

## CHAPTER II

### THEORY AND LITERATURE REVIEWS

Temperature Rising Elution Fractionation (TREF) has been known as the most effective method for polyolefin fractionation, such as PE and PP. These polymers are semi-crystalline and show various degrees of branching distribution which affects on their solubility. Unfortunately the drawback of preparative TREF is that it is time-consuming, particularly, in the crystallization step. To solve this problem, the use of mixed solvents for crystallization has been attempted. LLDPE resins produced commercially from ethylene and various comonomers such as 1-butene, 1-hexene and 1-octene were used in this study. It was found that the total analysis time depended on the strength of solvent used in the crystallization step.

Temperature Rising Elution Fractionation (TREF) is the most efficient technique [4] generally used for separating non-volatile materials. TREF is composed of two sequential steps as described in Figure 1, namely crystallization and elution. In the first step, the polymer is dissolved in a suitable solvent and then put in contact with an inert support [5]. The crystallization is carried out under well controlled conditions by slowly decreasing the temperature. In the elution step, solvent flows through a column packed which the polymer coated the inert support while the temperature is raised stepwise at an interval. Recently, there are many research reports that have successfully used the preparative TREF to determine the short chain branching density of ethylene/ $\alpha$ -olefin copolymers which used the long time in the crystallization step. Since the cooling rate is

## 2.1 Waxes

Wax [6] usually refers to a substance that is a plastic solid at ambient temperature and on being subjected to moderately elevated temperatures, becomes a low viscosity liquid. Because of its plastic nature, wax usually deforms under pressure without the application of heat. The chemical composition of waxes is complex: they usually contain a broad variety of molecular weight species and reactive functional groups, although some classes of mineral and synthetic waxes are composed totally of hydrocarbon compounds.

### Classification of waxes

1. Insect and animal waxes.
2. Vegetable waxes e.g., candelilla, carnauba, japan wax, Douglas-fir bark wax, rice bran wax, jojoba, castor wax, and barberry wax.
3. Mineral waxes e.g., montan wax, peat waxes, ozokerite and ceresin waxes, and petroleum wax.
4. Synthetic waxes e.g., polyethylene waxes, Fischer-Tropsch waxes, Chemically modified hydrocarbon waxes, and substituted amide waxes.

For centuries, the honeycomb of bees, i.e., beeswax, was the material commonly referred to as wax. Substances having typical wax characteristics have traditionally come from insects, e.g., beeswax; from vegetables, e.g., carnauba. and from animal, e.g., spermaceti, origins. Waxes from mineral and synthetic Supplies have been developed both as substitutes for waxes from traditional Supplies and for new applications. Waxes

from minerals and synthetic Supplies now surpass waxes from traditional Supplies in tonnage and commercial importance.

Waxes[7] obtained from natural Supplies such as vegetables or insects are subject to weather conditions, which may severely affect the stability of supply and price and, to a lesser extent, the consistency of the products. Waxes from minerals and synthetic Supplies are less susceptible to weather conditions, and thus have a more stable supply and price structure.

### **2.1.1 Insect and animal waxes**

#### **Beeswax.**

Beeswax has been known for over 2000 years, especially through its use in the fine arts. Beeswax is secreted by bees and is used to construct the combs in which bees store their honey. Removing the honey and melting the comb in boiling water harvests the wax; the melted product is then filtered and cast into cakes. The yellow beeswax cakes can be bleached with oxidizing agents to white beeswax, a product much favored in the cosmetic industry.

The composition of beeswax varies, depending on its geographic origin. The major components are esters of  $C_{30}$  and  $C_{32}$  alcohols with  $C_{16}$  acids, free  $C_{25}$  to  $C_{31}$  carboxylic acids, and  $C_{25}$  to  $C_{31}$  hydrocarbons. Beeswax typically has a melting point of  $64\text{ }^{\circ}\text{C}$ , a penetration (hardness) of 20 dmm at  $25\text{ }^{\circ}\text{C}$  and 76 dmm at  $43.3\text{ }^{\circ}\text{C}$  (ASTM D1321), a viscosity of  $1470\text{ mm}^2/\text{s}$  at  $98.9\text{ }^{\circ}\text{C}$ , an acid number of 20, and a saponification number of 84.

