BEESWAX THROUGH THE AGES.

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1. Introduction

Beeswax is the lipid secretion from special abdominal glands of the honey bee, Apis mellifera and related Asian species. Beeswax is employed by the bee for comb construction and for capping individual cells.
The secreted wax contains special substances (flavonoids) in order to protect it from oxidation and micro-organisms. Beeswax obtains its many colours from contact with plant material collected by the bee, in particular from propolis and pollen. As pollinators, bees perform a very important function in agriculture. The use of modern apiary techniques has been reported to increase crop yields by up to 50 % and more.
Many bee products, such as honey, wax, royal jelly, propolis, pollen, etc. are used by man for food purposes and the production of cosmetics and pharmaceuticals. Without beeswax, many quality cosmetic products such as lipsticks, creams, lotions, mascaras and suncare products could not be produced as we know them today. Furthermore beeswax is used for candles, polishes, coatings, sealants, etc. and a myriad of industrial applications.

2. Short history of beeswax usage in medicine and cosmetics.

Beeswax is one of the oldest cosmetic raw materials known to man. Many ancient civilisations used bee products for medicinal and cosmetic purposes, or practices bearing relation to cosmetics.
Beeswax was used in embalming in Egypt and other areas of the Near East. Embalmers used wax to cover eyes, ears and nose during mummification. The coffin was made airtight with beeswax (Ref. 24). According to Herodotus the ancient Iranians sometimes covered their deads with beeswax before burying them. Our word mummy is derived from a Persian word meaning 'wax'. Clearly the wax functions as a preservative and as a barrier against air and moisture.
The ancient Egyptians used wax for retaining the permanency of wig curls (Ref. 24) and also beeswax together with pigments was used for cosmetic purposes. Beeswax was also used to preserve papyrus scrolls and to protect paintings (Ref 24 etc.).
The Greek physician Galen (Rome, 2nd century A.D.) used beeswax, olive oil, water and most likely potash for his "*ceratum refrigerans*" (cooling ointment), the prototype of cold cream emulsions (Ref. 22). Undoubtedly Galen derived at least part of his knowledge from older sources, such as from Mesopotamia, Egypt and Greece.
The famous Iranian physician Avicenne (10th century A.D.) recommended beeswax in medicine.

China has a long history in using bee products in medicine, health care products and personal care (Ref. 1).
In China's most famous medicine book, "Shen Nong Bencao Jing" or "The Shen Nong's Book of Herbs" (ca. 1st- 2nd B.C., Han dynasty), or its revised version from the Ming dynasty, titled

"Bencao Gang Mu", beeswax is classified as a top-grade, non-poisonous medicinal ingredient of the 'Ping' category. It is praised for its beneficial influence on blood and energy systems and the overall balance of the body. The author attributes beauty enhancement and anti-aging properties to beeswax.
Combined with other ingredients it is applied on the skin for treating wounds and as a health food for dieting. Many recipes are given is this authoritative source of traditional Chinese medicine.
Ge Hong (about 284-364, Jin dynasty) and Sun Simiao (581-682) recommend 'beeswax therapy', i.e. a heat treatment of skin areas with cloths impregnated with molten beeswax.
Liu Yuxi in 841 gives a detailed description of beeswax therapy more than 1000 years earlier than the paraffin wax therapy from the Frenchman Barthe de Sandford (1909).
"The Sages Prescriptions", edited by the Song Dynasty Imperial Hospital (992), mentions diet therapy, health-improvement and anti-aging prescriptions containing honey, beeswax and honeycomb.
The Chinese also invented "Bee Acupuncture", a form of acupuncture employing living bees.

Traditional Chinese and Tibetan medicine is enjoying increased popularity as the West realises the value of traditional medicinal practices, complementing western medicine (Ref. 23). With research, centuries old experience in traditional Chinese medicine will have increasing value in the West.

