1

Introduction

1.1 General Survey of Waxes

> Since I nor wax nor honey can bring home,
> I quickly were dissolved from my hive,
> To give some labourers room.
>
> Source: William Shakespeare, "All's Well That Ends Well," King of France, I,2.

Waxes, in the broadest sense of their definition, have been playing a great role in history, science, and technical application. So, first we would like to address some of the most relevant kinds and uses of waxes of in the past millennia, starting with the first known touch of humanity with these very special materials.

But before all, what are waxes? Probably you may think of beeswax, of candles, or of polish – all still relevant but representing only a very small selection out of dozens of kinds of waxes, and more than 2000 known uses of waxes. Indeed, until the early nineteenth century, "wax" was a synonym for beeswax only. With the advent of chemical analysis, beeswax was identified with several different components. Then more and more natural and later also synthetic substances with similar properties were classified as waxes – see below.

Nevertheless, it makes sense to first set the focus on beeswax and closely related substances, as beeswax may be regarded as the "queen of waxes" throughout human history.

1.2 Definitions of Waxes

Wax is a generic term for a range of natural or synthetic products. For convenience, the range can be roughly subdivided as follows:

- Natural waxes: plant, animal, etc.
- Modified natural waxes
- Fully and partially synthetic waxes
- Mineral hydrocarbon waxes
- Petroleum waxes

Natural and Synthetic Waxes: Origin, Production, Technology, and Applications, First Edition.
Ernst J. Krendlinger and Uwe H. Wolfmeier.

Waxes today are usually defined by their characteristic properties (see also International Customs Tariff, Harmonized System HS 3404), and less so, or not, by their chemical composition.

Probably the most conclusive definition has been drawn up – in Europe – by the "Deutsche Gesellschaft für Fettwissenschaft" (DGF, German Association for Fat Science).

This was first established in 1957 and – slightly modified – confirmed in 1974 [1]. In the modified form, it entered the customs tariff of the European Union [2, 3].

According to this definition,

1. waxes should have a drop (or melting) point (mp) >40 °C;
2. their melt viscosity must not exceed 10 000 mPa s at 10 °C above the drop point;
3. they should be polishable under slight pressure and have a strongly temperature-dependent consistency and solubility;
4. at 20 °C they must be kneadable or hard to brittle, coarse to finely crystalline, transparent to opaque, but not glassy, or highly viscous or liquid;
5. above 40 °C they should melt without decomposition;
6. above the melting point (mp) the viscosity should exhibit a strongly negative temperature dependence and the liquid should not tend to stringiness;
7. waxes should normally melt between c. 50 and 90 °C (in exceptional cases up to 200 °C);
8. waxes generally burn with a sooting flame after ignition;
9. waxes can form pastes or gels and are poor conductors of heat and electricity (i.e. they are thermal and electrical insulators).

All substances that differ in more than one point from these items are not 100% waxes if this quite strict definition is applied; however, there are borderline cases.

Other attempts to define waxes have been made and published by, e.g. the European Wax Federation (EWF: see their website):

- solid at 30 °C, varying in consistency from soft and plastic to brittle and hard;
- as solids as coarse to finely crystalline, transparent to opaque, but not glass-like;
- have relatively low viscosity slightly above the melting point;
- melt above c. 40 °C without decomposition;
- consistency and solubility are highly temperature dependent;
- buffable under slight pressure;
- burn with yellow flame and can form pastes or gels when dispersed in solvents;
- exhibit low thermal and electrical conductivity.

With this broader definition, more substances have been classified as "wax" or at least "wax-like." From experience, we learnt that an exact definition of wax turned out to be unattainable, and some disputes are ongoing. We should accept that waxes cannot, in any case, be precisely separated from related species such as oils, fatty acids, or plastics.

An overview of the most relevant waxes is given below. It may demonstrate the broad variety of this fascinating organic material.

1.2.1 Natural Recent Waxes

Natural waxes have either vegetable or animal origin. The predominant, and perhaps the best known wax of *animal* origin is [4]

- beeswax (EU Marketing Standard E 901: see EU regulation 2016/673, April 2016)

  Important representatives of *vegetable* origin are

- carnaúba (E 903; from carnaúba palm tree: Cera Carnaúba)
- candelilla (Spanish: "little candle"; E 902); plant wax from candelilla scrub
- sugarcane wax (from sugarcane grass).

1.2.2 Mineral Hydrocarbon Waxes

Mineral hydrocarbon waxes are mostly mined and their application importance is continuously declining. There are two main types:

- Montan wax – manufactured by solvent extraction of Oligocene lignite;
- Ozokerite (naturally occurring earth wax).

1.2.3 Petroleum Waxes

Petroleum waxes are hydrocarbons derived from petroleum. There are four main types:

- slack wax – unextracted wax derived from dewaxing distillate lube oil streams
- paraffin – deoiled slack wax consisting predominantly of straight chain alkanes
- microcrystalline – branched and cyclic alkanes from deoiling residual bright stock lube oil stream
- petrolatum – bright stock deoiled residual lube oil or blends of oils and waxes – petroleum jellies

Remark: Although petroleum waxes are based on natural resources, they are not covered in Part I of this volume dealing with natural waxes: in their structure, they are more similar to fully synthetic waxes.

