NATURAL POLYMERS 3
WAXES

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Time schedule

LECTURE	SUBJECT
1	Introduction to the subject – Structure & Terminology of nature polymers, literature
2	Derivatives of acids – natural resins, drying oils, shellac
3	Waxes
4	Plant (vegetable) gums, Polyterpene –natural rubber (extracting, processing and modification)
5	Polyphenol – lignin, humic acids
25.10. & 1. 11.	**Polysaccharides I – starch**
8.11. & 15. 11.	**Polysaccharides II – celullosis**
22. & 22. 11.	**Protein fibres I**
29. 11. & 6. 12.	**Protein fibres II**
13. & 20. 12.	**Casein, whey, protein of eggs**
20. 12.	**Identification of natural polymers**
	Laboratory methods of natural polymers' evaluation

Latest news – CASEIN's Return? (Download in December 2017)

EU funds 'plastics from protein' project in France

French company Lactips says that its bioplastics project, Ecolactifilm, has attracted funding of €1.5m from the European Union's H2020 SME phase 2 programme.

The company produces water-soluble and biodegradable thermoplastic pellets from casein, a protein found in milk. The material, called Ecolactifilm and can be used in water-soluble or edible packaging.

Lactips said the funding would allow it to expand from 20 to 30 staff, and generate a turnover of €20m ($24m) by 2020, according to a report in Dairy Reporter.

The process begins by making pellets of the material, which can then be extruded into film. The company says that its first application will be to make a dissolvable film for dishwasher tablets.

Lactips has won funding to turn milk protein into plastic

The material will biodegrade in less than three weeks, says the company. In addition, it has an oxygen barrier and can support printing.

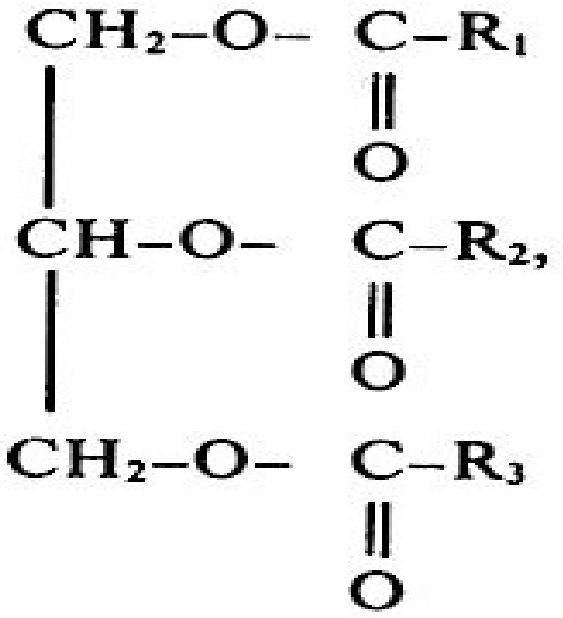
Lactips will also expand its research with the Jean Monnet University of Saint Etienne with a project called Hydroprint.

This project will look to develop water-soluble plastic filaments for use in 3D printing.

› **www.lactips.com**

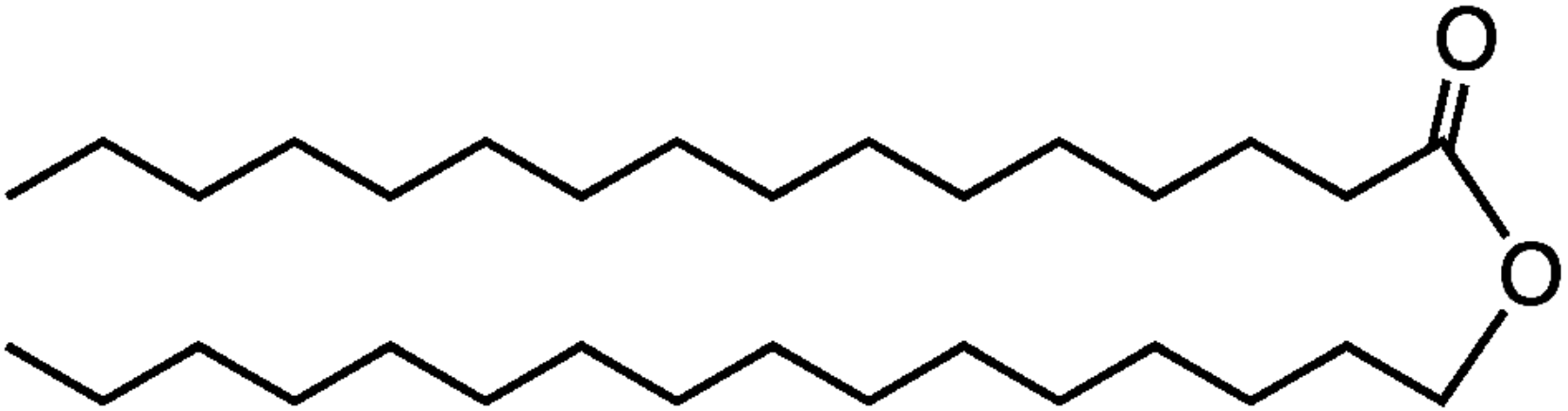
FATS –for a Reviving the Knowledge only (Lecture 2)