3. Modernisation of Chinese apiculture in the 20th century.

The Chinese have more than a 3000 year history of beekeeping.
In the 20th century the native Chinese bee (Apis cerana sinensis) has for a large part been replaced by the European bee (Apis mellifera ligustica and other types) (Ref 1). In many countries the European bee has been imported together with European beekeeping techniques (movable-frame hive technology). The main reason for the systematic introduction of the western bee, initially from Japan and the USA, was its superior honey production and easier beekeeping behaviour. Now more than two third of the bee population of China (1991: 7.5 million colonies) is of the European race.
However the western bee has also its disadvantages. For example, it is more vulnerable to disease and is less adaptable to extreme climates.
The introduction of modern beekeeping techniques and western bees revolutionized Chinese apiculture. The bee population grew enormously, dramatically increasing the production of honey, beeswax and other bee products.
In cooperation with the Chinese government, the production of the honey has increased manyfold to 208.000 tons (1991, Ref. 1) and the production of beeswax to more than 3000 tons (1991, Ref. 1).

China is at this moment the world's largest producer and exporter of honey, beeswax and royal jelly.

The European bee has also successfully been introduced into other Asian contries, notably Japan, Vietnam and Korea. In other countries the introduction either failed (for example Sri Lanka) or occurred at a much smaller scale.

Tulloch (Ref. 6,7) and Stransky, Streibl and coworkers (Ref. 3,4,5) used a combination of Preparative Column Chromatography and GC/MS for a very thorough analysis of the composition of European Apis mellifera wax (see Table 1, first column). It is now clear that beeswax is not just the mixture of simple (mono)esters, acids and hydrocarbons as it is often quoted to be. Routine statements about beeswax's composition neglect important aspects of its composition and do not do justice to the complex and unique character of this natural wax. Beeswax contains ca. 35 % of complex polyesters. It is precisely this complex ester fraction, which is largely responsible for the unique and plastic character of beeswax. The large content of (ω-1)- and (ω-2)-hydroxy fatty acids give these complex polyesters their special characteristics. This is the reason why beeswax is more than just a thickener in cosmetics formulations.

Comparison of wax from European and native Asian bees.

Referring to Fig. 1 it can be seen that the carbon chain length distribution of the hydrocarbons and esters of the two Asian beeswaxes (C,D) are totally different from European and African beeswaxes (A,B). Also the two Asian beeswaxes differ considerably.

As no detailed analysis of Asian beeswaxes has been published, as far as we have been able to find, we started an investigation to determine the composition of oriental beeswaxes.
In this article we present the preliminary results of this analysis (second and third column of Table 1). By GC we have identified and quantified the main fractions.
In Table 1 we have summarised the composition of European(African), Chinese and Indian beeswaxes.

Not only do both Asian beeswaxes have much lower acid values than European and African beeswaxes, but surprisingly they (almost) lack a free fatty acid fraction. The acid value must come almost entirely from esters with free carboxyl groups, such as acid monoesters and acid polyesters. In European and African beeswaxes the acid esters account for ca 1/5 of the acid value.

4. Analysis of Beeswax: Composition.

Comparison of wax from European and native Asian bees.

Western beeswax has been extensively investigated using such modern instrumental techniques as Gas Chromatography (GC), Mass Spectrometry (MS), GC/MS, Thin Layer Chromatography (TLC), Column Chromatography etc. and combinations, which give detailed information of its composition. Especially High Temperature Capillary Gas Chromatography is a powerful tool for routine analysis of beeswax. Figure 1 (A,B,C,D) give typical examples of gas chromatograms of four beeswax types.