1.2.4 Fully Synthetic Waxes

For about a hundred years, waxes can be produced synthetically. We distinguish between two main types:

- Polyolefin waxes
- Fischer–Tropsch wax.

1.3 Brief History of Waxes

Beeswax marks the beginning of the use of any kind of wax by humans. According to recent scientific research, bees – they obviously existed already in the early Cretaceous period – started to dust flowering plants about 110 millions of years ago, long before man entered the world. We dedicate a few pages to the history of the use and application of beeswax.

Only since about 10,000 BC, at the beginning of the Holocene era, beeswax has been verifiably collected by humans from bees' hives [5]. It is assumed that the home of bees is the present Indian subcontinent. In addition, they were also located in a narrow zone from the east to the west – running from China through Tibet: the Himalayas, Afghanistan, Persia, the northern part of the Arab States, Syria, and Asia Minor. The Indo-European peoples collected honey and wax from wild bees that lived in the natural caves of forest trees.

We credit the first evidence about beeswax – probably the only wax being used all the time before – to the Egyptians, some 7000 years before the present. So, to the best of our knowledge Ancient Egypt may be considered as the origin of beekeeping. The first written records in hieroglyphs originate from the Fifth Dynasty of the Old Kingdom (2494–2345 BC). Earthenware pots were provided as beehives.

As to the European proof of early use of waxes, we may refer to cave paintings in Spain dating from the Mesolithic period (10.000–5.000 BC). The painting of a female honey hunter harvesting honey and wax from a bee's nest in a tree was discovered in one of the Cuevas de la Araña (Bicorp, province of Valencia) [6]. The anonymous artist created the first documented encounter of a human being with a wild beehive, beautifully colored in red on a rock.

Whether the people of the Mesolithic period really used the wax and for what purpose it was used remain speculative as can be seen and interpreted from Figure 1.1. But what seems to be clear is that the painting shows a woman who dares to approach the beehive on the rock wall.

Figure 1.1 Woman gathering honey; watercolor copy by F. Benitez Mellado of a Mesolithic (c. 6000 BC) painting in the Cueva de la Arana, near Bicorp, Spain; in the Museum of Prehistory, Valencia, Spain.

Traceable evidence for the use of beeswax has recently been published by Jones et al. [7] for the fourth and fifth millennium BC.

It makes sense to go back to Old Egypt for a moment, because the application of wax became more and more sophisticated at that age, and this is undoubtedly proved by archeological findings, scientific research, and later, written documents.

1.3.1 Waxes Used by Ancient Egyptians

The word “wax” (beeswax) is called “mum” in Old Coptic, most certainly the latest stage of the Egyptian language. Since “mum” was a basic material for the mummification process, it may sound reasonable that the word “mummification” originally just meant “preserved in wax.”

The procedure of mummification was quite complex, long-lasting, and thus expensive. Recent chemical analysis [8] provided an astonishingly broad variety of individual ingredients. The ancient Egyptians discovered already 6000–7000 years ago that beeswax exhibits an antibacterial effect: therefore, it was essential to safeguard the durability of mummies. The chemicals required for mummification were based on natural resources, however rare, exclusive, and expensive. That is why only the “upper class” – like members of the Pharaoh’s court, High Priests, etc. – were subjected to mummification after death.

1.3.1.1 The Mummification Process

Here we step into some details of mummification, because some principles of the methods of wax refining and application that still exist were already being practiced at that time. *Beeswax* intended for use in the mummification process had to be bleached before use. The Egyptians did not have access to “modern” chemicals applicable as bleaching agents such as chromic acid, hydrogen peroxide, or mixtures of nitric acid and hydrochloric acid. In contrast to the present, they just made use of the influence of the sun and moon to serve this process.

Indeed, bleaching beeswax can be technically achieved just by sunlight. However, the Egyptians also considered the position of the moon, planets, and stars: they strictly adhered to astronomy and astrology. As a result, the mummification ceremony was restricted to very limited hours. Thus, the bleaching of wax – “mum” – was more of a ritual act than just manual work in Old Egypt. It meant a form of conjunction with the Egyptian Sun God Ra.

It is plausible that the Egyptians transformed the originally dark yellow to brown beeswax by bleaching into a highly refined substance, becoming bright at the end. They believed that this process could only be performed with the support of Divine power.

As we know, the “holy bleached wax” prevented a bacterial infection of the dried bodies of mummies for a long time – in many cases until the present. The Egyptians did not rely on the sun, moon, and stars alone when preparing waxes, not only for mummification but also for other uses: they had already gained some experience in several other chemical substances of natural origin. Cox [9] examined a wig from the British Museum, which dates from the fourteenth century BC. He noted that unbleached beeswax was mixed with a special resin. This mixture of wax and resin was probably used to make wigs handsome and looking more brilliant. So, waxes may have served among the first aids of coiffeurs!

