CHAPTER II

THEORETICAL CONSIDERATION

2.1 Waxes [5, 6, 9, 10]

Wax usually refers to a substance which is a solid at ambient temperatures with a relatively low melting point, and softening when heated and hardening when cooled. They are generally smooth, lustrous, glossy, insoluble in water, and combustible. Originally, the term “wax” refered to beeswax, which is probably the oldest wax, obtained from the honeycomb of the bee. Today the term wax has broader meaning of all material that have wax-like properties. They may be either natural or synthetic, and of petroleum, mineral, vegetable, or animal origin. Waxes compose of various types of chemical composition, such as paraffin hydrocarbons, fatty esters, acids, alcohols, and ketones.

The main compositions of vegetable and animal waxes are high molecular-weight acids, alcohols, esters, and saturated hydrocarbons, which esters usually being predominant. Table 2.1 shows some of the common wax acids and alcohols and Table 2.2 shows the physical and chemical properties of commercial natural waxes.

Table 2.1 Some common acid and alcohol waxes.

Name	Formula	Melting Point (°C)	Occurrence
<u>Acids</u>			
Cerotic acid	$C_{25}H_{51}COOH$	87.7	Free in beeswax, montan, carnauba; as ester in Chinese wax and carnauba
Lauric acid	$C_{11}H_{23}COOH$	44.2	As laurin in Japan wax
Palmitic acid	$C_{15}H_{31}COOH$	63.1	As palmatin in Japan wax; cetyl palmitate in spermaceti; myricyl palmitate in beeswax
<u>Alcohols</u>			
Cetyl alcohol	$C_{16}H_{33}OH$	49	As cetyl palmitate in spermaceti
Myricyl alcohol	$C_{30}H_{61}OH$	85	As esters in beeswax, carnauba

Table 2.2 Chemical and physical properties of commercial natural waxes.

Wax	Melting range, °C	Acid Number	Iodine Number	Saponification number
Beeswax	62 - 70	17 – 21	8 – 11	86 - 96
Carnauba	83 - 91	1 – 8	8 – 13	73 - 86
Candelilla	65 - 69	15 – 16	14 - 37	46 - 65
Japan	50 - 56	0.2 - 13	1.4 - 2	78 - 93

2.2 Methods of processing [9]

The physical operations used in the processing of natural waxes are :

- heating
- shredding
- selective and non-selective solvent extraction
- filtration with and without filter aid
- vacuum distillation

The chemical processing of natural waxes, used in the manufacturing of synthetic waxes are consists of :

- chemical bleaching
- esterification
- chlorination
- oxidation
- condensation
- hydrogenation

2.3 The major classes of waxes

Waxes are obtained from either natural or synthetic sources, so there are various types of waxes. The major classes of waxes are as follow :

- vegetable waxes
- animal and insect waxes
- petroleum waxes
- mineral waxes
- synthetic waxes

2.3.1 Vegetable waxes [5, 6, 9, 10]

Vegetable waxes are obtained from the coating on stems, fruits, leaves, grasses and seeds. They are mixtures of esters of fatty acids and high molecular weight alcohols and unsponifiable materials. Carnauba, candelilla and Japan are the most important commercial vegetable waxes. Physical properties of these waxes are shown in Table 2.3.

Table 2.3 Physical properties of commercial vegetable waxes.

Waxes	Characteristics	Color	Melting point, °C	Penetration	Flash point, °C
Canauba	very hard, brittle, not tacky, lustrous	pale yellow to greenish brown	83 - 86	1 - 3	298
Candelilla	hard, briltle, slightly tacky, lustrous	brownish to light yellow	68.5 - 72.5	1.5 - 5	240
Japan	resembles hard fat	pale cream	46.5 - 51.5	6 - 20	196

Carnauba Carnauba wax is obtained from the leaves of the carnauba palm and has a high melting point, hardness. It can take a lasting polish. These waxes can use to increase the melting point of paraffin waxes in the preparation of hot melt adhesives and coatings. So it often used to mix with other waxes to raise the melting point. Carnauba wax is generally used in conjunction with resin such as acrylics, polystyrene and poly (vinyl chloride) to formulate the resin - wax polishes (e.g., floor waxes, shoe pastes). At present, the carnauba wax are used in various manufacturing such as insulation material, electric batteries, candles, matches, soaps, chalk and salves.

