WAXES

1. Introduction

Waxes is a term deriving from the old English "weax" for the honeycomb of the beehive. That natural compound was used in the ancient time since its uses were quoted in the Roman times by Pliny (23–79 AD) and Virgil, but was already used by the Egyptians in funeral ceremonies. It can be also considered as the man's first plastic used to make writing tablets and models in Egypt. The first analyses have shown that beeswax was made of fatty acid esters of fatty alcohols. This academic definition is yet used to a restricted part of waxes, the wax esters, the others having various chemical structures. Now, for the wax chemist, waxes are usually defined by their physical properties more than by their chemical properties. Thus, the German Society for Fat Technology described wax as "a collective term for a series of natural or synthetically produced substances that possess the following properties: kneadable at 20°C, brittle to solid, coarse to finely crystalline, translucent to opaque, relatively low viscosity even slightly above the melting point, not tending to stringiness, consistency, and solubility depending on the temperature, and capable of being polished by slight pressure".

Although these properties can be given in a generalized form, it is convenient to subdivide waxes into natural and synthetic waxes. The former may be again subdivided into animal, vegetal, bacterial, and mineral waxes.

Animal waxes include either waxy depots (wax of honeycomb, spermaceti of the sperm whale, the fatty depot of planktonic crustacea), or waxy coatings or secretion (surface lipids of insects, skin lipids, wool wax, uropygial secretion of birds).

Vegetal waxes include the apolar lipids found in the outer layers of plants (cuticle, epicuticular wax), which help to prevent water loss and insect attack, but also those stored in some seeds (jojoba oil).

Microbial waxes (or cerides) are ester wax with the fatty acid or the alcohol component or both may have complex structures. They were mainly studied in tubercle bacteria.

Some waxes are of mineral origin, the most known being Montan wax. That fossilized compound represents a late step of the transformation of vegetal into hydrocarbon.

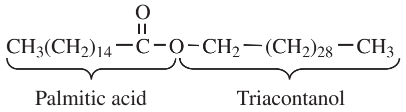
To ensure a constant supply and definite chemical and physical characteristics, chemists have synthesized several waxy substances that range through polyethylenes, alkyl esters, Fischer-Tropsch waxes, fatty amides, and polyethylene glycols. Commercialized waxes, either natural or of synthetic origin, are mainly used in industry, but also cosmetics and pharmaceutics.

As said above, the various materials named waxes do not form a chemically homogeneous group. They are made up of various substances including monoesters (wax esters), hydrocarbons, ketones, alcohols, aldehydes, acids, sterol esters, terpenes. All these substances have long or very long carbon chains (from 12 up to ~38 carbon atoms) and are solid in a large range of temperature (60–100°C).

2. Wax Constituents

Among the numerous wax components, the most important in commercial waxes are described below. We have included acids and alcohols, frequently found in an esterified form (wax esters), hydrocarbons, and ketones. The compositions of waxes may also include aldehydes, terpenes, and phenolic substances as minor compounds.

2.1. Wax Esters and Polyesters. These waxes are esters of a long-chain acid and an alcohol other than glycerol. The alcohol may be a long-chain alcohol, a sterol, a terpenoid, a hydrocarotenoid, or the vitamin A. The most frequent combination is a fatty acid esterified by an alcohol. Examples of wax esters are dodecylhexadecanoate (lauryl palmitate), octadecyl octadecanoate (stearyl stearate), etc. The structure of the main component of beeswax, triacontanyl palmitate, is given below.

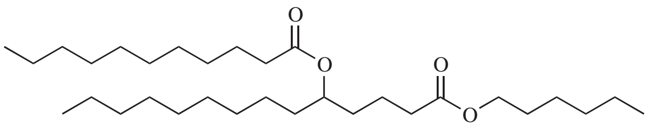


$$\underbrace{CH_3(CH_2)_{14}-\overset{\overset{O}{\|}}{C}-}_{\text{Palmitic acid}}\underbrace{O-CH_2-(CH_2)_{28}-CH_3}_{\text{Triacontanol}}$$

The acid or the alcohol chain may be unsaturated and some wax esters may be mono- or dihydroxylated enabling the construction of a polyester structure where the cross-linking depends on the availability of secondary hydroxyl groups.

In plants, monoesters are an ubiquitous class of lipids (up to 80% of the whole wax) found in almost all the outer surface. Saturated long-chain acids (C12−C30) and alcohols (C20−C32) are very common and thus, the total chain lengths cover the C34−C62 range. In some waxes, the acid moiety is unsaturated.

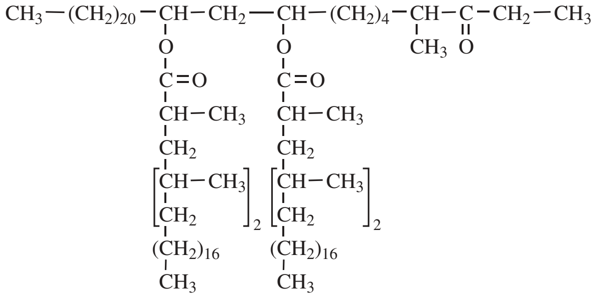
Uncommon esters are constituted by benzoic acid esterified with C22−C26 alcohols (1). There are several types of diesters, but the most frequent, the estolides, are formed from a hydroxyalkanoic acid (C12−C18) esterified with a similar molecule or from a normal fatty acid esterifying a long-chain diol. Complex structures made of various combinations of diols, hydroxy acids, and fatty acids have been identified in the needle surface lipids of conifer species and were shown to have molecular weights in the range of ∼800−1500 (2). An example of an estolide is given below.



In insects, wax esters have been described as predominant compounds (up to 80%) of the lipids spread on the body surface or secreted by specialized glands. These waxes are characterized by long-chain alcohols (up to C34), oxoalcohols or very long-chain methyl-branched alcohols (up to C44 with one, two or three methyl branches) esterified to short- (from acetate) to long-chain (up to C26) fatty acids.

Oceanic zooplankton species are known for the storage of wax esters as natural energy reserves. The calanoid copepods have a large sac in which wax is stored, the total reserve amounting up to 70% of the animal's dry weight. It is thus estimated on a worldwide basis that about one-half of all the organic substances synthesized by the phytoplankton is converted by the zooplankton for a time into wax. It has been established that waxes were used during the reproductive process under starved conditions (3). The wax of copepods that live in surface waters is rich in C20–C22 alcohols, whereas the wax in copepods that live in the depths is characterized by C16 alcohols, which remain liquid at low temperatures. In Arctic and Antarctic zooplankton, the high energy wax esters have long-chain monounsaturated fatty acids and alcohols (C20–C22) as major components (4). Furthermore, it has been shown that carnivorous zooplankton species are characterized by the presence of short-chain alcohols (C14–C16), whereas herbivorous species, as the calanoid copepods, contain mainly long-chain alcohols (C20:1–C22:1). Wax esters may play an important role in the buoyancy control in fish and mainly in species with regressed swim bladders, where wax esters comprise up to 90% of total fish lipids (5).