The major use of beeswax is in the cosmetic industry, with smaller amounts used in pharmaceuticals and candle production.

## **Spermaceti.**

Spermaceti is derived from the head oil of the sperm whale. Owing to the present status of the sperm whale as an endangered species, however, the material is no longer an item of commerce and has been replaced by other natural and synthetic waxes.

### **2.1.2 Vegetable waxes**

#### **Carnauba.**

The source of carnauba wax is the palm tree, whose wax-producing stands grow almost exclusively in the semiarid northeast section of Brazil. Carnauba wax forms on the fronds of the palm, and is removed by cutting the fronds, drying, and mechanically removing the wax. Impurities are removed from the wax by melting and filtering or centrifuging. Wide fluctuations in price and availability have caused markets served by carnauba wax to seek replacements. Whereas there is no other single wax, which combines all the properties of carnauba, suitable substitutes are available for most applications.

The major components of carnauba wax [8] are aliphatic and aromatic esters of long-chain alcohols and acids, with smaller amounts of free fatty acids and alcohols, and resins. Carnauba wax is very hard, with a penetration of 2 dmm at 25 °C and only 3 dmm at 43.3 °C. Carnauba also has one of the higher melting points for the natural waxes at 84 °C, with a viscosity of 396 mm<sup>2</sup>/s at 98.9 °C, an acid number of 8, and saponification number of 80.

The hardness and high melting point, when combined with its ability to disperse pigments such as carbon black, allows Carnauba wax increasing use in the thermal printing inks. Carnauba is also widely used to gel organic solvents and oils, making the

wax a valuable component of solvent and oil paste formulations. Carnauba polishes to a high gloss and thus is widely used as a polishing agent for items such as leather, candies, and pills. Other uses include cosmetics and investment casting applications.

### **Candelilla.**

Candelilla wax is harvested from shrubs in the Mexican states of Coahuila and Chihuahua and, to a very small degree, in the Big Bend region of Texas in the United States. The entire mature plant is uprooted and immersed in boiling water acidified with sulfuric acid. The wax floats to the surface and is filtered. The major components of Candelilla wax are hydrocarbons, esters of long-chain alcohols and acids, long-chain alcohols, sterols, and neutral resins, and long-chain acids. Typically, Candelilla wax has a melting point of 70 °C, a penetration of 3 dmm at 25 °C, an acid number of 14, and saponification number of 55. Principal markets for Candelilla include cosmetics, foods, and pharmaceuticals

### **Japan wax.**

Japan wax is a fat and is derived from the berries of a small tree native to Japan and China cultivated for its wax. Japan wax is composed of triglycerides, primarily tripalmitin. Japan wax typically has a melting point of 53 °C, an acid number of 18, and a saponification number of 217. Principal markets include the formulation of candles, polishes, lubricants, and as an additive to thermoplastic resins. The product has some food-related applications.

**Ouricury wax.**

Ouricury wax is a brown wax obtained from the fronds of a palm tree, which grows in Brazil. Ouricury is difficult to harvest, as it does not flake off the frond as does carnauba wax; rather, it must be scraped free. Ouricury is sometimes used as a replacement for carnauba in applications that do not require a light-colored wax.

**Rice bran wax.**

Rice-bran wax is extracted from crude rice-bran oil. It can be degummed, the fatty acid content reduced by solvent extraction, and bleached. The wax is primarily composed of esters of lignoceric acid (~43 wt %), behenic acid (16 wt %), and C<sub>22</sub>-C<sub>36</sub> alcohols (28 wt %).

**1. Origin**

Rice wax is a vegetable wax extracted from rice bran while extracting rice bran oil. As a by-product at a refining of rice bran oil from rice bran, it is potentially a treasure biological wax resource in East Asia where rice is one of the most important cereal. The wax has no odor and bleaches readily. Its impurities can be eliminated easily. It has many applications.