The chemical composition of carnauba wax is approximately as follow [10] :

Component	Weight %
aliphatic and aromatic ester	84 - 85
aliphatic esters	40
ω - hydroxy esters	13
cinnamic aliphatic esters	8
free fatty acids	3 - 3.5
alcohols	2 - 3
lactides	2 - 3
hydrocarbons	1.5 - 3.0
resins	4 - 6
moisture and inorganic residue	0.5 - 1.0

Candelilla Candelilla wax is harvested from candelilla plant. The approximate chemical composition is :

Composition	Weight %
wax esters	28 - 29
alcohols, sterols and neutral resins	12 - 14
hydrocarbons	49 - 50
free acids	7 - 9
moisture	2 - 3
inorganic residue	1

Candelilla is a hard and brittle wax. It composed of 50% hydrocarbons with small amounts of esters and free acid. It is used in chewing gum and in the cosmetic industry including paper coating and polishes.

Japan wax Japan wax is a fat and is derived from the beries, that is a small tree native of Japan and China. The wax, occurring between the skin and the kernel of the berry. These wax is used in candles, rubber vulcanization, polishes, textile finishes, lubricants, and as an additive in thermoplastic resins.

2.3.2 Animal waxes [5, 6, 10]

Animal waxes are obtained from insect or mammalian origin. Beeswax and wool wax are the most important commercial animal waxes. Their properties are shown in Table 2.4 below.

Table 2.4 Properties of beeswax and wool wax

	Beeswax	Wool wax
color	pale yellow to dark brown	brownish - yellow
melting point, °C	62 - 70	37 - 43
specific gravity at 15 °C	0.96 - 0.98	0.93 - 0.95
acid number	7 - 30	6 - 22
saponification number	83 - 104	84 - 127
iodine number	5 -13	15 - 47

Beeswax is separated from the honeycomb of a bee by melting the comb in boiling water and then filtered the melted products to obtain the yellow beeswax. It is bleached with oxidizing agents, e.g., peroxide or sunlight, to white beeswax. Its components are nonglyceride esters of carboxylic and hydroxy acids with some free carboxylic acids, hydrocarbons, and wax alcohol.

The major use of beeswax are in manufacturing of candles and cosmetic. Small amount of it is used for polishes and medicine. The industrial market of beeswax are limited because of its price, except in a cosmetic manufacturing.

2.3.3 Petroleum waxes [5, 6, 9]

Petroleum waxes are essentially saturated hydrocarbon mixture obtained from the refining of crude waxes from petroleum. Petroleum waxes are classified into paraffin and microcrystalline waxes.

Paraffin waxes These waxes consisted of normal alkane, obtained from distillation of crude oil. Paraffin waxes are macrocrystalline and brittle. The quantities of normal alkane in these waxes usually exceeds 75% and may reach almost 100%. The molecular weights of the hydrocarbon in paraffin wax range of about 280 to 560 (C_{20} - C_{40}). Its physical properties are shown in Table 2.5. Paraffin waxes are generally lower melting, lower molecular weights, and lower viscosities in liquid state than microcrystalline waxes. They are soluble in nonpolar organic solvent such as benzene, chloroform, carbon tetrachloride, and insoluble in polar solvent such as water and methanol.

Table 2.5 Physical properties of petroleum waxes

Property	Paraffin	Microcrystalline
flash point, °C	204, min	260, min
melting range, °C	46 - 68	60 - 93
viscosity at 98.9 °C, mm^2/s (=cst)	4.2 - 7.4	10.2 - 25

Microcrystalline waxes Microcrystalline waxes are the solid hydrocarbon mixtures refined by deoiling crude petrolatums, which are derived from the dewaxing of residual lubricating oil stock and tank - bottom wax. These waxes are called microcrystalline because they are small crystals but give an amorphous structure in the solid state. Microcrystalline waxes are consisted of isoparaffinic and naphthenic saturated hydrocarbons along with some normal alkane. The molecular weights range from about 450 to 800 (C_{35} - C_{60}).

Physical properties of microcrystalline waxes are given in Table 2.5, which are higher melting point and have a higher viscosity than paraffin waxes.

About 60% of petroleum wax are used for various packaging applications (e.g., paper wrappers and paper board containers). Other applications include hot melt adhesives, printing inks, protective coating (e.g., rushproofing formulations), candles, crayons and dental wax, etc.