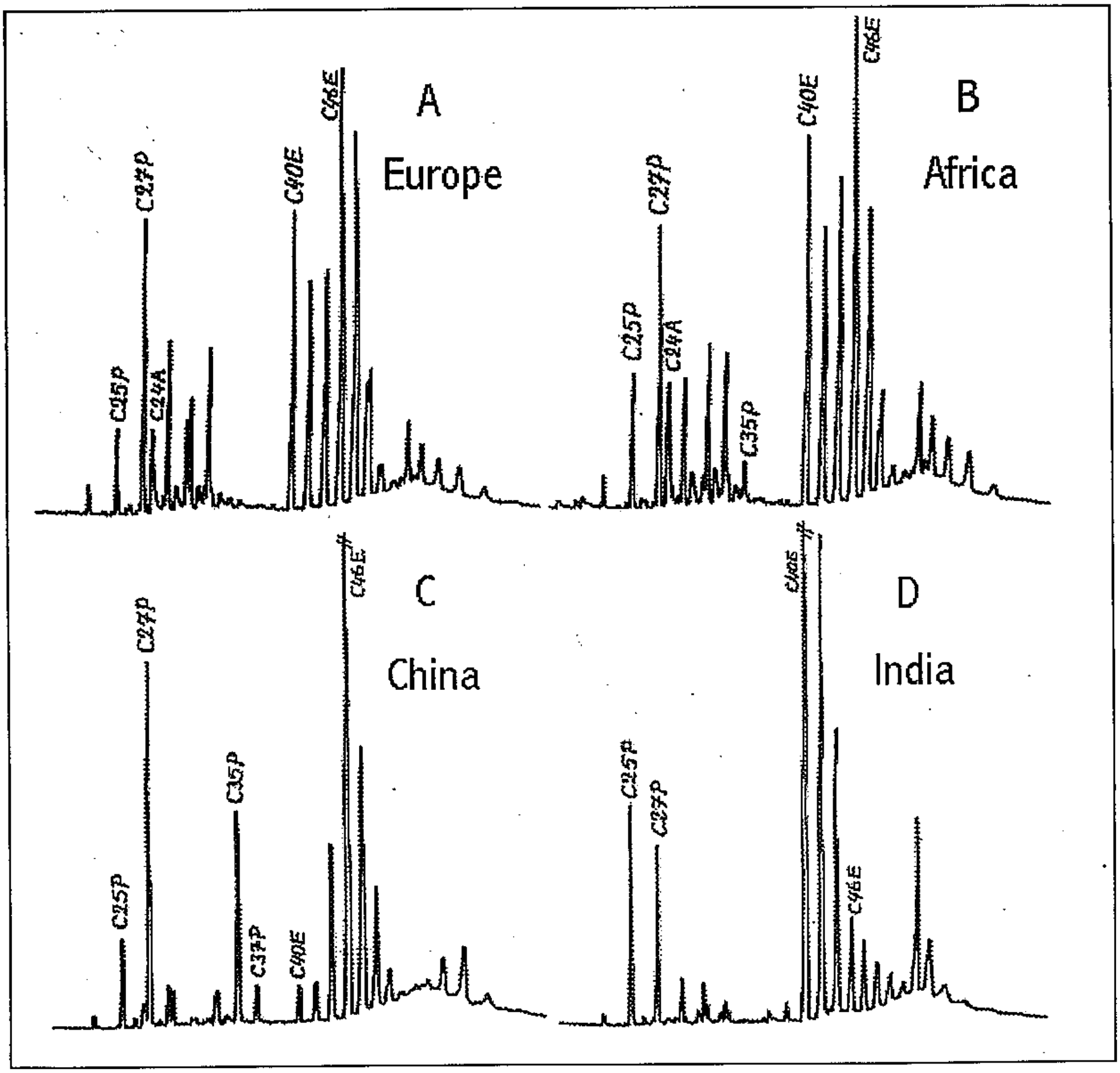

Fig.1 High Temperature Capillary Gas Chromatographic analysis of beeswaxes.

1A. Beeswax from European bees.
1B. Beeswax from African bees.
1C. Beeswax from native Chinese bees.
1D. Beeswax from native Indian bees.

Table 1 Composition of beeswax from European and native Asian bees.

	Europe[1,2]		China[3]		India[4]	
	C. No.	%	C. No.	%	C. No.	%
Hydrocarbons	C21-C35	13-16	C23-C37	ca.15	C23-C35	ca. 8
- % saturated	C21-C35	ca. 66				
- % unsaturated	C29-C35	ca. 32		small		small
- % branched	C14-C38	ca. 2				
Free fatty acids	C16-C36	11-12		small		small
Esters	C38->C66	71-74	C40->C66	ca. 84	C38->C66	ca. 90
- monoesters	C38-C54	27-33	C40-C52	ca. 26	C38-C52	ca. 27
- hydroxymonoesters	C40-C52	7-9	C40-C50	ca. 11	C40-C52	ca. 19
- diesters	C56-C68	14				
- triesters	C72-C84	3				
- hydroxypolyesters	C56-C100	8				
- acid monoesters	C32-C44	1		ca. 2?		ca. 2?
- acid polyesters		2		ca. 3?		ca. 3?
- unident. polyesters		8				
- glycerides		traces		traces		ca. 3
Typical cong. point	62 °C		63.5 °C		59 °C	
Typical AV	18-20		6-7		6-7	
Typical EV	70-75		80-83		85-89	