Waxes are not common constituents of bacteria, but have been described only in some species (*Acinetobacter, Moraxella, Corynebacterium, Mycobacterium*). Unique waxes are found in the cell envelope of mycobacterial species including the tubercle bacillus *Mycobacterium tuberculosis* (6). These waxes, named mycoserosates, are composed of a branched-chain alcohol (phthiocerol) esterified with long-chain and methylated fatty acids. The branched-chain alcohol may have 34 or 36 carbon atoms with hydroxyl groups in positions 9 and 11, or 11 and 13. The fatty acids have a chain length from C18–C26 and with two to four methyl branches that may occur at the 2, 4, 6, and 8 positions. One of these forms is shown below.



These waxes have been shown to be involved in the pathogenicity of the tubercle bacillus (7). *Acinetobacter* has been shown to accumulate a large amount of hexadecyl hexadecanoate (0.17 g/g dried cells) from hexadecane as substrate (8). The microbial production of wax esters has advantages over other sources since their composition can be experimentally controlled (9). Recently, the report on the biosynthesis of jojoba oil-like wax esters in engineered *Escherichia coli* opened new perspectives for the biotechnological production of waxes from inexpensive resources (10).

2.2. Hydrocarbons. Plant surface lipids may contain various amounts of straight-chain alkanes (from traces to 50%). The high range of chain length (from C15 to C38) of these ubiquitous components was the basis of their use as chemotaxonomic indicators. Branched alkanes have been isolated from plant surface lipids, but only in small percentages.

In insects, the amount of long-chain alkanes may vary from trace amounts to 100% of the surface lipids. In contrast to plant waxes, insect waxes contain frequently alkenes, the dienes accounting for a high proportion. Methyl-branched alkanes are also more common in insects than in plants. They occur in a diversity of structures up to tetramethylated molecules. Besides physical functions, several hydrocarbons have been described as having sex attractant activity in insects.

Long and very long chain hydrocarbons have been described in crude oils (petroleum) that derive from marine or lacustrine source materials. The wax (or paraffin wax) present in petroleum crudes mainly consists of straight-chain hydrocarbons (80–90%). The balance consists of branched hydrocarbons (isoparaffins) and some naphtenic hydrocarbons (C30–C60). All these compounds with a carbon chain in the range C18–C36 may represent up to 8% of a whole oil. High temperature gas chromatography (gc) has revealed a wide range of hydrocarbons extending from C40 to C120 amounting to ∼2% in oil and concentrated in the fraction referred to as microcrystalline waxes predominantly solid at room temperature (11).

2.3. Fatty Acids.

A large range of fatty acids is found as component of wax esters (see above), but some free acids may also be isolated in plants. Free straight- and branched-chain fatty acids with 16–34 carbon atoms are present at various concentrations in plant waxes. In the wax covering sorghum leaves, fatty acids amount to ∼40% of the total lipids (12).

2.4. Alcohols.

If long-chain alcohols are known as components of plant and animal wax esters, they are found also in the free state. If free alcohols are absent in some plant species, they may amount, as in maize seeds, to ∼60% of the whole wax. They have generally an even straight chain in the C20–C34 range with one species dominant in some plants: C32 in maize, C28 in sugar cane, rice and corn, and C26 in barley. Free long-chain diols (27 and 29 carbon atoms) are mainly encountered in surface lipids of conifer trees (13), but diols with chain lengths ranging from C22 to C28 have been detected in leaf waxes of castor oil plants (14).

In insects, many descriptions of free alcohols in surface waxes have been reported since the first discovery of a C34 alcohol in a cochineal insect in 1885. Some insect waxes are composed up to 90% of long-chain alcohols (tria- and tetratriacontanol) or oxoalcohols.

2.5. Ketones.

Ketones were first discovered in the wax of cabbage leaves in 1934. Symmetrical ketones are found in the surface wax of many angiosperms. They have the common formula $[CH_3(CH_2)_n]_2$ C=O with $n = 2–20$. α-Diketones ($R_1{-}COCH_2CO{-}R_2$) are more frequent and have been described in waxes of numerous plants. Diketones with a 31 carbon chain were isolated from the leaves of cereals while those with a 33 carbon chain were isolated from leaves of *Eucalyptus* and *Acacia* species (15).

3. Animal Waxes

Commercial animal waxes are obtained mainly from insects, but mammalian skin and fat depots are also valuable sources. Insect waxes are cuticular or surface productions that either protect the animals from desiccation and various predators or are used to store honey and protect immature animals. In mammals, spermaceti from the sperm whale is officially no longer used, and wool wax secreted by sheep skin remains a valuable by-product of wool shearing.

3.1. Beeswax. White [8012-89-3] and yellow [8006-40-4] beeswax is an abdominal secretion of bees (*Apis mellifera*), which is used by insects to form the hive cells. Beeswax is a by-product of honey industry since ancient times. Its presence was detected in the wall pictures of the Lascaux cave (17,000 BC) and in Egyptian mummies (700 BC). In the Roman period, beeswax was used as a waterproofing agent and treatment for painted wall (100 BC). In the Middle Ages, beeswax was valuable and exchanged as a form of currency. Now, it is used as modeling material, as component of seals, coatings, polishes, and candles. References to wax prior to the nineteenth century are near exclusively to beeswax. The world production amounts to ~7000 metric tons/year, 60% being used in the cosmetic industry and in pharmaceuticals and candle production. The majority of beeswax is produced in Brazil, China, Thailand, and Canada.

Crude beeswax is produced by melting and filtration, impurities being removed by water washing. For cosmetic uses, bleaching may be processed by diatomaceous earth or carbon black treatment, chemical reactions (oxidizing agents) or ultraviolet (uv) exposition.

Chemical characteristics: Acid number is between 3 and 30, saponification number from 80 to 150, and iodine value from 7 to 16.

The composition of beeswax varies, depending on its geographic origin, but its main components are palmitate, palmitoleate, hydroxypalmitate, and oleate esters of long-chain alcohols (C30–C32). The total esters, with 36–54 carbon atoms, amount to 70–90% of the total weight. The ratio of melissyl palmitate (C30 alcohol esterified by C16 fatty acid) to cerotic acid (C26), the other major component of beeswax is 6:1. Ethyl esters are also present, the most abundant species being ethyl palmitate, ethyl tetracosanoate, and ethyl oleate (16). Free fatty acids amount from 12 to 15% and hydrocarbons from 10 to 15%. Hydrocarbons have saturated (from 15 up to 35 carbon atoms) or unsaturated (from 21 up to 35 carbon atoms) chain. Minor quantities of sterols, diols, and terpenoids are also found in low quantities. Beeswax is soluble in chloroform, diethyl ether and warm benzene.

Beeswax typically has a melting point of 64°C, a penetration (hardness) of 20 dmm at 25°C and 76 dmm at 43.3°C (ASTM D1321), a viscosity of 1470 mm^2/s at 98.9°C.