Bleaching wax stood for progress in chemical knowledge, but Egyptians were already more capable: to produce beeswax *dispersions*: in chemistry, a dispersion means a system in which particles – formed by wax – are dispersed in a continuous phase of different composition, usually a liquid. This dispersion-making technique is being widely used to date, for many different purposes such as paints, glues, sun creams, lotions, etc. For the Egyptians, however, preparing dispersions was a very laborious issue, as anything had to be performed manually, without the assistance of modern technology.

1.3.1.2 Punic Wax

What are "Punic waxes," and why have they been important?

Punic wax – or cera punica – is a beeswax soap of paste-like consistency. The term "Punic" is equivalent to "Carthagian," and the Punics were also known as Carthagians.

[For the interested but nonhistorian reader: the Punic Wars, a series of three wars, were fought between Rome and Carthago from 264 to 146 BC; the famous Carthaginian general Hannibal crossed the Alps, won the famous battle of encirclement of Cannae, but in the end Carthago lost against the Romans and Hannibal lost his life.]

When wax is treated with a caustic soda, it results in a water-soluble soap. Saponification is not always just an easy procedure, at least not for people living a long time ago.

The numerous recipes and instructions for the preparation and processing of Punic Wax are somewhat mysterious: faith and ritual ceremonies played a great role. Egyptians believed that only during certain full moon phases the sea water would contain higher concentrations of sodium chloride (NaCl) and other salts necessary for the production of Punic Wax.

[Surprisingly, the salt content of water can depend on the moon phases, e.g. in zones where river water meets sea water. This is due to the different water layers near the surface and at depth.]

In short, to achieve chemical saponification wax had to be bleached with the aid of the sun and the moon, in combination with proper planetary alignments, by cooking with mineral soda, and heating with potash and other unknown, secret ingredients.

Since beeswax darkens rapidly in melted form through oxidation, the process of bleaching and saponification had to be interrupted and repeated several times. This is the standard procedure for wax saponification to date: darkening of beeswax dispersions can be counteracted by interrupting the process, intermediate cooling, and addition of hydrogen peroxide (H_2O_2).

Exact formulations of Egyptian Punic Wax are unknown, because the priests in ancient Egypt kept their mysteries secret and took them to their graves. Neither the recipes nor the ingredients or procedures of the priests can be identified today; there are too many unknown variables.

The continual development of Punic wax into modified and, at the end, completely new products has taken several thousand years. By adding and mixing wax with rubber, mastics, isinglass, egg, fig milk, turpentine oil, olive oil, walnut oil, and others, the properties of the resulting product could be changed dramatically. Experts could adapt their formulations to many different purposes.

Punic wax, in its water-soluble form, could be used, e.g. as the basis for cosmetic applications. Another famous application is called **encaustic**, the art or process of encaustic painting: this means decoration of, e.g. ceramics by burning in colors as an inlay, especially using colored clays or pigments mixed with hot (Punic) wax. To prepare color pastes, people had to crush and grind the available pigments into very small particles, directly before use. Among the pigments or colorants were purple, anchusa (red), azurite, melinum, orpiment, abianum, malachite, cinnabar, earthy, tree bark, papyrus ash (black), heavy metal oxides such as cadmium (yellow) and lead oxide (white), or cadmium selenide (red). Some of these pigments are highly toxic and certainly left users with serious illnesses.

The chemical base for the use of waxes for colorant preparations is their binding power for pigments. On reliefs, stelae, etc. crafted before 3000 BC, we can still identify the waxes using analytical chemistry and determine the exact age using the radiocarbon method [10, 11]. It appears quite remarkable that the chemical composition and structure of beeswax, with its major components aliphatic hydrocarbons, acids, and alcohols, remain nearly unchanged over time.

In ancient Egypt, beeswax was already used in 3000 BC as a binding agent for pigments. This is seen in reliefs and stelae from this period [6, 7]. And the beeswax, even after all this time, did not change its original structure. This shows that aliphatic hydrocarbons, aliphatic acids, and aliphatic alcohols in beeswaxes guaranteed an almost infinite shelf life.

This is probably one of the most impressive examples of how long a color, protected by perfectly purified beeswax (the Punic wax), can resist the external environmental influences without changing itself. Visitors to the Egyptian "Valley of the Kings" are usually overwhelmed by the brilliance of colors of thousands of years of age.

1.3.1.3 Nefertiti

Nefertiti, Egyptian "Nfr.t-jy.tj," originally pronounced approximately "Nafteta" (in German: Nofretete) (c. 1370 to c. 1330 BC) [12], was an Egyptian queen and the Great Royal Wife (chief consort) of Akhenaten (German: Echnaton), an Egyptian Pharaoh (Figure 1.2).

In January 1925, Prof. Rathgen realized that the pupil of the limestone bust of Nefertiti is a black disk of wax (beeswax with carbon black).