Notes:

1. *Wax from European bees (such as Apis mellifera ligustica, etc.; Europe, Siberia, China, Japan, Vietnam, U.S.A., Canada, part S. America, Australia etc. (Ref. 16)) (see also Figure 1A).*
2. *Wax from African bees (such as Apis mellifera scutellata, A. m. adansonii, etc.; Africa and now also S. and C.America (Ref. 16)). is similar to wax from European bees. (see also Figure 1B).*
3. *Wax from native Chinese bees (Apis cerana cerana = A. c. sinensis; China and Central Asia, N. India, etc. (Ref. 16)) (see also Figure 1C).*
4. *Wax from native Indian bees (Apis cerana Indica; S. and C. India, Bangladesh, Malaysia, Indonesia, etc. (Ref. 16)) (see also Figure 1D).*
5. *C. No. = Carbon chain length; unident. = unidentified; cong. point = congealing point.*
6. *AV = Acid Value; EV = Ester Value.*

5. Beeswax Analysis: Morphology and Crystal Structure.

Techniques such as X-ray Diffraction, Electron Diffraction, Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC and related techniques), (polarised) Light Microscopy, Scanning Electron Microscopy (SEC), etc. also furnish information on the morphology and crystal (micro)structure of beeswax and other waxes.

It has been proven that beeswax and most other waxes, are definitely crystalline(Ref. 18,19). However their typical crystal structure combines crystalline and amorphous characteristics into one material.
During cooling and solidification of a liquid wax the long chain wax molecules allign, forming various sizes of crystallites: the crystalline zones. Because of the variation in chain lengths, zones with voids and loose ends are formed at the crystal borders. These zones are called the chain-end defect or rigid amorphous zones. Components which cannot be accommodated well into crystallites, such as shorter chains, branched chains, unsaturated chains and oils, usually fill up the room between the crystallites, creating the so called mobile amorphous zones (Ref. 19). In beeswax at least two types of crystallites are involved (Ref. 18).

Waxes derive their typical oil gelling properties from their characteristic crystal texture. Crystallisation occurs in such a way that a paste is formed, consisting of a network of interlocked wax crystallites immobilising the oil. In other words waxes impose their structure upon the oil/wax mixture.

The very long chain hydroxypolyesters (C70 to over C100) in beeswax strengthen the network structure by forming bridges between zones.The high viscosity of the complex polyesters also contributes to hold the structure together (Ref. 20,21).
This explains the binding and oil-retention capability of beeswax.
The complex polyesters suppress the crystallisation of the monoesters in beeswax and lend to beeswax its characteristic pliability and microcrystalline crystal structure.

6. Beeswax in cosmetics.

The cosmetic industry is one of the largest users of beeswax.
Beeswax is used in the whole range of cosmetics, demonstrating its versatility as a cosmetic ingredient. A recently published cosmetics textbook (Ref. 2) states: "Beeswax is still the most important wax in cosmetics and a classical component for creams".
Many renowned international cosmetic companies use beeswax and appreciate its properties.
The consumer tends to prefer natural products in stead of mineral or synthetic alternatives and this preference is likely to be maintained in the future.

The improved knowledge of the functional composition of beeswax sheds a new light on the extensive application of beeswax in cosmetics.

In cosmetic products beeswax performs the following main functions:

1. Oil gelling agent.
2. Binding agent.
3. Consistency regulator for both W/O and O/W cosmetic emulsions.
4. Primary emulsifying agent (by saponification with alkalis like KOH, TEA, borax, etc.).
5. Highly occlusive fatty emollient.
6. Plasticizer.
7. Water-proofing.