2.3.4 Mineral waxes [5, 6, 9]

Mineral waxes are obtained from fossil remains such as bitumens, lignite, peat and shale, except the waxes derived from petroleum. The major commercial mineral waxes are montan, ozocerite and ceresin. The properties of montan wax, ozocerite, and ceresin are shown in Table 2.6.

Table 2.6 Properties of some mineral waxes

Wax	Hardness	Acid number	Melting point, °C
Montan	very hard	40 - 50	84 - 90
Ozocerite	fairly hard	0	60 - 90
Ceresin	fairly hard	0	50 - 80

Montan wax is a bituminous wax, occurring in brown coals or lignites. It has been used along with various polymers such as oxidized polyethylene and acrylic resins, and as an internal lubricant for poly vinyl chloride.

Ozocerite is a hydrocarbon wax. It has been blended with polystyrene, in conjunction with a mixture of C_9 olefins to yield a wax that is suitable for impregnation and coating of fibrous products, e.g., textiles for improving of gloss, hardness and tensile strength characteristics.

2.3.5 Synthetic Waxes [11]

The production of synthetic waxes in recent years has been steadily increasing from year to year. Most of these synthetic waxes are only in the sense that they have the physical properties similar to that of the natural wax.

Fishcher - Tropsch Wax Fishcher - Tropsch Wax is a by product from the synthesis of fuel, such as gasoline and diesel oils, obtained by Fischer - Tropsch catalytic hydrogenation of carbon monoxide at high temperature and pressure. This wax is white and very hard (penetration of 0 - 5 at 25 °C) with a melting point of 95 - 110 °C.

Fischer - Tropsch wax is comprised of normal alkanes in the molecular weight range of 600 - 950. It is used to blend with other waxes for hot - melt coatings and adhesives to increase melting points and hardness, in rubber and plastic. It is used as a mold release in carbon paper coating to increase hardness, and in textiles for impregnation and sealing.

Polyethylene waxes Polyethylene waxes are produced by polymerization of ethylene that a gas received from petroleum, the basic structure is, $(CH_2 - CH_2 -)_n$. Polyethylene which have a molecular weight of 2,000 -10,000 have a properties of high molecular weight hydrocarbon waxes. The low molecular weight (2,000 - 7,000) grades are used in the applications listed below.

Applications	Percent (%)
Plastic manufacturing, processing aids, mold and extrusion lubricant, color dispersant	25
Modification of petroleum waxes, hot - melt coatings, waxed paper, cable compounds, candles	21
Paints, inks, antislip	16
Textiles, impregnant, lubricant	13
Polishes, industrial maintenance	8
Rubber, processing and mold release	8
Crayons, cosmetics, chewing gum base, dental wax, and other	9

Polyethylene polyol fatty acid esters and derivatives The polyethylene glycols ("Carbowaxes") reacted with fatty acids, e.g., oleic acid and stearic acid to from a series of useful liquids and solids. A few of the commercial polyethylene glycol esters are waxy solid. They include "Carbowax 400 (Mono) Laurate" (melting point 50 - 60°C), "Polyethylene Glycol 600 (Mono) (Di) stearate" (melting point 24 - 26 °C), and "Carbowax 4000 (Mono) Laurate" (melting point 54 - 57 °C), these are products of Carbide and Carbon Chemicals Co.

To produce polyethylene polyol esters, the polyhydric alcohol from the 2 carbon atom dihydric alcohol (ethylene glyol) or trihydric alcohol (glycerol) or a high molecular weight alcohol such as Carbowax 6,000 (polyethylene glycol) with a polyethoxy dihydric alcohol are reacted with fatty acids ranging from C_{12} to C_{18}. Esterifying one mol of fatty acid with one mol of polyhydric alcohol will obtain a monoester which is generally hydrophilic (water loving). The diester lipophilic, is produced by reacting one mol of polyhydric alcohol with two mols of fatty acid to give the high molecular weight of products of a wax-like nature. The major uses to this waxes are depend on their surface activity and emulsifying action. Some are detergents, plasticizers and lubricants for plastics.