**2. Component**

Up to now there has been many research efforts and reports concerning rice wax. The main component of rice wax is ester composed of senior fatty acid and senior mellowness. The range of carbon element is limited, so the fat of this ester is mainly composed of C<sub>22</sub>-C<sub>24</sub>, the senior ester is C<sub>24</sub>-C<sub>34</sub>. DSC (differential scanning calorimeter)

testing indicates that when the rice wax melts, the peak of each part is very steep.

According to this result, we can conclude that rice wax possesses high crystallinity.

### 3. Application

(1) Long before people had used rice wax for skin maintenance, coating for furniture and abacus, and so on.

(2) It is firstly used as the raw materials for cosmetics making. Now the wax is used more for food wrapping paper, insulating agents, polishing agents. Rice wax is also widely used in the high technology areas where properties such as biodegradability, resolvability, agglutination, are important for plastic lubricants, information record materials and so on

#### **Jojoba.**

Jojoba oil is obtained from the seeds of the jojoba plant grown in semiarid regions of Costa Rica, Israel, Mexico, and the United States. The oil is made up of ca 80 wt % of esters of eicos- 11-enoic and docos- 13-enoic acids, and eicos-11-en-1-ol, and docos-13-en-1-ol, ca 17 wt % of other liquid esters, with the balance being free alcohols, free acids, and steroids. Jojoba oil is used primarily in the formulation of cosmetics. Hydrogenated jojoba oil is a wax used in candles and other low volume specialty applications.

#### **Castor wax.**

Castor wax is catalytically hydrogenated castor bean oil. The wax has a melting point of 86 °C, acid number of 2, saponification number of 179, and an iodine number of 4. Castor wax is used primarily in the formulation of cosmetics. Derivatives of castor wax are used as surfactants and plastics additives.

**Bayberry wax.**

Bayberry wax is isolated from the surface of the berry of the bayberry (myrtle) shrub by boiling the berries in water and skimming the wax from the surface of the water. The wax is green and made up primarily of lauric, myristic, and palmitic acid esters. The wax has a melting point of 45°C, an acid number of 15, a saponification number of 220, and an iodine number of 6. The wax has an aromatic odor and is used primarily in the manufacture of candles and other products where the distinctive odor is desirable.

**2.1.3 Mineral waxes [9]****Montan wax.**

Montan wax is derived by solvent extraction of lignite. The earliest production on a commercial scale was in Germany during the latter half of the nineteenth century, and Germany continues to supply the majority of the world's production of Montan wax. Montan wax production at Amsdorf is part of a massive coal-mining operation from a continuous vein and raw material is expected to last for decades.

The composition of Montan wax depends on the material from which it is extracted, but all contain varying amounts of wax, resin, and asphalt. Black Montan wax may be further processed to remove the resins and asphalt, is known as refined Montan wax. White Montan wax has been reacted with alcohols to form esters. The wax component of Montan is a mixture of long. chain ( $C_{24}$ - $C_{30}$ ) esters (62-68 wt %), long-chain acids (22-26 wt %), and long. chain alcohols, ketones, and hydrocarbons (7-15 wt %). Crude Montan wax from ~ Germany typically has a melting point of 80°C, an acid number of 32, and a saponification number of 92.

The largest traditional use for Montan waxes was as a component in on~ time hot-



melt carbon-paper inks. With the decrease in the use of carbon-paper inks, uses for the refined grades have become predominant, mainly in the formulation of polishes and as plastics lubricants.

#### **Peat waxes.**

Peat waxes are much like Montan waxes in that they contain three main components: a wax fraction, a resin fraction, and an asphalt fraction. The amount of asphalt in the total yield is influenced strongly by the solvent used in the extraction. Montan waxes contain 50 wt % more of the wax fraction than peat waxes, and correspondingly lower percentages of the resin and asphalt fractions. The wax fraction in peat wax is chemically similar to that of the wax fraction in Montan wax.

#### **Ozokerite and ceresin waxes.**

Ozokerite wax was a product of Poland, Austria, and in the former USSR where it was mined. True ozokerite no longer seems to be an article of commerce, and has been replaced with blends of petroleum-derived paraffin and microcrystalline waxes. These blends are designed to meet the specific physical properties required by the application involved.