Beeswax provides structural viscosity to lipsticks, lip balms, lip care sticks, mascaras, eye liners and other colour cosmetics.
Beeswax having good oil retention properties functions as a binder holding together the different components of a formulation, improving texture and pay-off. Beeswax also has excellent pigment compatibility and skin adhesion properties.
The moderate shrinkage properties of beeswax contributes to mould release in the production of sticks.
By partial saponification of its free fatty acids beeswax can perform as a primary emulsifier in creams and lotions. A well known example is "cold cream".
Beeswax is compatible with other emulsifying systems, such as modern non-ionic emulsifiers.
The various hydroxyesters of beeswax stabilise the emulsion by acting as coemulsifiers.

In addition to its function as a rheological additive beeswax softens, conditions, moisturizes and lays a protective barrier on the skin.
Beeswax is highly occlusive, but still enables the skin to "breathe".
The presence of unsaturates and polyesters in beeswax regulate the permeability for water vapour and oxygen. An analogy can be drawn to the protective function that natural (cuticle) waxes have for animals and plants.
To the film cosmetic products leave on the skin, the high plasticity of beeswax emparts flexibility, lubricity and therefore prevents cracking.
Once again the complex polyesters are responsible for this effect.

7.1. Quality Control and Specifications.

	USA[1]	EC[2]	China[3]	Japan[4]
Specific gravity	-	-	0.954-0.964	-
Melting point	62-65	-	62-67	60-67
Drop point	-	61-65		
Acid value	17-24	17-24	15-23 or 4-9	17-22 or 5-9
Ester value	72-79	70-80	-	-
Sap. value	-	87-104	75-110	80-100
Ratio (EV/AV)	-	3.3-4.3	-	-
Iodine value	-	-	6-3	-
additional purity tests:				
- test carnauba	+	-	-	-
- test paraffin, ceresin and certain other waxes = Sap. cloud test	+	+	-	+/-
- test fats, fatty acids, Japan wax, rosin, soaps	-	+	-	-

Notes:
1. United States Pharmacopeia / National Formulary.
2. European Pharmacopeia III.
3. The Quality Standard for Beeswax, Ministry of Commerce, Peoples Republic of China, No. GH013-82, May 1, 1983. No information was available to us concerning specifications for cosmetic or pharmaceutical usage.
4. Japan JSCI -II.

7.2. Toxicological Evaluation of beeswax.

Beeswax has world-wide Pharmacopeia, and Food Additive status (USA: GRAS, EC: E901). In a CTFA safety assessment review (Ref. 8) beeswax is concluded to be safe for use in cosmetics.

8. Suggested Formulations.

Formulations will be discussed and handed out during the presentation.

9. New Cosmetic Specialty Waxes.

Formulators choice of natural waxes, especially in the higher melting ranges, is relatively limited.
A case can be made for using modified or derivatised waxes.
The cosmetic industry in its never ending quest for innovative products, demand waxes which can provide properties not found in natural waxes.
We have succeeded in modifying beeswax and other natural waxes to meet this demand.
Polar and non polar derivatives and new synthetics have been developed.

These waxes aid formulators to incorporate otherwise destabilizing ingredients into their formulations.
Our beeswax esters (Ref. 9,12) and our siliconyl beeswax stabilize many multi functional products.
The context of this article on beeswax does not allow us to elaborate on the many varieties and their functions.
Please refer to the patent literature (Ref. 12-15) and to our publications (Ref. 9, 17).

- New natural waxes.

In search of novel vegetable waxes we introduced a wax from the orange peel (Ref. 10, 11), the sunflower seed, and from certain exotic flowers.
These waxes perform well in the trend for naturals.

- New synthetic specialty ester waxes.

The composition of beeswax served us as an inspiration source for the creation of new specialty ester waxes. We were interested to see what properties the individual fractions of beeswax have.

Kester Wax K82H imitates the monoester fraction of beeswax and introduces its oil gelling properties in a concentrated form (Ref. 13,14).

Kester Wax K80P imitates the complex hydroxypolyester fraction of beeswax and introduces its plasticity in a concentrated form. This wax melts at 80°C but remains pliable at low temperatures (Ref. 15).

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