2.4 The test methods

2.4.1 Color [5, 10, 11, 12]

The color of many waxes is judged when they are in molten state. The two most widely used color standards are ASTM D1500, which is used to measure dark brown to off - white color, and ASTM D156, which is used to measure off - white to pure white. In ASTM D 1500, the color of molten wax is evaluated in a standardized glass container by comparing the color of the transmitted light with that transmitted by a series of numbered glass standard. This test is used for manufacturing control, so the color is readily observed by the customer. In ASTM D156, the special heating coil to maintain the wax in liquid state must be used while the color is being read and the color of melted wax is matched with the color of standard glass color discs. The exact match being contained by varying the depth of the column as required. Color determined by this method values ranging from -16 to + 30. The higher positive values denote the lightest colors.

2.4.2 Melting point [5, 6, 10]

The melting point is reported depend on the method used and the characteristics of the wax. ASTM D 127 is the method used to measure the drop melting point, suitable for amorphous waxes, e.g., microcrystallines wax. Waxes whose time - temperature cooling curves show plateau, e.g., paraffin wax, which determined by ASTM D 87. ASTM D 938 evaluates the temperature at which a wax, on cooling, develops a resistance to flow. The melting point of many natural waxes is determined with either open or closed capillary tubes. Differential scanning calorimetry is widely used on all type of waxes and gives a quantitative melting point profile.

2.4.3 Hardness of Penetration [5, 6, 10]

The standard test for the hardness of waxes in industry is the penetration test, ASTM D 1321. This test measures the depth in tenths of a millimeter that a needle of a certain configuration under a given weight penetrates the surface of a wax at a given temperature. The lower the numerical value, the harder the wax. Generally, harder waxes contain less oil impurity and are more useful in polymer application. Figure 2.1 demonstrates the penetrometer that use for the penetration test.

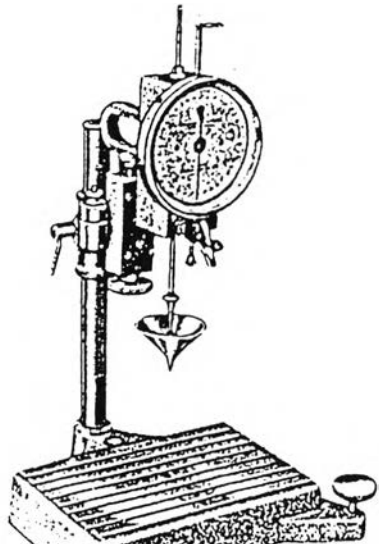

Figure 2.1 The penetrometer

2.4.4 Total acid number [5, 6]

For the total acid number ASTM methods D 974 and D 1386 can be used to determine the free acidity in oxidized petroleum waxes or natural waxes such as carnauba. It is an indication of the degree of oxidation of an oxidized wax or of the purity and composition of a natural wax.

The definition of total acid number is the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate a sample to a specified end point. This method is determined by dissolved the sample in a mixture of toluene and isopropyl alcohol containing a small amount of water and the solution is titrated at room temperature with potassium hydroxide. The end point indicated by color change from orange to green - brown color of the *p* - naphtholbenzein indicator. The total acid number is calculated as follows :

$$\text{Total acid number, mg of KOH/g} = [(A - B)\, M \times 56.1] / w$$

where :

A = KOH solution required for titration of the sample, mL

B = KOH solution required for titration of the blank, mL

M = molarity of the KOH solution

W = sample used, g.

2.4.5 Flash point [5, 11]

The flash point is determined by ASTM D 92, when a small sample of wax is melted and then gradually heated in the Cleveland open cup. A temperature will be eventually reached at which a small test flame passed over the entire surface will cause a flash. This temperature is called the flash point. This test indicates the amount of low molecular weight hydrocarbons, cracked material, and solvents present.

2.4.6 Viscosity [5, 6, 10, 11]

The property of a liquid which offers resistance to a change in shape is called viscosity. There are many instruments used in determining viscosities which depends on the rate of flow through an orifice under well controlled temperature conditions. Viscosity is an important test for mineral and synthetic waxes. ASTM D 88 and ASTM D 445 provided the measurement of the viscosities of waxes with reading in seconds. These methods are measurement of the Saybolt viscosity in Saybolt Universal sec (SUs) and of kinematic viscosity in mm^2/s unit or centistokes. ASTM D 2161 is used for the conversion of kinematic viscosity into Saybolt viscosity. The viscosity values indicate the component of petroleum wax. Lower values are paraffinic waxes and higher values are microcrystalline waxes.

The relation between kinematic viscosity and Saybolt viscosity at 210°F (98.9°C) is illustrated by the following example.