Ceresin wax originally was a refined and bleached ozokerite wax, but now is a paraffin wax of very narrow molecular weight distribution or blend of petroleum waxes.

#### **Petroleum waxes.**

Waxes derived from petroleum are hydrocarbons of three types: paraffin (clay-

treated); semi microcrystalline or intermediate; and microcrystalline (clay-treated). Semi-microcrystalline waxes are not generally marketed as such. Others include acid-treated, chemically neutralized, and hydro treated; and paraffin and hydrocarbon waxes, untreated. The quality and quantity of the wax separated from the crude oil depends on the source of the crude oil and the degree of refining to which it has been subjected prior to wax separation. Petroleum waxes are produced in massive quantities throughout the world. Subject to the wax content in the crude, paraffin and, to a substantially lesser degree, microcrystalline waxes are produced in almost all countries of the world that refine crude oil.

A paraffin wax is a petroleum wax consisting principally of normal alkanes. Microcrystalline wax is a petroleum wax containing substantial proportions of branched and cyclic saturated hydrocarbons, in addition to normal alkanes. Semi microcrystalline wax contains more branched and cyclic compounds than paraffin wax, but less than microcrystalline. A classification system based on the refractive index of the wax and its congealing point as determined by ASTM D938 was developed.

**Table 1.** Typical Properties of Petroleum Waxes

Properties	Paraffin wax	Microcrystalline
Flash point, closed cup, °C	204	260
Viscosity at 98.90°C, mm <sup>2</sup> /s	4.2-7.4	10.2-25
Melting range, °C	46-68	60-93
Refractive index at 98.9°C	1.430-1.433	1.435-1.445
Number average molecular weight	350-420	600-800
Carbon atoms per molecule	20-36	30-75

Ductility crystallinity of solid wax	Friable to crystalline	Ductile-plastic to tough-brittle
Value is minimum.		

Paraffin wax is macro crystalline, brittle, and is composed of 40-90 wt % normal alkanes, with the remainder  $C_{18}$ - $C_{36}$  isoalkanes and cycloalkanes. Paraffin wax has little affinity for oil content: fully refined paraffin has less than 1 wt %; crude scale, 1-2 wt %, and slack above 2 wt %. Within these classes, the melting point of the wax determines the actual grade, with a range of about 46-71°C. Typical properties of petroleum waxes are listed in Table 1.

The separation of paraffin wax from crude oil occurs during distillation, as shown in Table 1. The distillate is processed to remove oil to the degree desired through solvent extraction. It is then decolorized, usually by hydrogenation, but percolation through bauxite is also used. Microcrystalline wax is produced either from the residual fraction of crude oil distillation or from crude oil tank bottoms. After deasphalting of the residual fraction, heavy lubricating oil is removed by solvent extraction. The degree of solvent extraction is dictated by the economics of the lubrication oil market. The filtrate is crude petrolatum, a dark-colored, unctuous material containing oil and microcrystalline wax. Percentages of each may vary, but are usually about 40 wt % wax and 60 wt % oil. This material is then solvent-extracted for the wax. Because microcrystalline wax has great affinity for oil, the oil content of the wax is 1-4 wt %, depending on the grade of the wax. Unlike paraffin wax, oil is held tightly in the crystal lattice of the microcrystalline wax, and does not migrate to the surface. The microcrystalline waxes obtained from petrolatums are generally known as plastic grades, with penetrations greater than 11 dmm

at 25°C. Crude oil contains high molecular weight fractions, which are soluble at the high temperatures found in underground formations, but not very soluble at ambient conditions once the crude oil is produced. These high molecular weight fractions precipitate onto the walls and floors of storage tanks, and are known as crude oil tank bottoms. The microcrystalline waxes obtained from crude oil tank bottoms are generally known as hard grades, with penetrations less than 11 dmm at 250°C.