The FDA affirmed beeswax as Generally Recognized as Safe (GRAS) in 21 CFR 184-1973.

3.2. Chinese Wax. This wax is also known as insect wax. Chinese wax is deposited on the branches of certain trees by the scale insect, *Ceroplastes ceriferus*, common in China and India, or by another insect, *Ericerus pela*, in China and Japan.

Chinese wax is harvested by boiling in water animals and their secretions. About 1500 insects are needed to produce 1-g Chinese wax. It is used chiefly in the manufacture of polishes and candles.

Chemical Characteristics. Besides an important content in esters (~83%), Chinese wax includes some free alcohols (1% max), hydrocarbons (2–3%), and traces of free acids. Esters form chains with 46 up to 60 carbon atoms, the majority of alcohols and acids having 26 or 28 carbon atoms.

Chinese wax has a white or light-yellow crystalline aspect resembling spermaceti, but harder, more friable, and with a higher melting point (80–82°C).

3.3. Shellac Wax. Shellac wax [97766-50-2], known also as lac wax, is produced as a protective covering by a cochineal insect native of India, *Laccifer lacca*, which lives on trees called lac host trees. India and Thailand are the main countries where lac insects are cultivated.

As the scraped wax includes insects, twigs and lac dye, the whole product is crushed, washed, and dried. The clean wax is then converted into shellac by hand or machine after melting by steam heat and squeezing through filter by means of hydraulic presses. Exports from India (~50% of the world production) reached 40,000 tons in the recent years.

Commercial shellac wax is hard, brown, and has excellent shine-producing characteristics comparing with those of carnauba wax. Shellac wax is usually added to polishes to give a highly shining surface.

Chemical Characteristics. Shellac wax is mainly a mixture of fatty esters (70–82%), which are formed of chains of 28 up to 34 carbon atoms. The balance is composed of fatty alcohols (8–14%), fatty acids (1–4%), and hydrocarbons (1–6%). The acid number is 73–95, the saponification number is 185–210, and the iodine value is 10–18. The melting point is 115–120°C.

3.4. Spermaceti. Spermaceti [8002-23-4] is extracted from adipose tissues contained in the skull of a cachalot, *Physeter macrocephalus*, known as sperm whale. The frontal organ, used as a sonar by the animal, contains ~3 tons of spermaceti for a 15-m animal. The sperm oil drained from the skull is chilled at 0°C for several days to form a precipitate. The oil is eliminated by squeezing the whole mixture several times. The wax is then washed with water and crystallized as a white solid.

Spermaceti was used in medicine in England in the fifteenth century and later in cosmetics, pharmacy and also in candles. After the recent international regulation concerning whale captures, spermaceti is no longer produced and sold. It is replaced by synthetic wax made of pure cetyl palmitate or mixtures based on jojoba. The last usages of spermaceti were the treatment of leathers and lubrication.

Chemical Characteristics. Spermaceti contains a large amount of wax esters (65–95%), but also triglycerides (5–30%), free alcohols (1–5%), and acids (0–3%). Fatty esters are formed essentially of hexadecyl palmitate (C32) and hexadecyl myristate (C30). Spermaceti can be considered as the first wax chemically defined, first by Chevreul in 1823 and Dumas in 1835. Acid value is between 2 and 5, iodine value from 5 to 6, saponification number from 108 to 135. The melting point is from 42 to 50°C.

3.5. Wool Grease or Lanolin. This lipid mixture [8006-54-0] is secreted by sheep sebaceous glands and collected from crude wool (10–25% of the raw wool) by washing with dilute alkali or a mixture of soap solution and organic solvent. After an acid treatment, the precipitated grease is distilled. As an alternative, the alkali washings may be concentrated and the grease collected by centrifugation, this producing the best quality grease. The final grease may be bleached with sodium hypochlorite, or sulfur dioxide. Better grades of wool grease will yield lanolin, a fraction with the lowest level of impurities, including free fatty acids. The name lanolin comes from a trademark registered in 1902.

Wool grease acts as a waterproofing wax and aids sheep in shedding water from their coats. Certain breeds of sheep produce such a large amount of wax that extraction can be performed by a simple squeezing of the wool. Note that all the wax must be removed from wool before its processing into textiles.

Wool grease is used as lubricating grease, concrete mould lubricants and rust prevention. It also may be used as a component in leather softeners. Lanolin is used in cosmetics for its emollient properties and in pharmaceutical products as an ointment basis that readily absorbs through skin and facilitates absorption of medicinal chemicals. Medical grade lanolin has the property of being hypoallergenic and bacteriostatic.

Among numerous derivatives of wool grease, a complex mixture of fatty alcohols is produced by saponification and removal of fatty acid soaps. These lanolin alcohols are powerful oil-in-water emulsifier used in cosmetics and pharmaceuticals. Wool grease is also a starting material for the manufacture of alcohol derivatives and cholesterol which may be chemically transformed into vitamin D3.

Chemical Characteristics. Lanolin contains fatty esters (14–24%), free alcohols (6–20%), sterols, and triterpene alcohol esters (45–65%). Some hydroxylated fatty acids are free or esterified. Fatty acid chains have from 14 to 35 carbon atoms, many of them have branched chains. Acid number is from 7 to 15, ester number from 85 to 100, saponification number from 100 to 110, iodine value from 15 to 30. The melting point is 35–42°C.

4. Vegetal Waxes

Plant waxes are formed most frequently as components of the cuticle that covers the outer surface of aerial plant tissues. The cuticular wax has important functions vital for plant life, such as reduction of water loss, protection against uv radiation, defense against bacterial and fungal pathogens and against insect attack.

Despite their heterogeneity, plant waxes as an entity, is one of the most important biological production on the earth surface estimated to 10^9 metric tons spread over a surface that represents the largest interface between the biosphere and the atmosphere (17). This amount can be compared with the world production of fats and oils (~80 million metric tons). Besides these outer-surface locations, plant waxes are also found in some seeds equivalent to vegetal tallow or oil.

Several vegetal waxes are collected and purified around the world for commercialization. They tend to replace waxes of animal origin, but themselves, they tend to be replaced by much cheaper synthetic waxes.

4.1. Carnauba Wax. Carnauba wax [8015-86-9], known as "Queen of waxes" is secreted by the leaves of a Brazilian palm tree, *Copernicia cerifera*, ~100 g for one tree in a year. The wax is collected by cutting the fronds and drying. After melting, wax is purified by a simple filtration or centrifugation.

Carnauba wax is used in the composition of oil paste formulations, in the paper industry for paper coating (the largest application in United States) and as component of thermal printing inks. The hardness and high melting point allow carnauba wax, after mixing with beeswax, increasing uses in polishes for shoes, floor and furniture. Other uses include cosmetics (lipsticks, creams) and food industry (E 903: glazes for candies, gums, fruit coatings). The FDA affirmed carnauba wax as GRAS for certain food applications.

