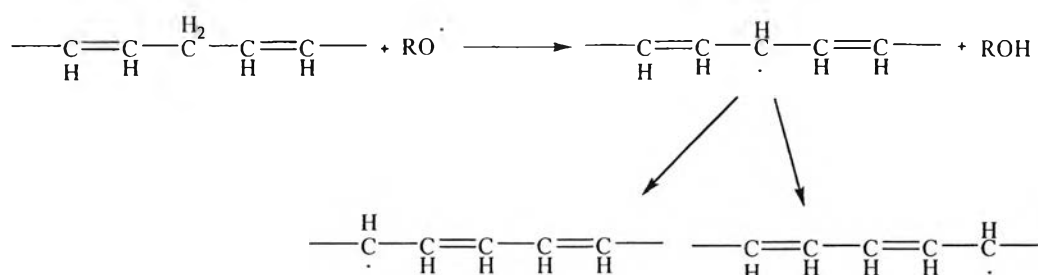
The alternative opinion is that the methylene group between two double bonds is particularly prone to direct oxidation. With oxygen, a hydroperoxide is formed.



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



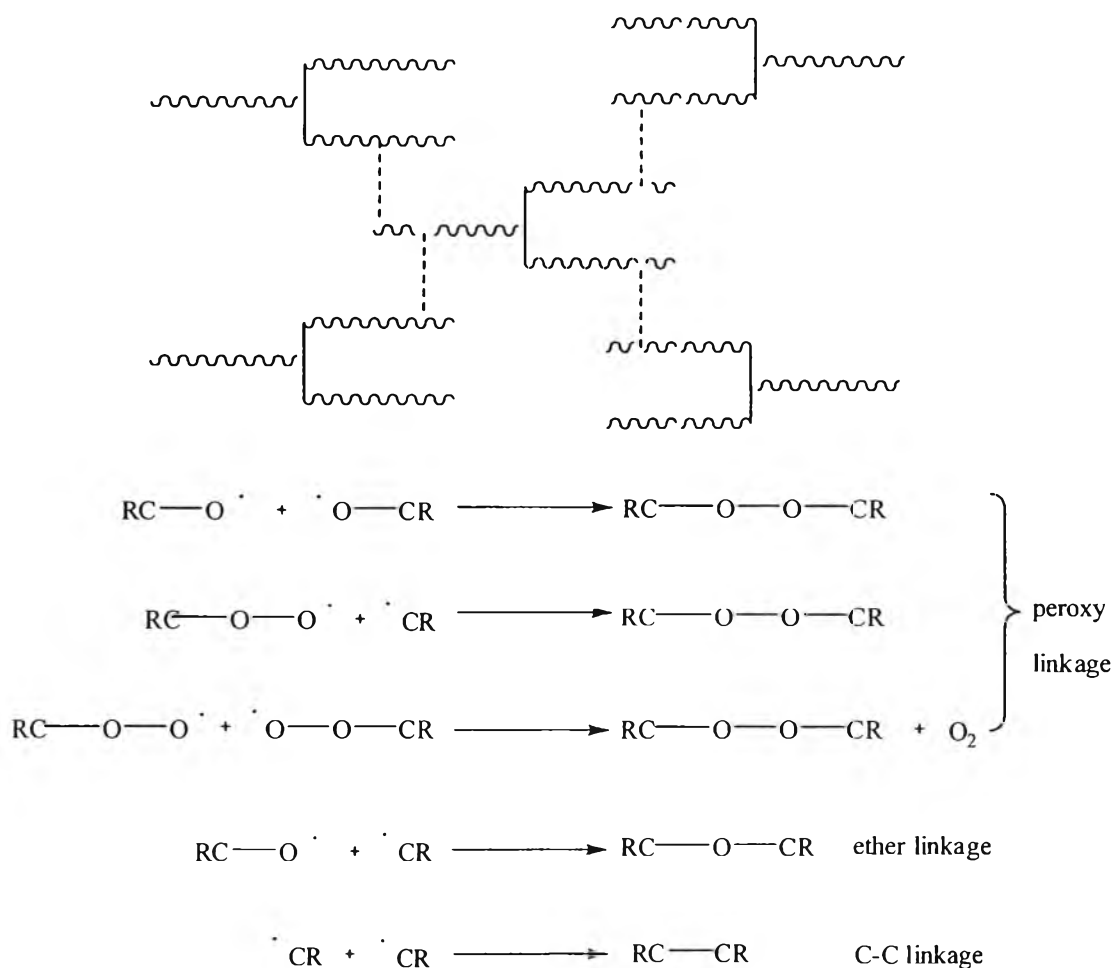
A free radical will readily remove a hydrogen atom from the active methylene group between double bonds, transferring its free radical nature to the attacked carbon atom. The new free radical may then rearrange to a conjugated form.