- **Vegetable Fats (Oils)**
  - Glycerides
  - Higher fatty acids (> 10 C)
    - **Saturated**
    - **Unsaturated**
      - One double bond only
      - More double bonds
        - » Isolated
        - » Conjugated



What are the WAXes?

Waxes are organic compounds that characteristically consist of long alkyl chains. They may also include various functional groups such as fatty acids, primary and secondary long chain alcohols, unsaturated bonds, aromatics, amides, ketones, and aldehydes. They frequently contain fatty acid esters as well. Synthetic waxes are often lo ack fu



Cetyl palmitate, a typical wax ester.

What is the Difference between Oils and *Wases*?

Oils

- Glycerides
- Higher fatty acids(> 10 C) **Unsaturated**
  - One double bond only
  - More double bonds
    - Isolated
    - Conjugated

Wases

- *Alcohols with longer aliphatic chain (approx. C > 15)*
- *The Waxes based od the DIOLS exist also*
- *Higher fatty acids (approx. > 15 C), mostly* ***SATURATED***

Whye are OILS liquid and and WASES are solid (USUALLY, at standard temperature)?

OILS

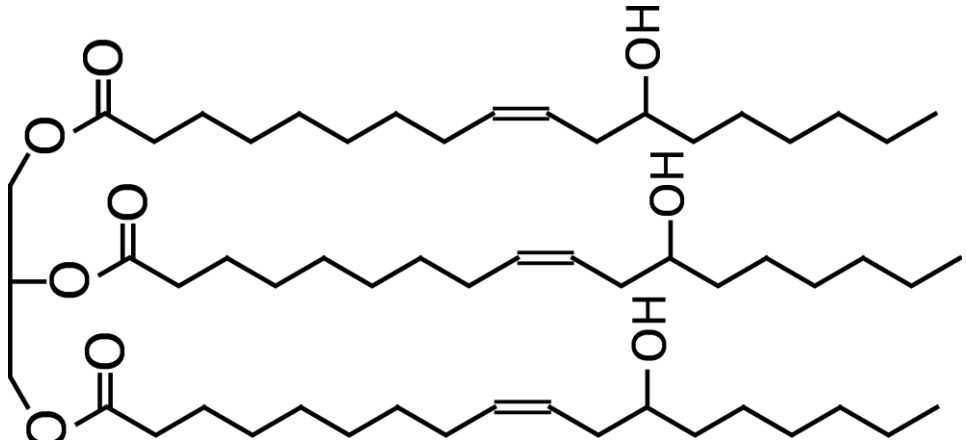
- **Unsaturated**
  - One double bond only
  - More double bonds
    - Isolated
    - Conjugated
- What is the movability around the DOUBLE BOND?
- How it influence the Crystallization Possibility?