Chemical Characteristics. Carnauba wax contains mainly fatty esters (80–85%) with C18–C30 fatty acids, free fatty alcohols with 30–34 carbon atoms (10–15%), free fatty acids (3–6%) and hydrocarbons (1–3%). As a peculiarity, carnauba wax contains esterified fatty diols (~20%), hydroxylated fatty acids (~6%) and cinnamic acid (~10%). This last phenolic acid compound, which is a potent antioxidant in free form, may be hydroxylated of methoxylated. Carnauba wax has an acid number of ~8 and a saponification number of ~80. It has the highest melting point and hardness among the natural waxes: The melting point is ~78–85°C, the viscosity is 3960 mm^2/s at 98.9°C, the penetration is 2 dmm at 25°C and 3 dmm at 43.3°C.

4.2. Candelilla Wax. This wax [8006-44-8] is produced by small shrubs from Mexico and Texas, *Euphorbia cerifera* and *Euphorbia antisyphilitica*. The wax is extracted by boiling the entire plant in acidified water. The floating wax is skimmed off, filtered, and decolorized with charcoal. It has been used in cosmetics (lip balms and lotion bars), in pharmaceutics and in food stuffs (E 902) to improve stability and texture as a substitute to beeswax. One of candelilla major outlets is a binder for chewing gums. The FDA affirmed candelilla as GRAS for certain food applications. Its adhesive properties allow its use in polishes for floor or furniture.

Chemical Characteristics. Candelilla wax contains mainly hydrocarbons (~50% of C29 to <C33). The balance is composed of fatty esters (28–30%), free alcohols and acids (7–9%), and triterpenoid esters (12–14%). It has an acid number of 13–18, a saponification number of ~55 and an iodine value of 20–45. Typically, the refined wax has a melting point from 67 to 80°C, its penetration is 3 dmm at 25°C.

4.3. Japan Wax. That product [8001-39-6] is not a true wax, but like a vegetal tallow found in the kernel and outer skin of the berries of various *Toxicodendron* and *Rhus* species, shrubs native to Japan and China. The collected berries are steamed and pressed to produce a greenish tallow that must be bleached with charcoal before use. That wax is much used in Japan in cosmetics (ointments), in the formulation of candles, polishes, and lubricants. It has limited food-related applications as it becomes rancid with age.

Chemical Characteristics. Japan wax contains a high amount of palmitic acid triglycerides (~95%), long-chain dicarboxylic acids (~4% of C22 and C23) and free alcohols (~1%). It has typically an acid number of 6–20, an iodine value of 10–15, and a saponification number of 205–240. Its melting point is 45–53°C.

4.4. Ouricouri Wax. Ouricouri wax [68917-70-4], also known as licuri wax, is a brown wax extracted from the ouricouri palm trees (*Cocos coronata, Syagrus coronata*), which grow in Brazil. Wax is collected by scraping the leaf surface. It was first exported from Brazil in 1937 but has fallen in use in recent times. Only ~7000 metric tons are produced annually. Ouricouri wax is used as a cheaper substitute for carnauba wax in applications that do not require a light-colored wax as in carbon paper inks, mould release lubricants and polishes. The wax contains a high resin content and, for that reason, is regarded as inferior.

Chemical Characteristics. For the refined wax, the acid number is 8–20, the ester number 75–85, the saponification number 70–100, and the iodine value 6–8. Its melting point is 81–84°C.

4.5. Esparto Wax. This wax is a by-product in the artisanal preparation of paper from a reed known in northwest Africa and southern Spain as “Halfah grass”, *Stipa tenacissima*.

Chemical Characteristics. While its composition is highly variable, it contains hydrocarbons, esters, alcohols (C28) and triterpenoids. It melts at 73°C.

4.6. Bayberry Wax. Bayberry wax [8038-77-5] is not a true wax, but a vegetable tallow since it is contained in the fruit coat of *Myrica cerifera*, a small tree native to Central and Southern America. After boiling the fruit in water, the molten wax is collected by skimming the water surface and pressed. It is grayish-green in color and has an aromatic odor. It is fairly hard and somewhat brittle, it can be used at 100% or blended with beeswax. Bayberry wax has been used in medicine but now it is used to make high grade candles and tapers with pleasant fragrance. Other common uses include lip and eyeliner makeup, buffing compounds, and laundry wax.

Chemical Characteristics. Bayberry wax contains mainly triglycerides (~95%), the main carbon chains being myristic, palmitic, and stearic acids. It has typically a saponification number of 210, an acid number of ~4 and an ester number of ~205. The melting point is ~45°C.

4.7. Rice Bran Oil. The milling of rice, *Oryza sativa*, produces a bran containing a wax [8016-60-2] and triglycerides that can be extracted with hexane. The wax is isolated by cooling the oil at 20–25°C, followed by a filtration or centrifugation. An efficient process for the preparation of food grade rice bran wax followed by the determination of its composition has been reported (18). Rice bran wax is much used as a constituent of chocolate enrobers, various fruit and vegetable coating, and lipsticks. It has also potential applications in cosmetics, pharmaceutics, polymer and leather industries.

Chemical Characteristics. The bran wax consists of fatty esters containing mainly saturated C22 and C24 fatty acids and C24–C40 fatty alcohols. The major alcohols are triacontanol (C30) and octacosanol (C28). An efficient purification process of octacosanol from rice bran wax by molecular distillation has been reported (19). The acid number is 0.5–10, the saponification number is 57–104, and the iodine value is 11–20. The characteristic physical properties of purified rice bran wax are similar to those of carnauba wax. The melting point is 75–80°C.

4.8. Sugar Cane Wax. Sugar cane is a by-product of the sugar refining industry, known since 1841 in New Orleans and always a matter of interest.

There is a large potential source of wax available for industrial applications in cosmetic and pharmaceutical industry, but the recovery costs are high. New applications in pharmacy may lead to enhancement in the production of that by-product of sugar and rum factories. In all the growing regions for sugar cane, *Saccharum officinarum*, the cane juice is treated with lime to precipitate nonsugar products including waxes. After settling, the waxy sediment is removed, purified in a filter press, and extracted with solvent. Another solvent treatment is processed to purify the wax part. It has been shown that adsorbats of vinasses produced during fermentation and distillation of the crude sugar cane juice in rum factories can be used as a new low cost source of sugar cane waxes (20).

Chemical Characteristics. After extraction, a mixture of wax esters, linear alkanes (C19–C33), triterpenes, and methyl esters of fatty acids is obtained. The main fatty acid and alcohol components have 16–18 and 26–32 carbon atoms, respectively. Sugar cane is a valuable source of policosanol, a mixture of fatty alcohols with octacosanol (C28) as the major constituent (~66%). There is a significant body of evidence demonstrating the benefits of policosanol with respect to cardiovascular diseases (21). The wax has a saponification number of 65–80 and an iodine value of 17. The melting point is ~80°C.