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.



2.9 Driers [23]

Driers are materials that promote or accelerate the curing or hardening of film formers containing oxidizable or drying oil components. Air drying is the formation of a solid film at ambient temperature by oxidation process from an applied liquid coating. Such coatings are convertible coatings in that the film, after drying, does not re-dissolve in the original carrier solvent. The air-drying process can be described as autoxidation, as it takes place automatically after the coating has been spread. Autoxidation is a chemical process that is greatly affected by temperature and the presence of catalysts.

The autoxidation of unsaturated drying and semi-drying oils does not proceed rapidly enough to be commercially acceptable; for instance, linseed oil, non-

yellowing oil with conjugated unsaturation requires more than 24 hours to become non-tacky. The conversion of these oils into higher molecular weight polymers (alkyds) with greater propensity to oxidize still does not give commercially acceptable drying times unless autoxidation catalysts are added.

A major advance in drier technology occurred in the 1920s with the preparation of the metal naphthenates. The naphthenic acid is not of precise composition, but is a mixture of acid of the same general structure. As the mixture would vary, so would the acid number, or combining equivalent of the acid, so that the metal content of the drier was not always the same from batch to batch. The next major advance in technology was the preparation of solvent solutions of these metal naphthenates, which not only gave materials that were easy to handle but allowed the metal content to be standardized. Naphthenates soon became the standard for the industry.

Drying metals

The metals are divided into two major categories, active and auxiliary. These groupings, however, should only be considered arbitrary as a considerable amount of overlap exists between them. Active driers promote oxygen uptake, peroxide formation and peroxide decomposition. At elevated temperatures several other metals, such as bismuth, display this catalytic activity themselves, but appear to enhance the activity of the active drier metals. It has been suggested that the auxiliary drier improves the solubility of the active drier metal, can alter the redox potential of the metal, or most likely functions through the formation of complexes with the primary drier.

Cobalt

Cobalt is the most important and most widely used drying metal. It is primarily an oxidation catalyst and as such acts as a surface or top drier. Used alone, it may have a tendency to cause surface wrinkling and poor through-dry. Therefore, to provide uniform drying, cobalt is generally used in combination with other metals, such as manganese, zirconium, lead, calcium and combinations of these metals.

Cobalt drier has a strong red-violet color, which contributes a little color to a clear a clear varnish. However, if cobalt drier is mixed with gum turpentine, dipentene, or similar solvents prone to take up oxygen on storage, a strong green color develops. This color usually disappears from the dried coating, but will be more persistent if calcium is used with cobalt.

Cobalt is a transition metal, which can exist in two valence states, and is known for its ability to form coordination complexes. If cobalt drier is added to some undiluted resins, profound changes in viscosity may occur, although this does not happen when cobalt drier is added to the pre-diluted resin. This is usually restricted to resins containing high molecular weight fractions, such as very high viscosity alkyds and copolymers. A similar effect occurs with calcium and zinc drier. The wrinkling effect with cobalt is turned to advantage in the production of alkyd-based baking wrinkling enamels.