Wases

- *Higher fatty acids (approx. > 15 C), mostly **SATURATED***
- *What is the movability around the SIMPLE BOND?*
- *How it influence the Crystallization Possibility?*
- ***How POLYOLEFINES crystallize ?***

From the OIL to WAX

Castor Oil



Three DOUBLE BONDS

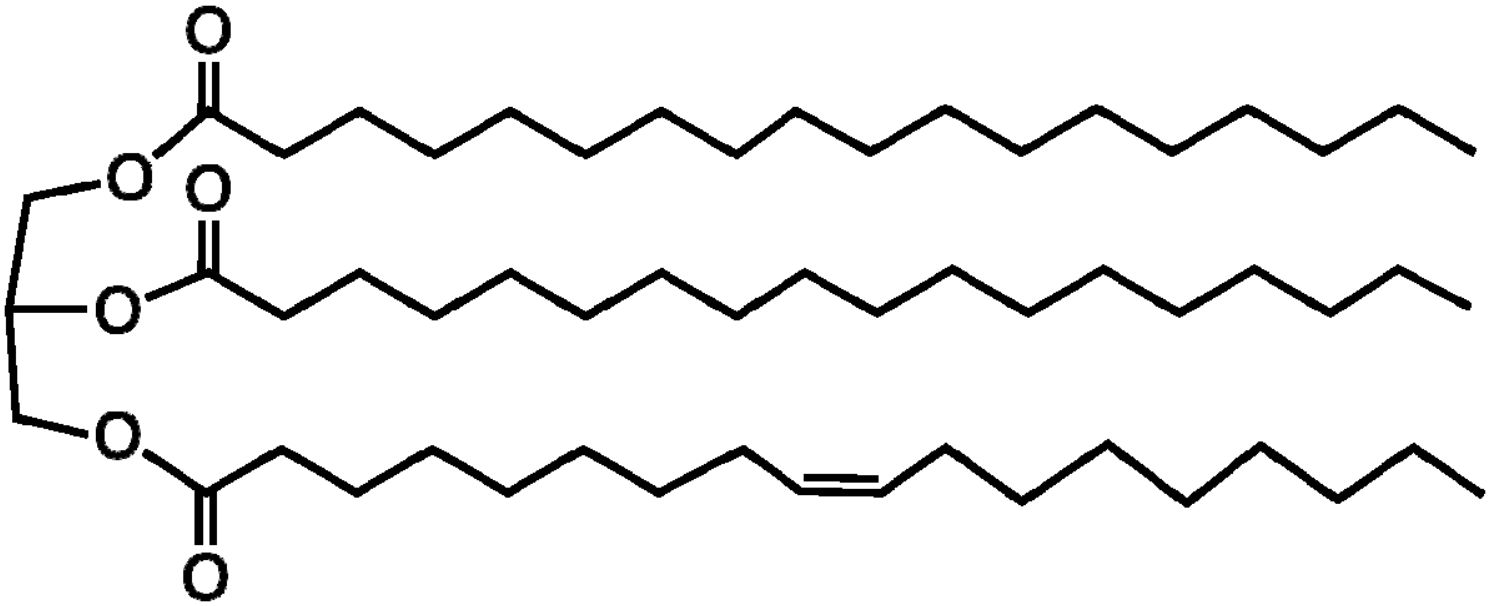
HYDROGENATION

Free –OH groups remains!

WAX > Castor Wax

Something between OIL and WAX is *Tallow, Suet*

One DOUBLE BOND (Oleic acid) + TWO saturated fatty acids (Stearic acid)



For what was TALLOW used in the past and for what is used now?

Waxes – natural X synthetic

- **Natural products**
  - Renewable sources
    - *Animal origin (very rarely)*
    - Vegetable product (prevails)
  - NONRENEWABLE RESOURCES
- **Modified natural products**

Synthetic products

Why put we WAXES in the Natural polymers?

Many of them have Molecular weight in the oligomeric region and many of them is possible to make by polymerysation of the alkenes or by **DEPOLYMERISATION OF POLYOLEFINS**

OLIGOMERS = bridge between low MW and POLYMERS

Comparison of Oils and Fatts

Type of fat	Total fat (g)	Saturated fat (g)	Monounsaturated fat (g)	Polyunsaturated fat (g)	Smoke point
Sunflower oil	100	11	20	69	225 °C
Soybean oil	100	16	23	58	257 °C
Canola oil	100	7	63	28	205 °C
Olive oil	100	14	73	11	190 °C
Peanut oil	100	17	46	32	225 °C
Rice bran oil	100	25	38	37	250 °C
Lard	100	39	45	11	190 °C
Suet (Tallow)	94	52	32	3	200 °C
Butter	81	51	21	3	150 °C
Coconut oil	100	86	6	2	177 °C