4.9. Soy Wax. Soy wax is a human-made substitute to beeswax, a cheaper alternative for making candles. Soy wax is not a true wax but consisted of hydrogenated soybean oil (22). Soy wax was invented in 1991 by Michael Richards and commercialized in 1995. Some soy waxes are pure soy, and some are blends with hydrogenated coconut oil, palm oil and with beeswax. Thus, mixtures with different melting points were obtained. The lower melting points are 120–135 for wax used in container candles and above for pillar and votive candles. They are known to have a longer burning time than paraffin and to be environmentally safe. Cargill bought in 2001 the patent of Michael's soy wax innovation (Soybean wax candles U.S. Pat. 6,599,334) and now supplies candle producers.

More recently, waxes prepared from hydrogenated soybean are used to render cellulosic materials resistant to water. These materials are recyclable using conventional paper recycling methods. Research are also developing to make fire logs using soy wax as binder combined with wood residue that, when combusted, emitted fewer pollutants than firewood or other fire logs.

4.10. Sorghum Wax. Sorghum wax is made from the coating on sorghum berries (sorghum hulls) and has physical characteristics similar to carnauba wax. Over 1.25% wax/g dry solids may be recovered from bran dry matter obtained from dry-milling operations. The wax melting point is ~180°C, thus valuable to make tough coating for fruits, vegetables and car or floor polishes. Some studies have shown that sorghum wax, as sugar cane wax, lowers plasma cholesterol in humans.

Chemical Characteristics. Sorghum wax is comprised of very long-chain fatty alcohols (37–55%), aldehydes (35–55%), and acids (~5%) with carbon lengths ranging from C28 to C32 (23). The high level of aldehydes in sorghum wax implies their oxidative conversion to acids during storage and may hamper some applications.

4.11. Castor Wax. Castor wax [8001-78-31] is, as soy wax, a human-made substitute to more expensive waxes. It is obtained by catalytic hydrogenation of castor bean oil. Castor wax is used primarily in the formulation of cosmetics. Some derivatives are used as surfactants and plastic additives.

Chemical Characteristics. The saponification number is ~80 and the iodine value is 4. The melting point is ~86°C.

4.12. Jojoba Oil. Jojoba oil [61789-91-1], known also as liquid wax, is obtained by pressing the green nuts of the bush *Simmondsia chinensis* (Euphorbiaceae). The jojoba tree is cultivated since the early 1980s mainly in Mexico and the southern United States (New Mexico, Arizona, California). Other countries (Israel, Africa, Australia, China) are experiencing the cultivation of jojoba tree. An extensive review on jojoba may be consulted (24). The seed contains 50–60% oil. The oil is a unique liquid wax, which is very resistant to oxidation and is largely used in cosmetic applications (soaps, shampoos, skin cream, antisolar oils). It is colorless and odorless with unique physical and chemical properties and is regarded as a replacement for spermaceti. Sulfonated jojoba oil is used as component in high pressure lubricants. Hydrogenation of jojoba oil yields a solid wax that is used in polishes, candles, and coatings. New uses are emerging as foam control agent in pharmaceutical industry, low calorie food additive, cooling fluid in electric transformers, and plasticizer in poly(vinyl chloride) (PVC).

New applications may derive from new products, such as jojoba ferulate, which absorbs strongly uv and is very stable at temperature up to 100°C (25).

Chemical Characteristics. Jojoba oil is formed quite exclusively of wax esters (>90%) with a total of 38–44 carbon atoms. The fatty acids are 20:1n-9 (~70%), 22:1n-9 (15–20%), and 18:1n-9 (~9%), while the esterified fatty alcohols are monounsaturated and have predominantly 20 and 22 carbon atoms. The balance is free alcohols, free acids and sterols. The saponification number is 92 and the iodine value is ~82. The melting point is ~7°C.

5. Mineral Waxes

5.1. Montan Wax. Montan wax [008002-53-7], known also as lignite-wax, is derived by solvent extraction of lignite. The earliest production of montan wax on a commercial scale was in Germany during the latter half of the nineteenth century, and Germany continues to lead the world in production of montan wax. Crude Montan Wax is found in Germany, Eastern Europe and areas of the United States in certain types of lignite or brown coal deposits that have been formed over millions of years by transforming the fossil plant material. Wax that once protected the plant leaves did not decompose and enriched the coal. After mining, the montan Wax is extracted from the coal by means of solvent that is distilled from the wax solution and removed with super heated steam. The largest manufacturer of montan Wax in the world is Romonta GmbH, Amsdorf, Germany. It supplies >80% of the montan wax into the United States (~900 tons in 2001). The largest traditional use for montan wax is in the formulation of carbon paper inks. The decrease in use of carbon paper resulted in montan wax being further refined for use in the formulation of polishes, rubber, and as plastics lubricants. Its uses are also extending to fruit coating, water proofing, as an asphalt additive and leather finishing. Montan wax emulsions are also used in temporary anti graffiti coatings (26). Because montan wax reduces hydraulic conductivity by up to five orders of magnitude and has a great chemical resistance, it is now being used for the underground encapsulation of hazardous waste sites. Montan wax is hard and brittle, its properties being similar to those of carnauba wax, which it can replace. Partially synthetic montan wax derivatives that are extremely hard with a light color and excellent polishing characteristics are manufactured from refined wax by saponification and esterification of the long-chain fatty acids with various alcohols.

Chemical Characteristics. The composition of montan wax varies geographically with production, but includes varying amounts of wax, resin and asphalt. Black montan wax may be further processed to remove resins and asphalt, and is known as refined montan wax. The quality of crude montan wax is estimated by the acetone soluble amounts (resin content) and isopropanol insoluble (asphalt content). The isopropanol insoluble indicates the amount of difficultly refinable parts of the wax. Samples with a content of $>8\%$ are very difficult to refine or the resulting products are unusable (26). The wax components are a mixture of long-chain (C24–C30) esters (50–60%), long-chain acids (20–25%), resin acids (10–15%), polyterpenes (3–5%), alcohols (1–1.5%), ketones (1–1.5%), and hydrocarbons (1%). Crude montan wax typically has an acid number of 32, and a saponification number of 92. Its melting point is $\sim$80°C.

5.2. 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 $\sim$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.

5.3. Ozokerite and Ceresin Waxes. Ozokerite wax [001-75-0] 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 [8001-75-0] occurs naturally as Ozokerite, market grades being purified ozokerite obtained from lignites. It has a zero value for acid number and saponification number. Normal grades of ceresin wax (either yellow or white) have melting points from 59 to 77°C. As ozokerite, it consists of high molecular weight saturated and unsaturated hydrocarbons (iodine value: 7–9). Paraffin waxes are incorporated in final products to give consistent performance. The inert properties of that wax are of importance in rubber compounding. It is also used as a substitute of beeswax or paraffin wax in polishes, insulating compounds, cosmetics, and waterproofing applications.