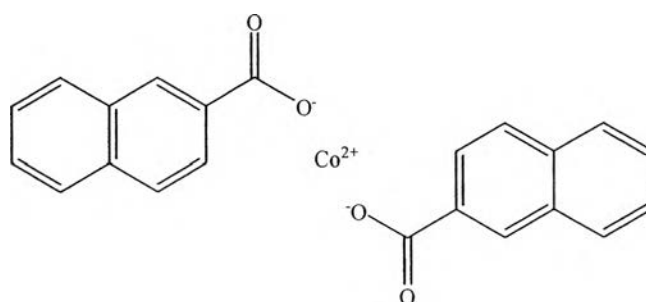
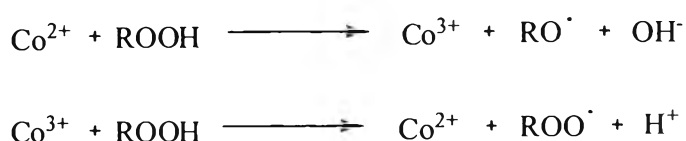


Figure 2.16 The structure of Cobalt naphthenate

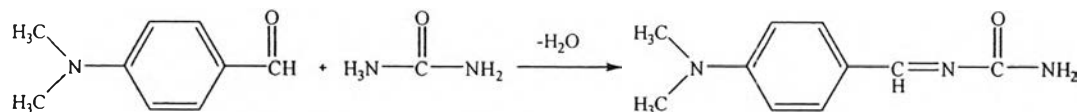
Driers containing transition metals with several oxidation states are called primary driers. They act as catalysts of hydroperoxide decomposition in a redox reaction called Haber and Weiss mechanism can be illustrated as follow:



Scheme 2.1 Mechanism of Cobalt naphthenate

2.10 Ehrlich's reaction [25]

The reaction between *p*-dimethylaminobenzaldehyde (*p*-DMAB) and urea in the presence of acid give a light yellow called lemon Kelly.



Scheme 2.2 The Ehrlich's reaction

2.12 Literature reviews

In 2003 Kiatkanarat [26] prepared prepolymer film for NPK fertilizers coating by reaction of epoxidized vegetable oils with amine compound, and cross-linking of vegetable oils using metallic salt as catalyst. The results showed that the most suitable oils preparing the prepolymer film were tung oil and 1:1 tung oil/soybean oil mixture in the presence of 0.5% cobalt naphthenate as catalyst.

In 2004 Saengrith [27] prepared controlled-release fertilizer coated with drying oil i.e. linseed oil, soybean oil and tung oil. The fluidized bed and pan coating were used for coating process. It was observed that pan coating was appropriate for the preparation of controlled-release fertilizers. Linseed oil and soybean oil were appropriate to be used as coating material but tung oil was not suitable. The optimum amount of linseed oil and soybean oil for coating by pan coating method was 10% and took 45, 120 minutes for drying.

In 2005 Ibrahim and Jibril [28] prepared controlled-release fertilizers with paraffin wax or a mixture of paraffin wax and rosin and study release profiles of KCl, NH_4NO_3 , KNO_3 , $(\text{NH}_4)_2\text{SO}_4$, and K_2SO_4 as fertilizers substrate. When the fertilizers were coated with wax/rosin or wax only, the rate of dissolution showed a higher decrease for wax/rosin samples than for wax-coated samples.

In 2005 Dutta et al [29] studied structural analysis and the performance of film for surface coating of heated and unheated Nahar seed oil. The film from heated

oil showed shorter drying time over the film from unheated oil. However, the film from heated oil did not show significant improvement of coating performance. There is only marginal improvement of hardness and acid resistance on the film from heated oil compared to unheated oil.

In 2008 Buttrees [30] prepared controlled-release fertilizer coated with drying oil from *O. canum* seed, linseed oil, and soybean oil. It was observed that the optimum amount of drying oils for coating process was 6% and using 2% cobalt naphthenate as catalyst at 60°C. In coating process, *O. canum* seed and linseed oils were pre-cured by heating at 150°C for 2 hours which could reduce coating time from 10 and 50 minutes to 2 and 10 minutes, respectively. The products obtained from this method were smooth, compact, glossy and water resistant. The releasing of urea could be prolonged for two months. The UV-Visible spectrophotometric method was used to determine the urea released from encapsulated urea fertilizer. It was observed that encapsulated urea fertilizer with drying oil from *O. canum* seed oil and linseed oil at the same average thickness had the same releasing rate of urea. The higher coating thickness showed the longer release time of urea. Furthermore, higher temperature and lower pH enhance releasing rate.