Petroleum waxes are also widely used in other industrial applications. Paraffin waxes are added to rubber during compounding, and exude to the surface during curing, which helps protect the rubber from degradation resulting from ozone. Paraffin and other waxes can be added to plastics, especially poly (vinyl chloride) (PVC) as lubricants. Both paraffin and microcrystalline waxes are widely used to help control the properties of hot-melt adhesives. Dispersions of microcrystalline are added to ink to improve slip and rub properties. Petroleum waxes are used in many consumer applications such as cosmetics, polishes, and candles. Unrefined petroleum waxes are often used in fireplace logs.

#### **2.1.4 Synthetic waxes**

##### **Polyethylene waxes.**

Low molecular weight (less than 10,000 Mn) polyethylenes having wax like properties are made either by high-pressure polymerization or low-pressure (Zeigler-type catalysts) polymerization. All the products have the same basic structure, but the processes yield products with distinctly different properties. Some polyethylenes have fairly low density owing to branching that occurs during the polymerization. Molecular weight distributions, expressed as the weight average molecular weight divided by the number average molecular weight, or polydispersity, also varies widely among the

different processes, as does the range of molecular weights available.

Differences among the processes have a major impact on the use of the products. Products from a particular process or manufacturer may dominate one market, while products from a different process may be preferred in a different application. Major uses include hot-melt adhesives for applications requiring high temperature performance, additives to improve the processing of plastics, slip and rub additives for inks and paints, and cosmetic applications.

Products used in food applications require regulatory approvals. This regulation includes a maximum amount of hexane-soluble material with other requirements. The amount of material extracted by hexane is a function of molecular weight and branching polyethylenes in the 500-1200-molecular weight range. In addition to molecular weight requirements, this regulation includes an absorbance test to verify the suitability of the product for food applications.

Some by-product polyethylene waxes have been recently introduced. The feedstock for these materials is mixtures of low molecular weight polyethylene fractions and solvent, generally hexane, produced in making polyethylene plastic resin. The solvent is stripped from the mixture, and the residual material offered as polyethylene wax. The products generally have a wider molecular weight distribution than the polyethylene waxes synthesized directly, and are offered to markets able to tolerate that characteristic. Some of the by-product polyethylene waxes are distilled under vacuum to obtain a narrower molecular weight distribution.

Several of the polymerization processes allow different functionality to be added to the backbone of the polymer, including copolymers of ethene, propene, hexene, vinyl

acetate, and acrylic acid, with wax-like properties. Copolymers of ethene with other olefins provide a method of extending the range of properties available. The addition of other olefins creates a branched polymer, which decreases the melting point and hardness, while increasing viscosity as compared to a linear polyethylene of the same molecular weight distribution. Longer branches created through the addition of hexene show a larger effect than those from propene. Copolymers with vinyl acetate and acrylic acid provide a method of introducing oxygen functionality. These products may be further reacted with metal salts to form ionomers.

In addition to copolymerization, polyethylene's terminated as ketones. Alcohols, and carboxylic acids with molecular weights as high as 700 Daltons are now available. The products offer the same chemical functionality as common fatty alcohols and acids, but are higher melting and harder. Similar to the fatty alcohols and acids, derivatives such as ethoxylates, esters, and amides also are available as higher melting versions of the fatty derivatives.

Functional polyethylene waxes provide both the physical properties obtained by the high molecular weight polyethylene wax and the chemical properties of an oxidized product, and one derived from a fatty alcohol or acid. The functional groups improve adhesion to polar substrates, compatibility with polar materials, and dispersibility into water. Uses include additives for inks and coatings, pigment dispersions, plastics, cosmetics, toners, and adhesives.

**Fischer tropesch waxes.**

Polyethylene wax production is based on the Fischer-Tropsch synthesis, which is basically the polymerization of carbon monoxide under high pressure and over special catalysts to produce hydrocarbons. Distillation is then used to separate the hydrocarbons into different products, including liquid fuels and waxes with melting points ranging from about 45-106°C. Currently the waxes are produced in large volumes in South Africa and Malaysia, with an estimated 12,000-14,000 ton consumed in the United States in 1994. Uses are similar to those for polyethylene waxes, including hot-melt adhesives and additives for inks and coatings.