By using Punic wax as a base for the makeup of the bust of Nefertiti, which is exhibited in the Egyptian Museum of Berlin, the Egyptians preserved this

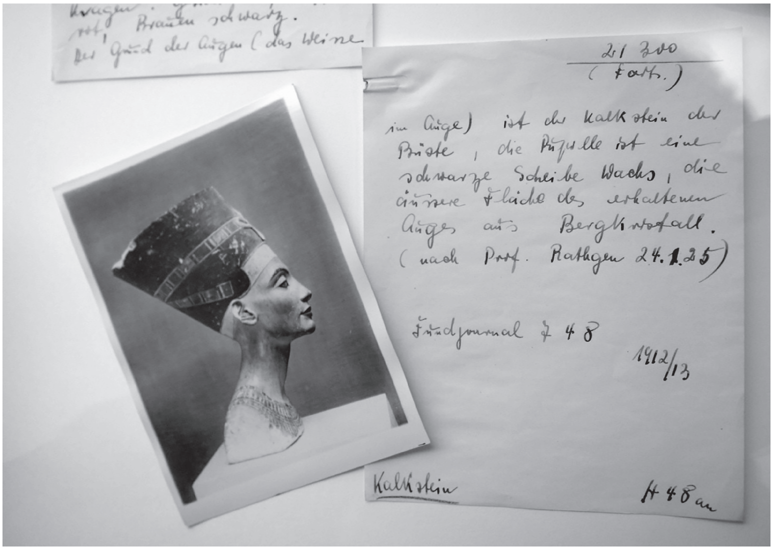

Figure 1.2 Fund journal card from the bust of Nefertiti – Egyptian Museum, Berlin.

beautiful image forever. The pigments for paintings were bonded in Punic wax, and subsequently, the bust was covered with an additional layer of Punic wax. Tulloch [13], when investigating the bust, found out that the makeup of the bust of Nefertiti was a mixture of beeswax with natural gum and resins. Stierlin [14] describes his first impression of the bust in his excavation diary with the note: "Colors as just launched. Work is quite excellent. Describe useless view. [...] Every other word is superfluous."

To be honest, there is still some doubt if the Nefertiti bust is a fake, a forgery [16]. Wax, which can be examined for its age using the C14 method, could help eliminate doubts.

Around 1920, the chemist Friedrich Rathgen had already drawn a sample, which survived in an old bag in the museum until its age was finally determined. Experts concluded that the material is probably more than 3300 years old. One may or may not find this proof convincing.

However, the material for analysis was not taken directly from the eye of the bust, where the wax had most probably been applied: this would be impossible today for reasons of conservation.

For the ancient Egyptians, Punic wax was not only processed locally but also traded and exported. Phoenician traders distributed this precious product over the entire Mediterranean region. All know-how of manufacture was kept as a secret. In the famous Edfu Temple of Horus [a Falcon deity; temple built in 237 BC] numerous recipes for cosmetics can still be deciphered, engraved on the walls in hieroglyphs (Figure 1.3).

[Anyone deeply interested in the medical and cosmetic treatments in ancient Egypt is referred to the so-called "Ebers Papyrus," written in hieroglyphics [17]. It is currently kept in the library of the University of Leipzig in Germany.]

Figure 1.3 Case presentation "Tumor against the deity Xenus." Source: Public domain, https://commons.wikimedia.org/w/index.php?curid=1504673.

1.3.2 Greeks, Romans, and Waxes

1.3.2.1 Bronze Casting

The Greeks and (later) the Romans are known to have adopted many cultural achievements from other people. No wonder that they especially admired Egyptian arts and techniques. Among other items, they further developed the refinement and use of beeswax.

With respect to the head of a Greek bronze statue from the fifth century BC, Farnsworth [15] describes another substantial advance in the use of beeswax. After mixing with quicklime (unslaked calcium carbonate), the mixture was converted into a hard cement-like mass. This could be processed and used as a casting mold.

1.3.2.2 Wax Tablets in Ancient Times

When today's people hear about "tablet" they think of "tablet computers." However, "tablets" are much older (Figure 1.4).

Wax tablets have been found in various forms, ranging from a single slab of wood with waxen surface to a 10 or more-paged book.

The Romans used wax tablets that were made of wood and covered with a layer of wax, often linked loosely to a cover tablet, as a "double-leaved" diptych. It was used as a reusable and portable writing surface until the Middle Ages (Figure 1.5).

Cicero's letters make passing reference to the use of *cerae*, and some examples of wax-tablets have been preserved in waterlogged deposits in the Roman fort at Vindolanda on Hadrian's Wall.

Writing on the wax surface was performed with a pointed instrument, a stylus. Writing by engraving in wax required the application of much more pressure and traction than would be necessary with ink on parchment or papyrus, and the scribe

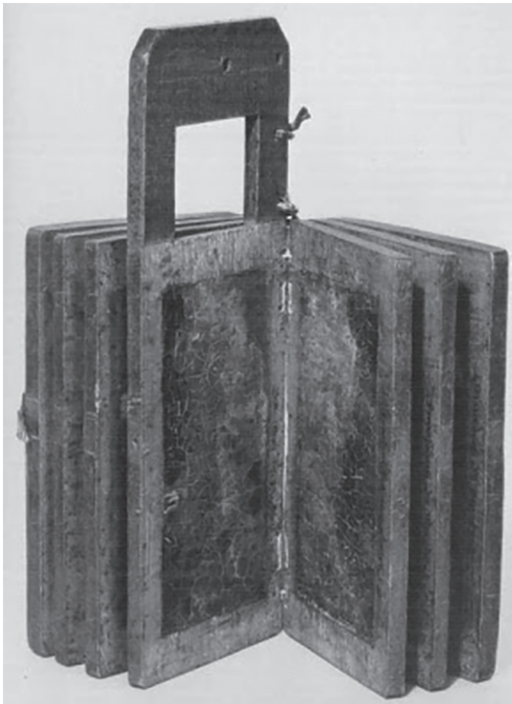

Figure 1.4 A book of wax tablets shown at the National Museum for Art and Cultural History in Bremen, Germany.