Kinematic Viscosity (centistokes)	Saybolt Viscosity (seconds)
2.0	32.8
2.5	34.6
3.0	36.3
3.5	37.9
4.0	39.4
4.5	41.0
5.0	42.6
5.5	44.2

2.4.7 Oxidation and Thermal Stability [12, 13]

The thermogravimetric balance (TG) is one of recent technique developed to evaluate thermal behavior of different chemical compounds. This instrument is used to indicate the effect of temperature on the weight loss of the compounds. Oxidation stability is the most important chemical property of lubrication. It is the degree in which atmospheric oxygen can react with lubricants under various conditions. This property can determine by thermogravimetric instrument under air condition.

The values obtained from the curve for thermooxidation stability by TG method are shown in Figure 2.1.

- The oxidation point is the point of temperature which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.

- The oxidative compounds is the weight of oxygenated compounds in milligrams of the substance remains in the pan of balance at oxidation point. Higher than this point the compounds will carbonize, and finally change completely to CO_2.

Figure 2.2 shows the thermal stability curve. At first the sample evaporates gradually, then faster which indicates the sample decomposition. Above 400 °C the residue and impurities start to be continued then remain stable up to about 600 °C.

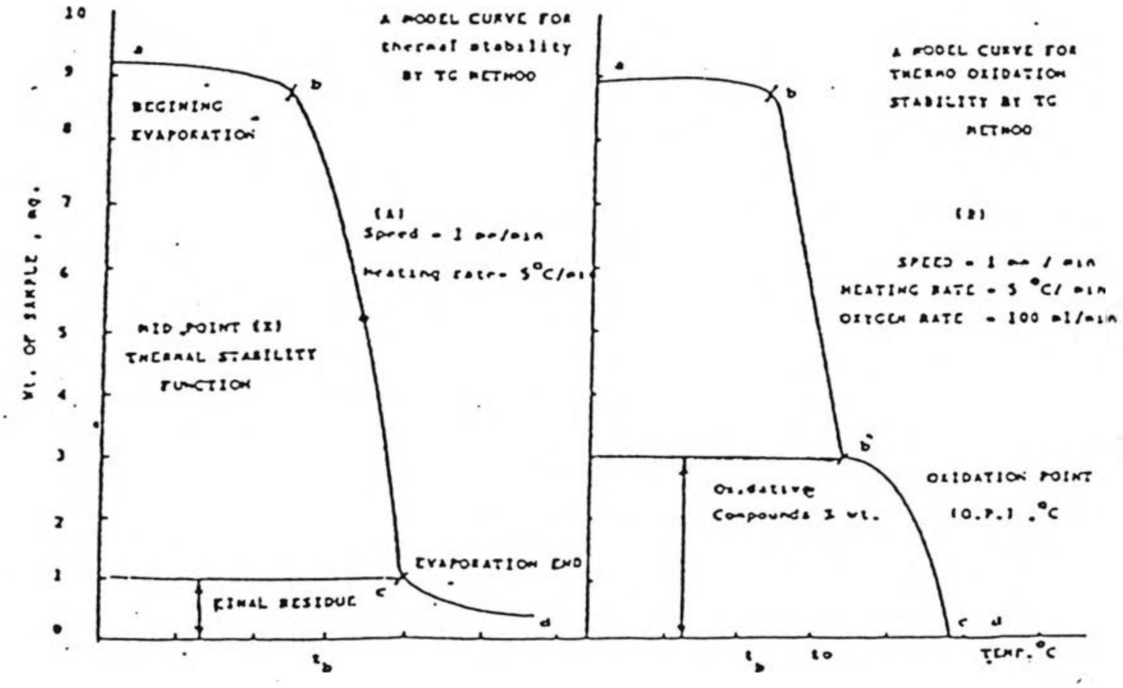

Figure 2.2 Comparison between typical model curves for both TG thermal and thermooxidation stabilities.

2.5 Economic aspects.

Waxes are important industrial raw materials, but the amount of waxes that produced in our country are insufficient. Every year, industries purchased a lot of waxes to use in their manufacturing of goods. Table 2.7 shows the imported quantity of various types of waxes per year.

If the efficient techniques for producing the synthetic waxes are available in Thailand, the amount of imported waxes is expected to decrease.