The **smoke point** of an oil or fat is the temperature at which, under defined conditions, enough volatile compounds emerge **when a bluish smoke becomes clearly visible from the oil.** At this temperature, volatile compounds, such as free fatty acids, and short-chain degradation products of oxidation come up from the oil. These volatile compounds degrade in air to give soot. The smoke point indicates the temperature limit up to which that cooking oil can be used.[1]

The **iodine value** (or "iodine adsorption value" or "iodine number" or "iodine index") in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. The higher the iodine number, the more C=C bonds are present in the fat.[1] It can be seen from the table that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints.

Acid value (or "neutralization number" or "acid number" or "acidity") is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance.[1] The acid number is a measure of the number of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. In a typical procedure, a known amount of sample dissolved in an organic solvent (often isopropanol) and titrated with a solution of potassium hydroxide (KOH) of known concentration using phenolphthalein as a color indicator.

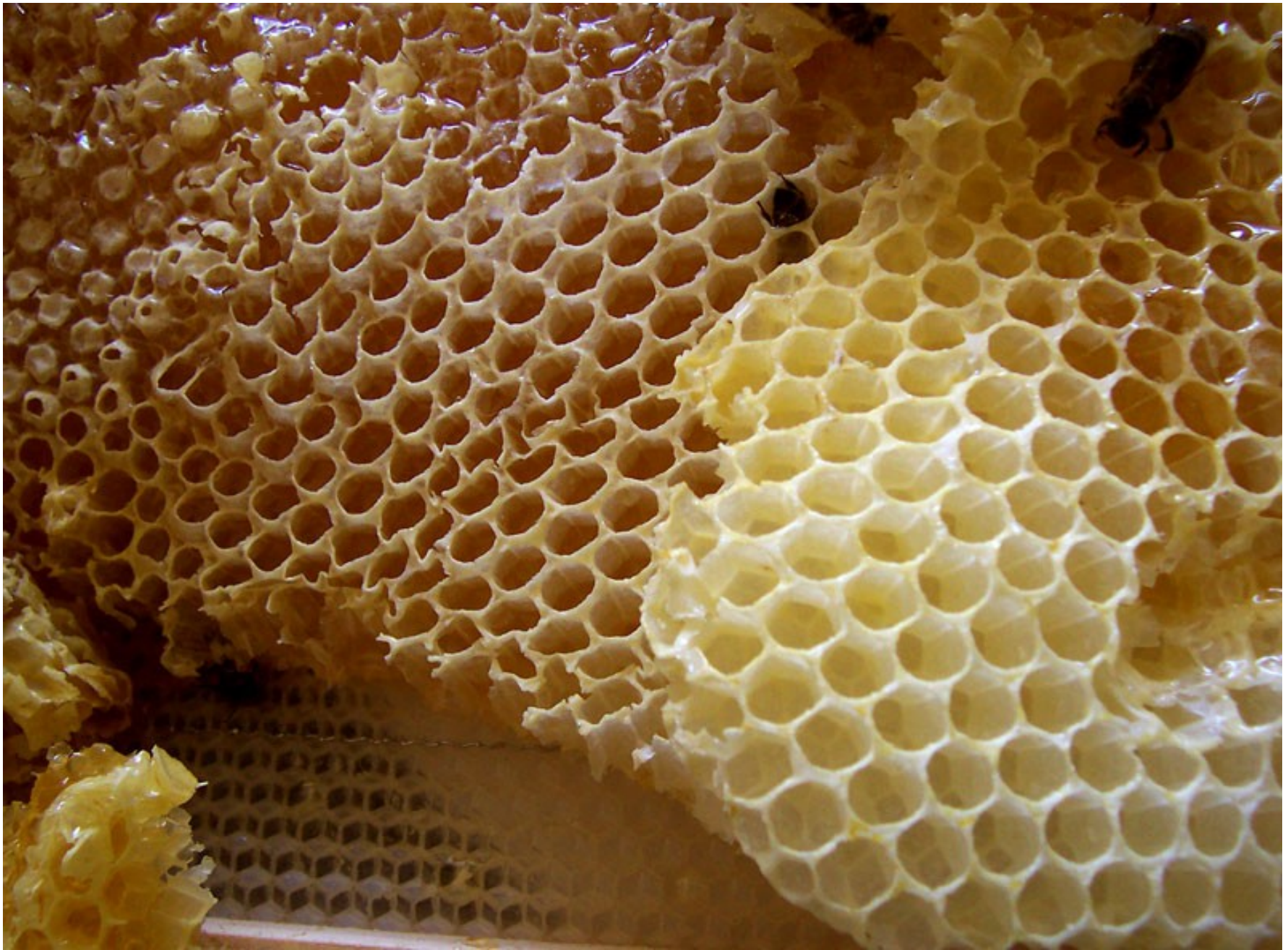
Saponification value (or "**saponification number**"/"**Koettstorfer number**",[1] also referred to as "**sap**" for short) represents the number of milligrams of potassium hydroxide required to saponify 1g of fat under the conditions specified.[2] It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/tri-ester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have a low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small, given the following relation:

Number of moles = mass of oil / average molecular mass

Physical & Chemical Properties of some WAXES

WAX	Density (kg/m^3)	Melting point (°C)	Iodine value (g I/100 g)	Acidity value (mg KOH/g)	Saponification value (mg KOH/g)
BeesWAX	950-970 (23 °C)	61-70	8-11	16-24	80-103
Lanolin (wool WAX)	917-940 (15 °C)	36-41	15-47	0,5	86-127
Japan WAX	975-992 (15 °C)	51-55	4,5-12,8	8-23	206-237
Carnauba WAX	990-998 (15 °C)	81-86	7-14	4-10	78-88
Montan WAX	980-985 (29 °C)	74-87	10-16	26	70-80
Ceresine	880-920 (?? °C)	55-80	7-10	0	0,0-0,1
Parafine	883-915 (?? °C)	55-88	0,5-2,5	0	0,0-0,3
Microcrystaline WAX	900-940 (?? °C)	63-85	0,0-1,5	0,1-0,2	0,05-2,00

Beeswax is the INSECT WAX



Beeswax is FOOD ADDITIVE („E numbers“) (E901 - Glazing substances)

E900 - E999 CATEGORY: Glazing substances, sweeteners, packaging gases, propelans

Beeswax in the Greek Mythology