Figure 1.5 Wax tablet and a roman stylus.

had to lift the stylus in order to change the direction of the stroke. Therefore, the stylus could not be applied with the same degree of dexterity as a pen. A straight-edged, spatula-like implement (often placed on the opposite end of the stylus tip) would be used in a razor-like fashion to serve as an eraser. The entire tablet could be erased for reuse by warming it to about 50 °C and smoothing the softened wax surface. The modern expression of "a clean slate" equates to the Latin expression "*tabula rasa*."

Wax tablets were used for high-volume business records of transient importance until the nineteenth century. For instance, the salt mining authority at Schwäbisch Hall employed wax records until 1812 [18].

Some experts believe that already Homer mentioned wax tablets:

> The king [Proetus] was angered by her words. He would not kill Bellerephon, as his heart shrank from murder, but he packed him off to Lycia, and scratching many deadly signs on a folded tablet, gave him that fatal token.
>
> Source: Iliad, Book VI

The dating of the Iliad of Homer varies greatly, between the thirteenth and the seventh centuries BC.

Unquestionable proof of wax tablets was first provided by Herodotus,[1,2] the famous Greek historian, in his great work "The Histories" (Figure 1.6).

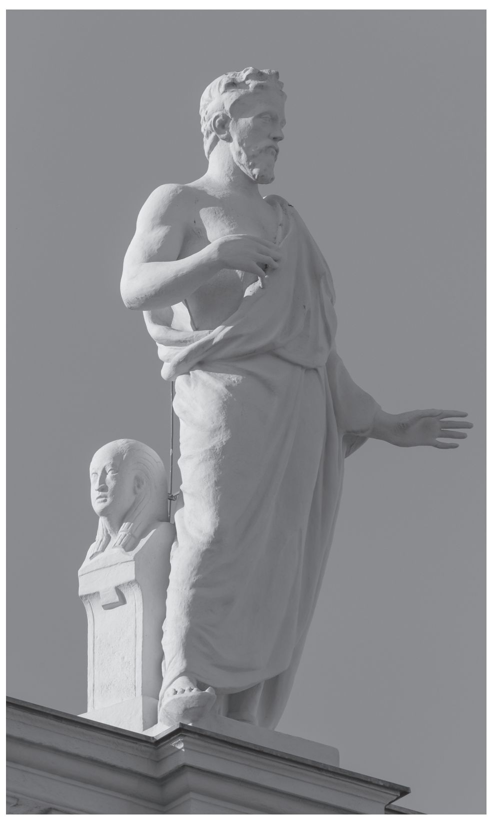

Figure 1.6 Herodot von Carl Kundmann auf der Attika des Naturhistorischen Museums in Wien. Source: Von © Hubertl/Wikimedia Commons, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=46495004.

1 490/480 BC.
2 Around 424 BC.

Back to the Romans: wax tablets became so popular that they became the largest scale application of waxes over centuries. An astonishingly large number of Roman wax tablets have been discovered, e.g. from Pompeii.

1.3.2.3 Wax Tablets at Later Times

There is a long, in certain areas still lasting, tradition of using wax tablets for learning at schools. Starting in the Mediterranean area, this application spread over Europe, and became quite common throughout the Middle Ages. It is not forgotten even today, in the computer age, in some regions. Wax tablets also won importance in the transmission of communication, like exchanging letters in later ages.

How was this done? With the tip end of a stylus made of wood, metal, or ivory, the writer scratches letters into the wax. The shallower end of the stylus serves as an eraser by simply stroking mistakes smoothly. For larger parts of mistakes, a broad wax putty knife was used by the writers. Wax tablets were particularly well suited for sending letters or messages with business contracts. Wax panels were knotted together and sealed with hot wax and a special stamp signet ring. The recipient of a message could check the seal, and if it was intact could feel quite sure that no unauthorized person had gained the information. And there was another advantage: the wax tablet could be reused – "recycled" – by the receiver after heating the tablet for a short time, for example, in the sun.

1.3.2.4 Candles

The first candles were invented in the Orient approximately 5000 years ago [19]. These were not fabricated from beeswax, but consisted of straw, hemp, or reed, which was soaked in fat or resin. They must have pitifully stunk and heavily smoked. Less sooty candles could later be produced by the ancient Romans, by replacing fat and resin with beeswax as burning material. From here, the candles could be used in the household with the beginning of the second century BC. They were curled up in papyrus and dipped in beeswax [19]. But initially they were prepared only for the upper segment of the population, because this type of lighting was not the cheapest.