5.4. Petroleum Waxes. All petroleum waxes are derived from crude oil during the refining process designed to produce lubricating oil. Three general categories of petroleum waxes are obtained during the refining. They include macrocrystalline wax (or paraffin wax) [64742-43-4], microcrystalline wax

[64742-42-3] and petrolatums. 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. A classification system based on the refractive index of the wax and its congealing point as determined by ASTM D938 was developed (27).

Paraffin wax is a petroleum wax consisting principally of straight-chain alkanes with an average chain length of 20–30 carbon atoms. According to the European Wax Federation (28) paraffin waxes have a carbon-number distribution of n-alkanes from 18 to 45 and a total content of iso- and cycloalkanes of 0–40%. It is obtained from light and middle lubricating oil cuts of vacuum distillation. This class also includes wax from heavy lubricating oil distillates, which is intermediate between macrocrystalline and microcrystalline waxes with regard to structure and composition (intermediate wax). Paraffin wax is extremely unreactive under normal conditions. Oxidation reactions occur only at elevated temperatures, particularly in the presence of oxygen and catalytically active metals. Under well-defined conditions, paraffin wax can undergo chemical reactions, such as chlorination, oxidation, dehydrogenation, and cracking, all being important in industry.

Microcrystalline wax is a petroleum wax solid at room temperature containing substantial proportions of branched and cyclic (naphtenes, alkyl- and naphtenes-substituted aromatics) hydrocarbons, in addition to normal saturated alkanes. It is produced from a combination of heavy oil distillates and from the sediments of paraffinic crude oil (settling waxes). The microcrystalline structure can be explained by the presence of strongly branched isoparaffins and naphtenes, which inhibit crystallization. This class differs from paraffin wax in that it has poorly defined crystalline structure, darker color, and generally higher viscosity and melting point. It tends also to vary much more widely than paraffin wax with respect to physical properties. Microcrystalline wax is more reactive than paraffin wax because of the higher concentration of complex branched hydrocarbons with tertiary and quaternary carbon atoms. These C–C bonds are not thermally stable (ie, the wax darkens and resinifies) on prolonged heating. In addition, it forms black tar-like substances on contact with aggressive chemicals such as concentrated sulfuric acid or antimony pentachloride. The reaction of microcrystalline wax with oxygen at elevated temperature and in the presence of catalytically acting heavy-metal soaps is used for the production of oxidized microwax. The last category of petroleum wax is petrolatum. It derives from heavy residual oils and is separated by a dilution and filtering process followed by cooling at about −20°C. It has a microcrystalline structure and is semisolid at room temperature. It has good oil-holding capacity such that when filtered and blended it becomes mineral jelly. When fully refined it becomes microcrystalline wax. When the petroleum jelly is adjusted with white mineral oil to give the required viscosity, Vaseline is obtained. The melting range is 48–85°C for an oil content from 3 to 7%.

Depending on the degree of refining, other terms are also used to refer to petroleum wax. These terms refer to the amount of oil contained in the product. Slack wax [64742-61-6] refers to petroleum wax containing from 3 to 50% oil content. Scale wax refers to wax containing 1–3% oil. Fully refined paraffin wax has <0.5% oil content.

Within these classes, the melting point of the wax determines the actual grade, with a range of ~46–71°C. Typical properties of petroleum waxes are listed in Table 1.

The physical properties do not completely define the suitability of a wax for a particular application. The functional properties of wax should be considered as well. These include the translucency and opaqueness of the wax, solid appearance, flexibility, etc. The combination of physical and functional properties ultimately determines if a particular wax is suitable for a given application.

Petroleum waxes are produced in massive quantities throughout the world. A recent report from Kline and Company Inc. provides information on the world petroleum wax market that accounts for close to 3.6 million tons, valued at nearly $2 billion. Production capacity in the United States and imports for 1995 were ~650,000 and 114,000 tons, respectively. Petroleum wax makes up 95% of the whole waxes consumed in the United States and in the EEC. Canada supplies >50% of the petroleum wax imported into the United States. Paraffin and, to a substantially lesser degree, microcrystalline wax are produced in almost all countries of the world that refine crude oil.

The separation of paraffin wax from crude oil occurs during distillation, as shown in Figure 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 ~40% wax and 60% 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%, 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 >11 dmm at 25°C. Crude oil contains high molecular weight fractions that 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. Crude oil tank bottoms are essentially crude oil with very high wax contents and are processed as indicated in Figure 1.

The microcrystalline wax obtained from crude oil tank bottoms is generally known as hard grades, with penetrations <11 dmm at 25°C. To produce a "fully refined" wax from a product wax requires that the wax be passed through a bed of clay to remove color and through a vacuum stripping tower for odor removal. The discoloring operation is known as "percolation" and is a batch process. The clay is regenerated before reuse by passing it through a multiple hearth furnace to remove the absorbed color bodies.

The use of refined grades of petroleum waxes in some food applications is regulated by the FDA in 21 CFR 172.886, and 21 CFR 178.3710. The Bundesgesundheitsamt (BGA) of Germany also has specifications for refined petroleum waxes used in food applications. Many other countries reference either the FDA or BGA specifications for their food regulations. Petroleum wax is widely used in chewing gum to modify the properties of the chewing gum base. The wide range of properties available help chewing gum base manufacturers formulate a broad variety of chewing gum, ranging from the traditional hard stick gum to the softer bubble gum. Petroleum wax can also be used as protective coatings for fruits, vegetables, and cheeses. Petroleum wax is outstanding as a cost-effective moisture and gas barrier, and food packaging applications are a major market for refined food grade petroleum wax. Blends of paraffin and microcrystalline wax are used by themselves or in combination with other additives, such as high molecular weight polyethylene and ethylene vinyl acetate copolymers to improve the performance of paper packaging, such as paperboard boxes, paper containers, and flexible packaging.

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 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 inks to improve slip and rub properties. Petroleum waxes are used in many consumer applications, such as cosmetics, polishes, and candles. Unrefined petroleum waxes (petrolatum) are often used in fireplace logs. Chlorinated paraffins are components of flame-retardants and plasticizers.

6. Synthetic Waxes

Synthetic waxes range through polyethylenes, alkyl esters of carboxylic acids or hydroxyacids, Fisher-Tropsch waxes, hydrogenated waxes and long-chain amides. Production figures for each of these waxes are not available except for the Fisher-Tropsch waxes that are imported in the United States in quantities reaching ~14,000 tons/year.

6.1. Polyethylene Waxes. Low molecular weight (molecular weight less than ~10,000) polyethylenes [9002-88-4] having wax-like properties. Polyethylene waxes can be made by direct polymerization of ethylene under special conditions (high or low pressure polymerization) that control molecular weight.

$$\underset{\text{monomer}}{CH_2{=}CH_2} \dashrightarrow \underset{\text{PE wax}}{-\!\left(CH_2-CH_2\right)_n\!-}$$

Another method involves breaking down high molecular weight polyethylene into lower molecular weight fractions. A third method involves separation of the low molecular weight fraction from high molecular weight polymer. All the products have the same basic structure, but the processes yield products with distinctly different properties. Some polyethylenes have fairly low densities, 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. Polyethylenes in the molecular weight range 2000–4000 are waxes, and in the range 4000–12,000 they are wax resins. The low molecular weight solids produce fluid-melts in the range 97–106°C. Annual production in the United States is estimated at 100,000–140,000 t.