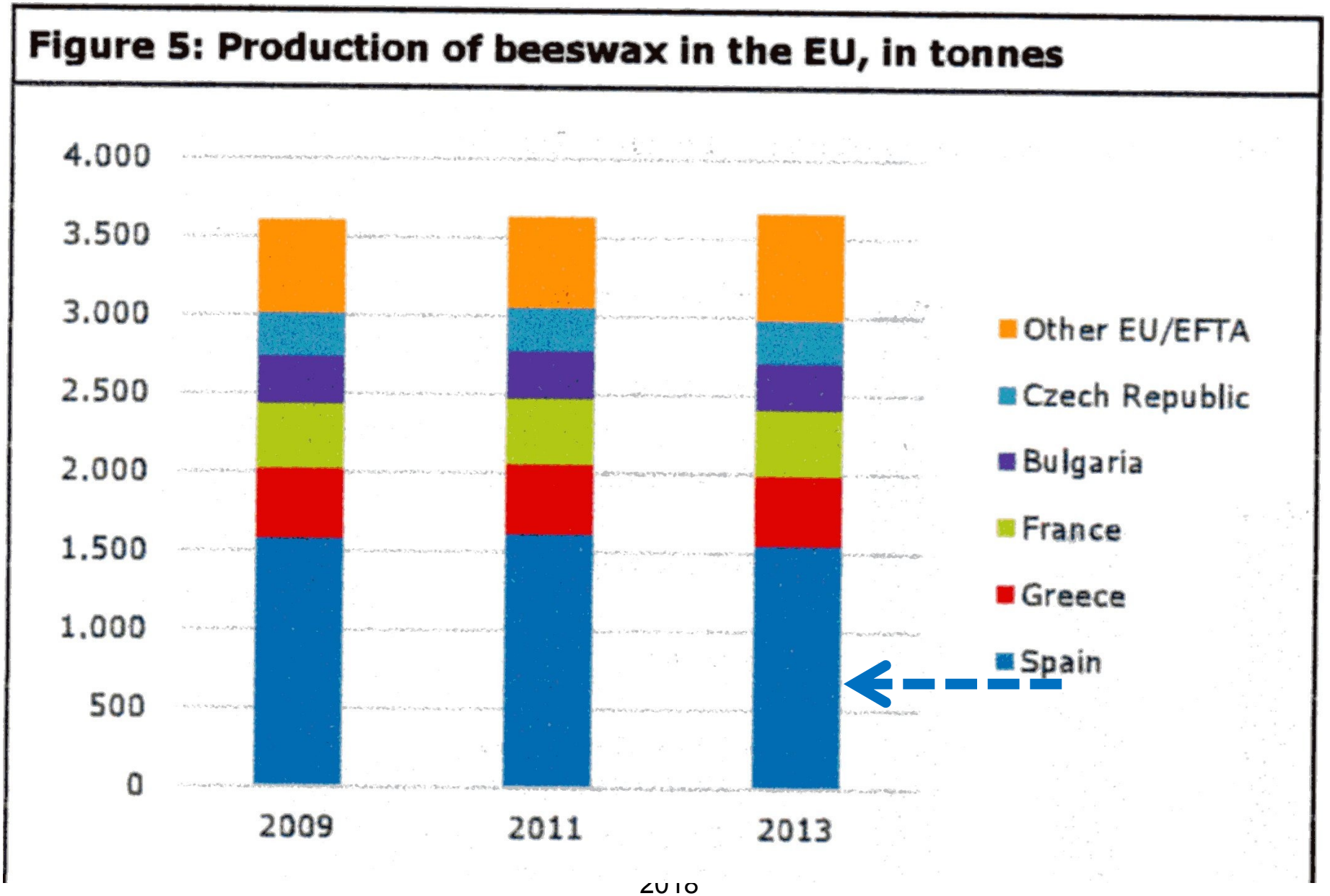
Odysseus was curious as to what the Sirens sang to him, and so, on the advice of Circe, he had all of his sailors plug their ears with beeswax and tie him to the mast. He ordered his men to leave him tied tightly to the mast, no matter how much he would beg. When he heard their beautiful song, he ordered the sailors to untie him but they bound him tighter. When they had passed out of earshot, Odysseus demonstrated with his frowns to be released. Some post-Homeric authors state that the Sirens were fated to die if someone heard their singing and escaped them, and that after Odysseus passed by they therefore flung themselves into the water and perished.

The current Price of BEESWAX Approx. 5 – 7 EUR/kg

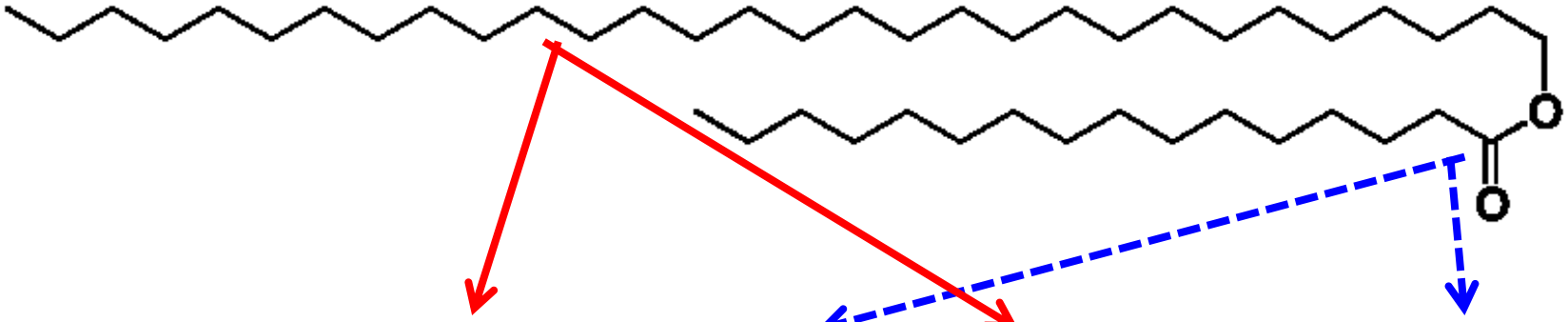
Table 1: Major food segments and applications for beeswax