Christianity and its development of liturgical actions were the driving forces for a rapid spread of the use of candles. By using beeswax instead of sooty fats and oils, candle technology was further developed and refined through the Middle Ages.

Constantine I, the Roman emperor from 306 to 337, determined that all the church processions should be accompanied by large wax candles, and that the Easter night should be turned into the brightest day by the burning of a huge number of high "wax columns" and fire flares.

As wax was used as in the form of wax candles, it became an integral part of the church liturgy.

A little later, Saint Ambrose (339–397), one of the four church fathers, glorified the bee and the wax in his Missale.

Hieronymus (347–420), another church father, recommended the burning of lights during the reading of the gospel. The light mess festival was also held in Jerusalem in the fourth century, and the Easter candle in Italy and Spain for the first time. The candle had become a symbol of divine light and divine purity. In wax, the product of the "virgin bee," the church fathers saw both a symbol of the virginity of Mary and the holy humanity of Christ.

Beeswax was only available in limited amounts and thus became a very valuable resource. It was reserved mainly for ecclesiastical liturgies, and for the rich princely houses. Only by the end of the fifteenth century could beeswax be harvested in higher quantities. Now the owners of wealthier town houses could also afford such an illumination in their homes!

The hassle of producing beeswax candles was well known to the manufacturers: the wicks of the candles had to be trimmed continuously, so that they could reduce the formation of soot and drops. Despite all the progress, the problem with the wicks remained for a long time. Even Goethe had the desire: "Do not know what they could invent better than the lights burned without brushing." This pesky problem, however, could not be solved until the nineteenth century. Many significant developments in today's candle making were realized through the nineteenth century.

In 1820, Eugène Chevreul (1786–1869), a famous French chemist, found out how to separate fatty acids from animal fats [20]. This ultimately led to the development of stearin: a substance that is quite tough, unperishable, and burning nearly without residues. Candles made of stearin are still popularly in use today.

After being able to separate the naturally occurring paraffins from petroleum, candle-making was revolutionized. Paraffins are wax-like substances, odorless, and can be refined up to extremely high purity. They are free from potentially troublesome by-products.

Economically, paraffins started a success story: cheap, burning clearly with little sooting, the ideal material for candles! The only technical disadvantage, its low melting point, can be compensated with "hard stearin." Beeswax was a loser, but not totally: a mixture of paraffin with 5% beeswax was, and is still, used as raw wax for candles, e.g. in the Catholic Church.

The candle – for most people still the typical wax product – has experienced a long development in different cultures since its first use. It has been the preferred light source of humanity, with unbeaten popularity.

Nowadays candles symbolize celebration, especially during religious festivals, standing for romance, soothing the senses, and setting accents for decoration. Candles generate a warm and wonderful glow to the delight of all people [19]. But with the invention of the light bulb by Edison in 1879, candle making lost its prime importance for general lighting purposes. From the ancient world to modern times, waxes were mostly used for a variety of applications.

But beeswax candles, marked with "100% natural origin," play a small but interesting role, despite – or because of – rarity and price.

1.3.2.5 Waxes in Medicines and Cosmetics

The Roman physician Galenus of Pergamom (129–201 AD) is considered as the originator of scientifically based preparation of medicines and cosmetics [21]. One of his inventions, a dispersion currently known as "cold cream" [Latin: ceratum refrigerans], is used as a cream for dry and itchy skin. This "classic" cosmetic is a formulation of olive oil, beeswax, and rose water. On application of the cream on the skin, the dispersion breaks and generates a cooling effect by evaporating water. To date, cold creams make use of this physicochemical effect.

Astonishingly, already the Romans warned against excessive use of cosmetics! They had determined that some preparations could have negative effects on health, e.g. leading to skin problems such as premature aging.

1.3.2.6 Waxes as Cosmetics in Early Christianity

In sharp contrast to Roman culture, early Christians strongly opposed the use of cosmetics. They were convinced – and many still are – that real beauty only comes from the inside. For Christians only their souls were relevant, not the outer, mortal beauty. Thus, cosmetics were deemed unnecessary and superfluous. This new belief resulted in an economic effect, a significant decrease in the use of beauty-promising cosmetics. A woman decorating face and lips with cosmetics could even be regarded and denounced as a prostitute!

The decline in cosmetic culture continued until the Middle Ages. But there was a very negative side effect of this originally religious attitude: parallel to the refusal to use cosmetics, medical and hygienic knowledge and applications decreased. So, for the beeswax "industry," wax tablets and candles became the prime business. For these purposes, it was no longer necessary to clean the beeswax, a simplification of production but a loss in know-how.

1.3.2.7 Wax Trading in the Middle Ages

Already from the Bronze Age the first traditions for the wax trade are available [22]. Nordic merchants brought skins, potash, honey, and wax to southern countries, to exchange it for bronzeware [23].