Table 2.7 Waxes : Quantity of import

waxes	amount (kg.) 1996	 1997	 1998
Paraffin waxes	14,231,057	14,074,627	13,817,627
Mineral waxes and synthetic waxes	11,676,617	16,019,881	12,297,635

Source : Customs Department (1996 - 1998)

2.6 Esterification

Esterification reaction of alcohol and organic acid leading to ester and water is as follows:

$$\underset{\text{alcohol}}{\mathrm{R'OH}} + \underset{\text{organic acid}}{\mathrm{RCOOH}} \rightleftharpoons \underset{\text{ester}}{\mathrm{RCOOR'}} + \underset{\text{water}}{\mathrm{H_2O}}$$

This reaction is reversible, but it can be pushed to get more product by using excess alcohol and removal of water as it forms by the azeotropic agent, e.g., toluene. The possible catalysts in this reaction are sulfuric acid, phosphorus oxides and anhydrous sodium hydrogen sulfate. After the ester has been formed, unreacted acid is neutralized by sodium bicarbonate or calcium hydroxide and removed by filtration.

2.7 Literature review

The naturally occurring waxes were used for a very long time in industry, and commonly used in such applications as candles, cosmetics, inks, carbon paper, crayons, rubber products, and lubricants. However, these waxes were in limited supply and were not always available, and when they were available they may be expensive. So the synthetic waxes were developed and become important waxes in certain application. The synthetic ester waxes were one kind of synthetic waxes that used in many applications because of the advantage in their properties.

In 1984, Richard L. McConnell [15 - 17], prepared new branched polyester waxes containing particular amounts of tri or tetrafunctional hydroxyl containing compounds. These waxes were prepared using at least one saturated aliphatic dibasic acid having 4 to 36 carbon atoms, at least one saturated aliphatic or cycloaliphatic glycol having 2 to 12 carbon atoms and controlled amounts of aliphatic triols and /or tetraols. These polyester waxes were used as modifiers for ethylene/vinyl acetate copolymer as adhesives and as additives to improve the hardness of polyolefin coatings. The synthesized linear polyester waxes from mixed aliphatic dibasic acids, reacted with glycol such as ethylene glycol, 1,3-

propanediol and 1,4-butanediol which had excellent properties in coating compositions for paper or metal foils. Moreover, in the same year, McConnell, prepared the linear polyester waxes by reacted 1,12-dodecanedioic acid with glycols such as ethylene glycol, 1,3-propanediol and 1,5-hexanediol, and obtained linear polyester waxes which may be viscous liquids, amorphous or semicrystalline solid with melting points less than about 100°C. These products were as useful as the new branched polyester waxes that discuss above. In many applications, the synthetic ester waxes were the important component used in cosmetic make up (e.g., propylene glycol monomyristate and myristyl myristate) [18], in hot melt jet ink [19], used to improve the extrudability of vinylidene chloride interpolymer (e.g., fatty ester and glycol esters) by decreasing the particulate degradation in the extrudate [20], and used in solid marking composition as a plasticizer which the solid marking composition was suitable for used in writing instruments [21, 22].

In 1995, Kawin Phattanaphakdee had synthesized the lubricating base oils from palm oil by transesterification with alcohol such as 1-butanol, 1-hexanol. The result was the synthetic monoester that had a good properties to be used as a lubricating base oil [1]. In 1996, Darunee Tubthim synthesized diester lubricating base oils by esterification of palm oil and its free fatty acid, e.g., oleic acid, stearic acid and palmitic acid with 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 2,2-dimethyl-1,3-propanediol, 2-ethyl-1,3-hexanediol. The products were obtained in two states, i.e., liquid state and solid state. Due to unable to determine the physical properties of the solid products, so these diesters were unsuitable for used as automotive lubricating base oil. However, every product from esterification and transesterification with 2-ethyl-1,3-hexanediol were liquid state that had the properties suitable to use as automotive lubricating base oil [2].

Thus this present study was concentrated on the solid diester products from fatty acids with glycols by esterification using concentrated sulfuric acid as catalyst. Because of the glycol diesters of some fatty acids had a characteristic similar to the waxy solid, so they were expected to be used in many applications e.g., as lubricants, as a plasticizer, as emulsifier, as friction modifier and as antifoaming agents.

These synthetic diester waxes were used to blend with the base oil as additives in order to study the new applications of these waxes, and then studied the properties of the lubricants, such as foaming, viscosity index, kinematic viscosity, flash point and pour point, compared with the properties of the base oil.