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. Most polyethylenes are regulated by the FDA under the olefin polymer regulation, 21 CFR 177.1520. This regulation includes a maximum amount of hexanesoluble 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 are regulated by the FDA under the synthetic petroleum wax regulation, 21 CFR 172.888. 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 are 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, polyethylenes terminated as ketones, alcohols, and carboxylic acids with molecular weights as high as 700 Da 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, or 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.

6.2. Fischer-Tropsch Waxes. Polymethylene wax [8002-74-2] production is based on the Fischer-Tropsch synthesis, which is basically the polymerization of carbon monoxide under high pressure (300–450 psi), high temperature (235–255°C), 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 ~45 to 106°C. The paraffin wax can be obtained by chilling and is composed of C17–C25 hydrocarbons. A second wax can be obtained from the catalyst that becomes saturated with the wax (melting point from 70 to 80°C). The waxes are as hard as the hardest vegetable waxes, and they can be produced with very high gloss. Ester waxes can be obtained by oxidation of Fischer-Tropsch waxes.

Currently, the waxes are produced in large volumes in South Africa and Malaysia, with an estimated 12,000–14,000 t consumed in the United States in 1994. Uses are similar to those for polyethylene waxes, including hot-melt adhesives and additives for inks and paper coatings. Additional markets are found in electrical insulation, as lubricants and antioxidants for rubber and resin-wax polishes. Oxidized Fischer-Tropsch waxes are largely used in the production of polishes and pastes for floors, furniture and cars.

6.3. Chemically Modified Waxes. Hydrocarbon waxes of the microcrystalline, polyethylene, and polymethylene 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 (29). 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, eg, maleic, at high temperature (30). 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.

6.4. Synthetic Esters. Synthetic ester waxes similar to those found in Nature may be obtained when fatty alcohols are allowed to react with long-chain fatty acids. Cetyl stearate may be prepared by heating stearic acid and palmitic alcohol at atmospheric pressure and raising the temperature from 220 to 270°C over 2 h. Efforts were made to synthesize jojoba oil substitutes and led to the production of liquid wax esters, such as oleyl erucate (Dynacerin 660 from Dynamit Nobel). The structure and properties of that product are very similar to those of natural jojoba oil. Other synthetic esters are based on diesters of ethylene glycol and other dihydric alcohols. The reaction of glycerol with vegetable fatty acids, isostearic acid and adipic acid produces substitutes of lanolin.

6.5. Substituted Amide Waxes. The product of fatty acid amidation has unique wax-like properties (31). Fatty acids are reacted with ammonia or amines at elevated temperature, catalyzed with boric acid at 180–250°C and 50–100 psi to form amides. Alternatively, methyl esters or triglycerides can also be used. Probably the most widely produced material is *N*,*N'*-distearylethylenediamine [110-30-5], which has a melting point of ~140°C, an acid number of ~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.

6.6. Polymerized α-Olefins. Some polymers of higher α-olefins, eg, $C > 20$, 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 α-olefin monomers and polymerization conditions. Melting points for the products range from 54 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.

6.7. Carbowaxes. Carbowaxes are solid polyethylene glycols, a family of water-soluble linear polymers formed by the addition reaction of ethylene oxide. The generalized formula for polyethylene glycol is with molecular weights ranging from 200 to 8000;

$$HOCH_2(CH_2OCH_2)_nCH_2OH$$

The chemical structure suggest a limited compatibility with the other waxes.

They have a great variety of uses in mechanics as lubricants, in a variety of food-related applications, and in laboratory practice (embedding medium, chromatography support, etc). For Carbowax 1000, the freezing point is 37–40°C, for Carbowax 4000, the freezing point is 53–56°C, and for Carbowax 6000, the freezing point is 60–63°C.

7. Analytical Techniques

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 vegetable or animal waxes. 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 that contain carboxyl groups, such as vegetable, montan, and oxidized waxes. Increasingly, instrumental methods, such as thin-layer chromatography (tlc), high performance liquid chromatography (hplc), gc, mass spectrometry (ms), gel permeation (also known as size exclusion) chromatography (gpc), refractive index (ri), differential scanning calorimetry (dsc), infrared (ir) spectroscopy, 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. Various aspects of class separation and analytical approaches has been reviewed (32).

7.1. Melting and Congealing Points. Selection of the proper melting point method depends on the characteristics of the wax. Drop melting point (ASTM D127) is suitable for amorphous waxes, eg, microcrystallines, but is not reliable for higher viscosity synthetic waxes, for which ring-and-ball softening point (ASTM D36) should be used. Waxes whose time–temperature cooling curves exhibit plateaus, eg, paraffin wax, may be evaluated by ASTM D87. Open or closed capillary tubes are used to measure the melting point of many of the natural waxes. For tiny samples (some mg), a microprocedure using Fourier-transform infrared spectroscopy has been described (33). Shortly, the sample temperature was increased in increments of $\sim 1^\circ$C, with an infrared spectrum being collected at each temperature. As alkyl chains melted, the frequency of $-CH_2-$ symmetric stretching vibrations increased from ~ 2849 to ~ 2854 cm^{-1}, and was used as an index of lipid melting. The midpoint of the phase transition (T_m) was calculated by fitting plots of frequency versus temperature to a logistic equation. 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.

7.2. Hardness (Penetration). 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.

7.3. 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, eg, carnauba, are based on the color of the solid wax. The accurate measurement of color in light-colored, ie, 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.

7.4. 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°C.

7.5. 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 mm^2/s (= cSt).

7.6. 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.

7.7. Saponification Number. The saponification number (ASTM D1387) is the milligrams of potassium hydroxide, which react with 1 g of wax under elevated temperatures, and indicates the amount of free carboxylic acid plus any ester materials that 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.

7.8. Iodine Value. Iodine value measures the number of double bonds to indicate the degree of wax unsaturation. The results are expressed in grams of iodine absorbed by 100 g of wax.

7.9. 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 vs temperature provide insight into the thermal characteristics of a wax, including crystalline transitions, eg, solid–solid, solid–liquid, and liquid–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.

7.10. Wax Component Separation. Before any quantitative determination can be done it is necessary to isolate a wax sample free of interfering compounds. Thus column chromatography (cc), solid-phase extraction (spe), and thin-layer chromatography (tlc) are classical techniques for the isolation of waxes and the separation of their various components.

On an analytical scale, a detailed tlc investigation of all wax constituents has been reported (34). On the preparative scale pure fractions can be isolated, suitable for further analysis. On the other hand, the quantification of wax esters was optimized using the combination of tlc with flame ionization detection by the system commercialized as Iatroscan (35).