According to historic reports from the year 973, in the early time of the Kievan Rus (882–1283), Russians could produce quite a large amount of honey- and beeswax. The volume by far exceeded their own needs. Some years, they could export more than 1000 tons of beeswax [24]. From contracts between Russian princes and Byzantine merchants in the ninth and tenth centuries, we are well informed about specific items and conditions of trade. The Byzantine merchants offered silk and spices; in exchange they bought slaves, wax, and furs from the Russian princes [25].

Wax was, in addition to fur, the outstanding commodity from Eastern Europe, which was needed in large quantities in Western Europe.

From the last third of the thirteenth century a French list of the countries and their products, which were traded in Bruges (Belgium), has been preserved. Wax was imported from Russia, Hungary, Bohemia, Poland, Castile, Andalusia, Granada, Portugal, and North Africa from Fez, Bugia, Tunis [26].

At the beginning of the sixteenth century, Albert Krantz, in his "Wandalia," explained that the beginning of trade with Russia was a golden time for the merchants. The heathens, who had no idea of the value of the wax, would have thrown this as trash behind their house, and be glad when strangers took it with them [27].

In his PhD thesis [28], Peter Heinz Stützel describes the select examples of wax trading in the Middle Ages in detail.

1.3.3 Waxes from the Indians

Long before Columbus discovered America, the Papago Indians collected the seeds of jojoba shrubs in the semi-deserts and dry areas of Mexico, California, and Arizona. By roasting the seeds, they obtained the jojoba wax. This was used as a remedy for skin diseases, external inflammations, pattern baldness, and head scales. Today, we know that jojoba oil – which actually is a wax – when applied to the skin, affects microorganisms and fungi (*Candida albicans*). Jojoba oil can stop the metabolic pathway of the said species.

This benefit is the reason why jojoba oil is a preferred raw material for the treatment of acne and unclean skin. Remarkably, the use of jojoba wax remained a secret of the Indians even after the settlement of North America by European immigrants. It was not before the last decades that the excellent cosmetic properties of jojoba wax were rediscovered, and the demand for this natural resource increased significantly.

When Columbus (Spanish: Cristòbal Colon) entered one of the islands of the Greater Antilles on his first voyage to the “New World,” he regarded one place to be suitable for a settlement.

In his board book, dated 29 November 1492, it is written as follows:

> In one house they found a cake of wax, which he [Columbus] brought to the [Castilian] Sovereigns, and he says that where there is wax there must also be a thousand other good things.

It is supposed that the wax was brought from Yucatan, Mexico – an early proof of trading in Old Latin America.

There is another impressive description of the value and use of wax by Bancroft, a physician and chemist (and, by the way, a double spy for the United States and Britain). Edward Bancroft (1745–1821), a Massachusetts-born chemist, became a plantation doctor in Dutch Guiana in South America. After returning home in 1776, he published the “Essay on the Natural History of Guinea” in 1769 [29].

The impure beeswax derived from black bees was melted and boiled with charcoal, and then filtered through linen cloths. After being treated this way, wax was significantly brighter and was suited, e.g. to cover wounds, like we use pavements nowadays. Clearly, it was the antibacterial effect of beeswax that offered this new opportunity. But the Native Americans also used purified, molten wax for the preparation of candles. They dipped long twisted cotton threads into the liquid beeswax several times, and then wrapped it into a ball shape, weighing up to 1 kg. The light thus generated was not as bright as that of European tallow and wax candles; however, the technique is applied even today with handcrafted candles, with slight modifications. A separate chapter on candles discusses the close relationship between wax and candles – see Appendix B Candles – A Most Popular Application Area for Waxes.

1.4 Origin of Natural Waxes

All waxes are organic materials, which indicates that they did not exist in the early ages following the birth of our planet earth. Earth formed around 4.5 billion years ago, according to the latest scientific evaluation [30]. The earliest evidence of life on earth dates at least 3.5 billion years ago but the origin of first living organisms from non-living matter (in biology called abiogenesis) is still an unsolved enigma of science.

So, nature took quite a long time from the beginning of the earth to the beginning of life, and only between 3.2 and 2.4 billion years ago the first photosynthetic organisms appeared on our planet. They began enriching the atmosphere with oxygen, switching it from a reducing to an oxidizing environment. Photosynthesis – Photosynthesis of Plant Waxes – has been and still is the most important biochemical mechanism to produce living organisms from "dead matter."

But the path from simple first organic substances and primitive organism to waxes was still very long. We must differentiate between waxes that were just built from organic predecessors, following chemical degradation of once living organisms, and waxes specifically "designed" by nature to serve special purposes such as protection against a hostile environment [31].

The beginning of waxes, as we know them today, starts with the decomposition of organic substances originating from the early years of our plant system.

1.4.1 Petroleum Waxes

Petroleum waxes are by far the oldest species within the world of waxes, as these are defined today. They are a minor constituent of crude oil, or petroleum, and can be roughly classified into paraffin wax, microcrystalline wax, and petroleum jelly. Petroleum – and hence these waxes – are derived from ancient fossilized organic materials, such as zooplankton and algae. Vast quantities of these remain settled at sea or lake bottoms, mixing with sediments and being buried under anoxic conditions. As further layers settled on the sea- or lakebed, intense heat and pressure built up in the lower regions. This process caused the organic matter to change, first into a waxy material known as kerogen, an insoluble organic material in sedimentary rocks that is found in various oil shales around the world. Petroleum and its associated "by-product" waxes were formed through many millions of years and certainly still are, however, on a time scale negligible to the rate of consumption at present.