Segment	Application	Benefits
Confectionery	Candy, cookies	Used to polish and seal, improving product's appearance, texture and shelf life
Bakery	Dough, croissants, doughnuts	Used to maintain moisture and softness in baked goods
Nuts and snacks	Nuts, raisins, dried fruit, liquorice	Used for coating/moisture barrier to keep the centre from drying out
Fruits	Citrus fruit, melons and apples	Coating material in fruits to improve appearance and to preserve quality

The major Producers of BEESWAX in EU



BEESWAX



triacontanyl (myricyl) palmitate $CH_3(CH_2)_{29}O\text{-}CO\text{-}(CH_2)_{14}CH_3$

- **This ester is considered as the MAIN COMPONENT in the approx. 285 up to now found items, approx. 111 NO identified items (Compounds) is waiting for your Effort!**
- ***Figures from different sources are different, so take the Figures as an Example of the Complexity of the Natural products only (see the next slide)***
- **BEESWAX could be different place and and Beespecies accordinglly**
- **Some Components are volatile**

FRACTION	PART	REMARKS
Hydrocarbons	14%	Mostly saturated C_{13-39} and cis alkenes C_{31-33}
Monoesters	35%	Mostly Palmitic acid with alcoholes C_{24-32}
Diesters	14%	Containing 15-hydroxypalmitic acid bonded to α, ω 1-diols with palmitic or unsaturated acid
Triesters	3%	Derived from triols
Hydroxy monoesters	4%	
Hydroxy polyesters	8%	
Acid esters	1%	
Acid polyesters	2%	
Free acids	12%	Mostly C_{24}, lesser C_{26} a C_{28}, but somewhere is presented as the main component „Cerotic acid“ – hexacosanoic acid
Free alcohols	1%	Myricyl alcohol & *CERYL ALCOHOL*
Unidentified	6%	

Cerotic acid = hexacosanoic acid
= *cerotic acid* ($C_{26}H_{52}O_2$)

myricylalcohol (triacontan-1-ol) $C_{30}H_{61}OH$

CERYL ALCOHOL

white crystalline alcohol $C_{27}H_{55}OH$ occurring as an ester in waxes (as beeswax)

BEESWAX - Properties

- **Melting point 61 – 70 °C**
- **Solubility:**
  - **Turpentine,**
  - Amyl alcohol,
  - Toluene,
  - Gasoline,
  - Chloroform,
- **BEESWAX is plastic at room temperature, hard and brittle after cooling**