The usual procedure to separate wax esters is cc. This method has been adopted by the European Union as an official method (36). The wax esters eluting just before the triglycerides, the addition of Sudan I allowed to visualize when the elution of wax esters ends (37). A simpler and faster procedure than the official one described in the EEC document has been reported (38). The use of silica gel impregnated with silver nitrate was proposed to improve the separation of wax esters (39). An adaptation of the previous methods using SPE silica cartridges was proposed to improved on the official EEC regulation method (36).

The isolation of the hydrocarbon fraction is performed usually after saponification. The unsaponifiable is fractioned on a silica gel column using light petroleum as eluent. The identification of the compounds is then carried out by ms (40).

7.11. Gas Chromatography. Gas chromatography has been used for many years, especially on the relatively simple structures of vegetable and insect waxes. Thus, the relative amount of fatty acids and hydrocarbons by gc was successfully used in comparing waxes used in pictorial artworks with animal and vegetal waxes (41). Use of the gc for petroleum and synthetic waxes was limited by the maximum carbon number that 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 that can resolve carbon numbers up to C100. Good resolution can be obtained on products with generally only one type of structure, eg, 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.

7.12. Mass Spectrometry (ms). A method for determining the relative amounts of isomers of straight-chain saturated wax esters has been reported (42). This potent method was based on single-ion monitoring values from gas chromatography–mass spectrometry (gc–ms) analyses. Unexpected wax ester species (diterpenic esters) have been identified in vegetal oil by gc–ms (43). The combination of ms and gc allowed to precise the structure of different ester isomers and to characterize various wax works of art in providing knowledge of the recipes elaborated by the sculptors (44). The composition of plant waxes, including fatty acids, triterpenoids, alkanes, alcohols, and aldehydes, is also efficiently determined using gc–ms (45). The combination of lc with ms (atmospheric pressure chemical ionization) was successfully applied to very long-chain fatty acids from sugar cane wax (46). It was thus possible to identify some of the longest fatty acids found in Nature (from C34 to C50).

7.13. Gel Permeation Chromatography. The gel permeation chromatography (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 gc. 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, P_d.

7.14. Infrared Spectroscopy. 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.

7.15. Nuclear Magnetic Resonance. The nmr analysis has been used in the polymer industry for some time 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.

7.16. Raman Spectroscopy. The application of Fourier transform Raman spectroscopy (rs) and microscopy to biomaterial characterization and particularly for the nondestructive analysis of biopolymers and fragile artifacts, involving little or no sample preparation, is now being realized (47). Individual animal, vegetal and hearth waxes may be qualitatively distinguished without pretreatment before analysis.

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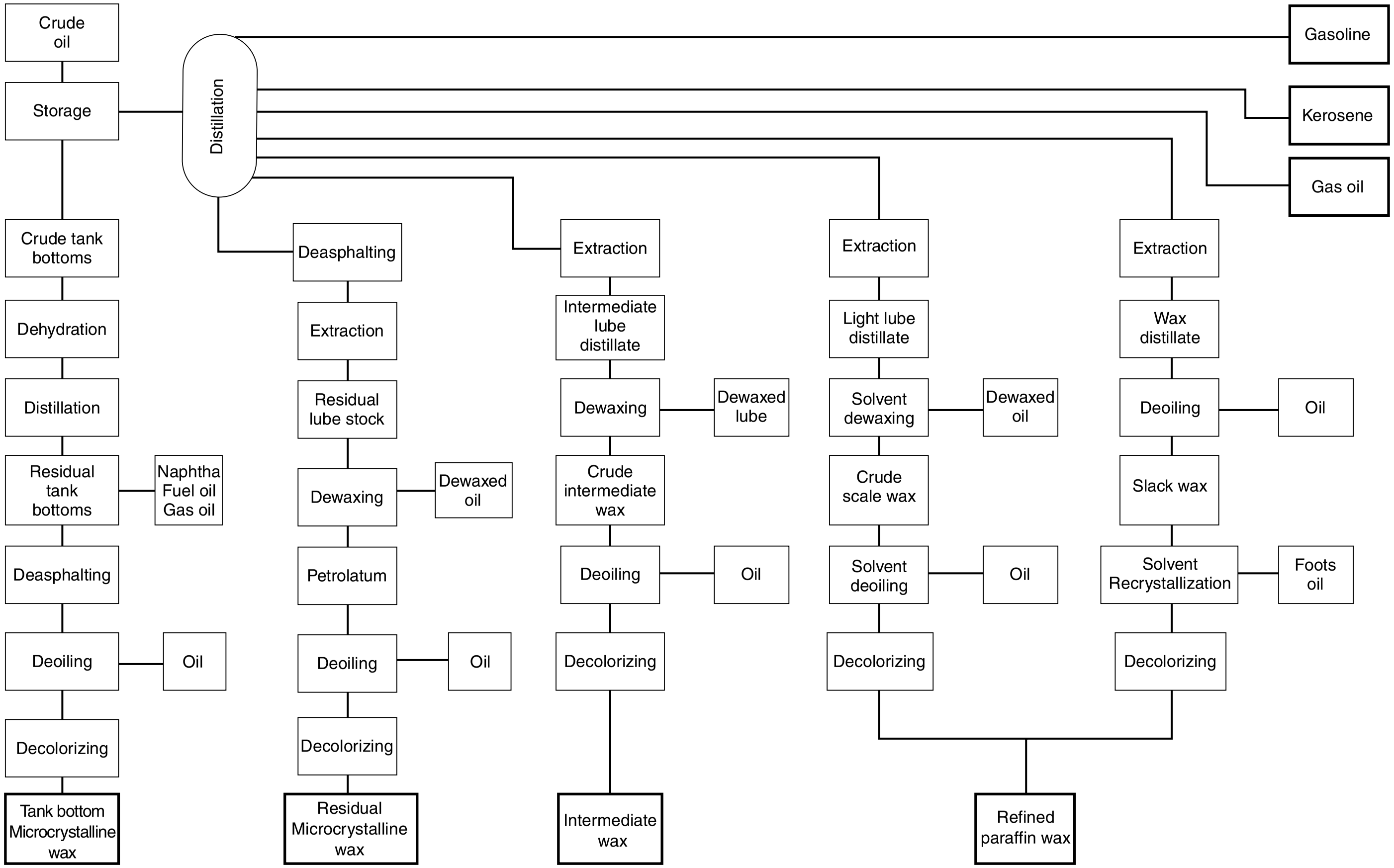

Fig. 1. Refining of petroleum waxes. Courtesy of Baker Petrolite Corporation.

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

Property	Wax: Paraffin	Wax: Microcrystalline
flash point, closed cup, °C	204	260
viscosity at 98.9°C, mm^2/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
average molecular weight	350–420	600–800
carbon atom per molecule	20–26	30–75
ductibility/crystallinity of solid wax	friable to crystalline	ductile-plastic to tough-brittle