[Although compliant with the general definition of waxes, petroleum waxes differ substantially in chemical composition from their cognate plant and animal species. In addition, their actual production volume exceeds that of other waxes by orders of magnitude. Chemically, they are much more related to partly or fully synthetic waxes. That is why they are not covered in this volume on natural waxes.]

1.4.2 Plant Waxes

Plant waxes were the next to appear on earth, following those just built from degradation of dead organic materials. They did not exist in the early days of life. While the earliest forms of life existed at least 3.5 billion years ago, it took more than at least another billion years before "waxes" became – surely not the most important but nevertheless indispensable – part of nature.

It was plants that developed waxes after leaving the oceans in the era of Ordovician (between 485.4 million years ago [Mya] and the start of the Silurian Period 443.8 Mya).

Some 450 million years ago, plants started to enter and conquer land – clearly one of the great breakthroughs in evolution. Ocean water had been protecting plants against the rigors of climate and weather, solar radiation, and changing environment. Now plants had to control their water supply and storage in an effective way, to survive the periods between rainfalls and dry periods. Like water, solar radiation had to be utilized most effectively: it was needed for the photosynthesis process, to build up the plant material, but a protective shield against too much sunlight was necessary to avoid desiccation. "Wax" as we will see later, was a key factor in solving the new challenges on land.

1.4.3 Animal Waxes

The history of animal waxes is much shorter, on a geological time scale. It started with insects, with bees, our favorite natural wax producer. A species called *Melittosphex burmensis* is the oldest known bee that has been discovered until today. It was found as an amber inclusion of the Cretacious Period (c. 100 millions of years ago) in the year 2006 by Poinar (Oregon State University). An impressive example of a honeybee, already much resembling a modern type of bee, was preserved in amber in the German Eifel low mountain range, aged c. 45 millions of years (Figure 1.7).

Figure 1.7 Honey mead from the Middle Eocene of the Eckfelder Maar [32].

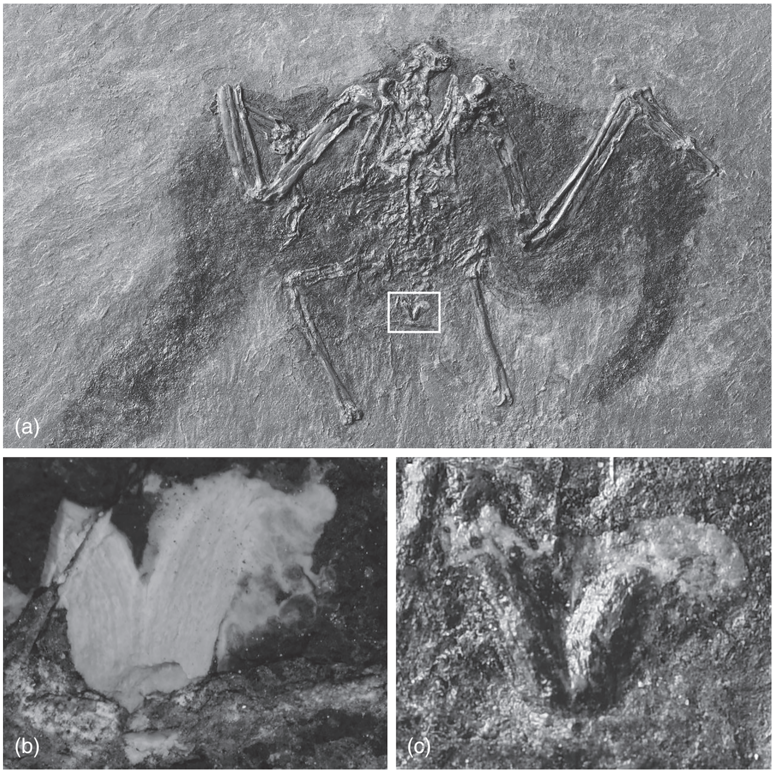

Figure 1.8 Preservation of uropygial gland lipids in a 48-million-year-old bird.

Last but not the least we may refer to a very recent finding: a group of researchers at the University of Bristol's School of Earth Sciences together with researchers at the Senckenberg Natural History Museum in Frankfurt, Germany, have analyzed a well-preserved preening gland in a 48-million-year-old bird fossil and discovered original oil and wax molecules within, which can be seen very well in the enlargement of the framed area (Figure 1.8) [33].

The fossil was discovered from the famous Messel locality in Germany, which is well known for preserved birds, mammals, fish, reptiles, insects, and leaves with exceptional details. We should not be surprised if some day fossil waxes are detected even from dinosaurs or early mammals – these had entered the earth long before the abovementioned bird fossil. There are some indications of lipids that are supposed to have been identified in dinosaur bones, but paleobiological science still needs improved analytical methods for confirmation of the first "dinosaur waxes."

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