**Chemically modified waxes.**

Hydrocarbon waxes of the microcrystalline, polyethylene, and polyethylene classes are chemically modified to meet specific market needs. In the vast majority of cases, the first step is air oxidation of the wax with or without catalysts. The product has an acid number usually no higher than 30 and a saponification number usually no lower than 25. An alternative step is the reaction of the wax with a polycarboxylic acid, e.g., maleic, at high temperature. Through its carboxyl groups, the oxidized wax can be further modified in such reactions as saponification or esterification. Oxidized wax is easily emulsified in water through the use of surfactants or simple soaps, and is widely used in many coating and polish applications.

**Substituted amide waxes.**

The product of fatty acid amidation has unique wax like properties. Probably the

most widely produced material is N,N'-distearylethylenediamine, which has a melting point 140°C, an acid number 7, and a low melt viscosity. Because of its unusually high melting point and unique functionality, it is used in additive quantities to raise the apparent melting point of thermoplastic resins and asphalts, as an internal-external lubricant in the compounding of a variety of thermoplastic resins, and as a processing aid for elastomers.

### **Polymerized olefins.**

Some polymers of higher  $\alpha$ -olefins, e.g.,  $C > 20$ , have wax like properties and are sold as synthetic waxes. The polymerization process yields highly branched materials, with broad molecular weight distributions. Properties of the individual products are highly dependent on the  $\alpha$ -olefin monomers and polymerization conditions. Melting points for the products range from 54 °C to 74 °C, with number average molecular weights 2600-2800, and penetrations at 25°C of 5-12 dmm. The unique structure makes these products very effective when used in additive amounts to modify the properties of paraffin wax, primarily for use in candles. The products can increase the hardness and opacity of the paraffin, without increasing the cloud point or viscosity. Other uses include mold release for polyurethane foams, additives for casting wax, and additives for leather treating.

### **2.2 Analytical techniques [10]**

Most waxes are complex mixtures of molecules with different carbon lengths, structures and functionality. Attempts to measure the exact chemical composition are extremely difficult, even for the vegetable waxes, which are based on a relatively few



number of basic molecules. Products such as oxidized microcrystalline wax not only have a mixture of hydrocarbon lengths and types as starting materials, but also add complexity through the introduction of various types of carboxylic functionality onto those hydrocarbons during the oxidation process.

Because of the difficulty in analysis of chemical composition, most of the routine test procedures on waxes are for the measurement of the physical properties of the waxes and are used to compare the properties of waxes within a class. Some properties, such as acid number or saponification number, give insight into the chemical functionality of the product, and are widely used for products, which contain carboxyl groups such as vegetable, Montan, and oxidized waxes. Increasingly, instrumental methods such as gas chromatography (GC), gel permeation (also known as size exclusion) chromatography (GPC), refractive index (RI), differential scanning calorimetry (DSC), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR) are being used to further characterize the products. Properties such as molecular weight distribution, degree of branching, degree of crystallinity, and functionality can be readily measured with these techniques.

### **2.2.1 Melting and congealing Points.**

Selection of the proper melting point method depends upon the characteristics of the wax. Drop melting point (ASTM D127) is suitable for amorphous waxes, e.g., microcrystallines, but is not reliable for higher viscosity synthetic waxes, for which ring-and-ball softening point (ASTM D36) should be used. ASTM D87 may evaluate waxes whose time-temperature cooling curves exhibit plateaus, e.g., paraffin wax. Open or

closed capillary tubes are used to measure the melting point of many of the natural waxes. The congealing point (ASTM D938) is the temperature at which a melted wax ceases to flow, and is more consistent than melting points for some waxes.

### **2.2.2 Hardness**

The standard test for the hardness of waxes in industry is the penetration test (ASTM D1321). 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. A series of penetrations measured at different temperatures, rather than at a single temperature, is preferred.

### **2.2.3 Color.**

On solidification of a wax and depending on factors such as the rate of cooling, the amount of occluded air, and surface finish, the color of solidified samples of the same wax may be different. For this reason, the color of most waxes is judged only while molten, although some commercial standards for certain waxes, e.g., carnauba, are based on the color of the solid wax. The accurate measurement of color in light-colored, i.e., amber to off-white to white, waxes is difficult but very important because of the additional processing costs required to achieve the light color. The two most widely used color standards providing numerical measurement 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.

#### **2.2.4 Oil content.**

The production of petroleum waxes involves the removal of oil; therefore, the oil content (actually the percentage of oil and low molecular weight fractions) is one indication of the quality of the wax. Oil content is determined (ASTM D721) as that percentage of the wax soluble in methyl ethyl ketone at  $-31.7^{\circ}\text{C}$ .

#### **2.2.5 Viscosity.**

Although traditionally of little importance in the evaluation of vegetable and insect waxes, viscosity is an important test for mineral and synthetic waxes. One of the most frequently used tests, ASTM D88, is used to measure the time in seconds required for a specified quantity of wax at a specified temperature to flow by gravity through an orifice of specified dimensions. This viscosity is expressed in Saybolt Universal Seconds (SUS) at the temperature of the test. The SI unit for kinematic viscosity is  $\text{mm}^2/\text{s}$  (=cSt).

#### **2.2.6 Acid number.**

The acid number (ASTM D1386) is the milligrams of potassium hydroxide necessary to neutralize one gram of wax, and indicates the amount of free carboxylic acid present. The test is widely used for vegetable and insect waxes, and synthetic waxes containing carboxylic acid groups.

#### **2.2.7 Saponification number.**

The saponification number (ASTM D1387) is the milligrams of potassium hydroxide, which react with one gram of wax under elevated temperatures, and indicates

the amount of free carboxylic acid plus any ester materials, which may be saponified. Both the acid number and saponification numbers are generally provided to give an indication of the free carboxylic acid and ester content of vegetable and insect waxes, and synthetic waxes containing carboxylic acids and or esters.

### **2.2.8 Differential scanning calorimetry (DSC).**

The DSC has become widely used to characterize waxes. Under controlled heating and cooling rates, the amount of energy consumed or released is measured. Curves of heat flow v/s temperature provide insight into the thermal characteristics of a wax, including crystalline transitions such as solid-to-solid, solid-to-liquid, and liquid-to-solid. Common values obtained from the curves include the initial and ending temperatures for heat flow, and heat of fusion, expressed as joules per gram.

### **2.2.9 Gas chromatography (GC).**

Gas chromatography has been used for many years, especially on the relatively simple structures of vegetable and insect waxes. Use of the GC for petroleum and synthetic waxes was limited by the maximum carbon number which could be eluted, and the number of isomers for each carbon number. Improvements in technology have allowed wider use of this technique, with columns and equipment available, which can resolve carbon numbers up to C<sub>100</sub>. Good resolution can be obtained on products with generally only one type of structure, e.g., paraffins with a high preponderance of primary alkanes. Products such as microcrystalline wax, which contain several different branched isomers for each carbon number, plus some cyclic compounds, cannot be completely

resolved, although useful information can still be obtained.

#### **2.2.10 Gel permeation chromatography (GPC).**

The GPC (also known as size exclusion chromatography) is widely used to measure the molecular weight distribution for synthetic polyethylene waxes. Whereas GPC cannot match the resolution available in GC techniques, useful information regarding the molecular weight, and molecular weight distribution can be obtained for products with molecular weights too high for gas chromatography. The molecular weight is normally reported using the number average,  $M_n$ , or the weight average,  $M_w$ . The ratio of the weight average to the number average is known as the polydispersity.

#### **2.2.11 Infrared spectroscopy (FT-IR).**

Infrared curves are used to identify the chemical functionality of waxes. Petroleum waxes with only hydrocarbon functionality show slight differences based on crystallinity, while vegetable and insect waxes contain hydrocarbons, carboxylic acids, alcohols, and esters. The IR curves are typically used in combination with other analytical methods such as DSC or GC/GPC to characterize waxes.

#### **2.2.12 Nuclear magnetic resonance (FT-NMR).**

The FT-NMR analysis has been used in the polymer industry to measure properties such as amount and type of branching, polymerized ethylene oxide content, and hydroxyl content. The same techniques are applicable to waxes, and are used for both characterization and quality control.