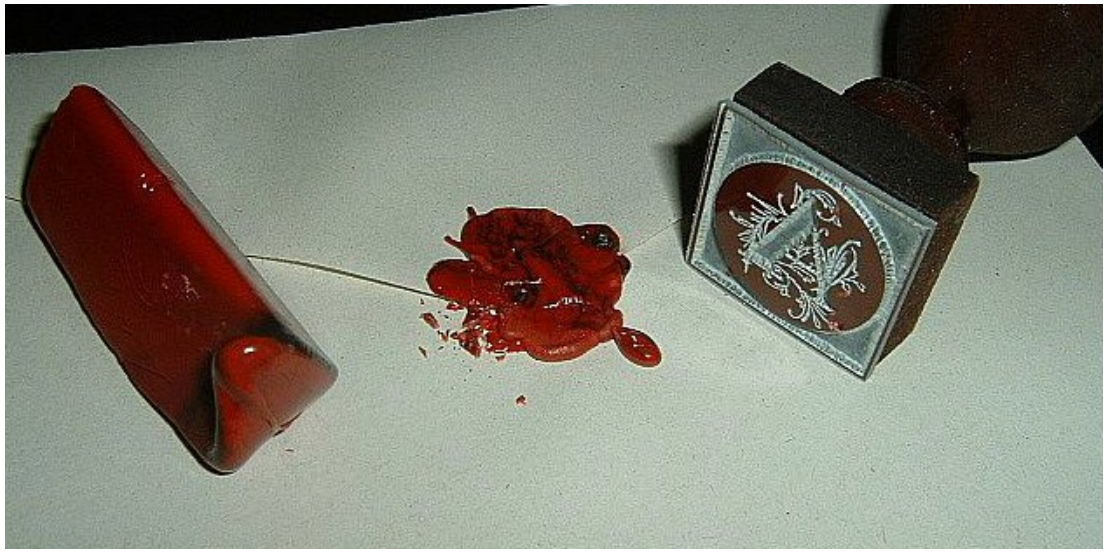
BEESWAX - modifications

- **Falsification** – addition of paraffin, stearic acid, …
- **Cleaning** – melting in the boiling water, oxidation, ……..
- **Tack ability improvement** > + resins, e.g. **colophony**
- **Stiffness improvement** **>** + harder waxes
- **Boiling with alkali solutions** > **PUNIC WAX** (soaps Na^+, K^+) with higher m.p.

BEESWAX in History

- **Casting of Metals „ Lost-wax casting “**
- **Candles –** probably by the Eastern Christians only now
- **Impregnation –** thanks to saturated acids is not so sensitive to oxidation
- **Seals**
- **……..**

Seals



From the 16th century it was compounded of various proportions **of shellac, turpentine, resin, chalk or plaster, and coloring matter** (often vermilion, or red lead), but not necessarily beeswax. The proportion of chalk varied; coarser grades are used to seal wine bottles and fruit preserves, finer grades for documents. **In some situations, such as large seals on public documents, beeswax was used.**

Another composition:

- **Beeswax,**
- **Carnauba wax,**
- **Colophony,**
- **Chalk,**
- **Pigments**

inorganic (WHY INORGANIC?)

BEESWAX in the modern World

- **Casting of Metals „ Lost-wax casting “**
- **Impregnation –** thanks to saturated acids is not so sensitive to oxidation
- **Glazing substances, Polishing agents**
- **Food industry &Pharmacy** – glossy surface of Candies and Pills
- **Conservation (Preservation) of metals and wood** – It remains soluble for Centuries, low water vapour permeability > Polish for furniture
- **Conservation (Preservation) of historical painting**

BEESWAX - verification of Purity

- **Ratio of ester value and acid value –** it should be 3,6 – 4,3
- **Ratio of the Main components** triacontanyl palmitate CH3(CH2)29O-CO-(CH2)14CH3 to cerotic acid CH3(CH2)24COOH, the two principal components, being 6:1 > **METHOD?**
- **Gas chromatography (GC)** after transformation to methyl esters of acids

BEESWAX a bit unusual use

Rice in the Packaging made of BEESWAX

BEESWAX a bit unusual use

It is not stated, what WAX was used

- **Beeswax?**
- **Paraffin wax?**
- **The other natural wax?**

Oil in the Packaging made of Wax & caramelized Sugar

We suddenly change direction of our Interest!

Natural Products > NONRENEWABLE SOURCES > **OZOKERITE (earth wax –** NATURAL PARAFFIN)

Ozokerite in history

- **Cleaning** – melting and filtration
- **Cleaning** - by H_2SO_4 and then by active carbon
- **Improvement** of colour and removing of the nonmelted impurities

WAX DESTILLATION

- CERESINE >Candles, Dilution of the **BEESWAX**
- VASELINE >lubricant, base of the salves and ointments in pharmacy

Ozokerite at present

- More likely mineralogical curiosity
- Substituted mostly by a products made by crude oil distillation- more cheap
- Substituted by metallocene waxes – possibility to set precisely properties, but they are more expensive

CERESINE 1

- It **WAS** made by refining of OZOKERITE (chemical & physical) originally
- **IT IS MADE mostly by mixing of various products from crude oil refinery > cheap**
- **It contains, unlike paraffin, branched and cyclic structures > plasticity at lower temperature, because having lower tendency to crystallize**

CERESIN 2

- Swelling in the many solvents and oils > WAX PASTES
- Melting point approx. 60 – 70 °C

SOLUBILITY

- **Turpentine,**
- **Toluen**
- **Chloroform,**
- **Gasoline,**
- **Petrolether (hydrocarbons with chain length of $C_{5–7}$ (Boiling point approx. 30–70 °C)**

CERESIN 3 - USE

- Conservation and oil tannage of leather
- GENERALY: surface protection (preservation) agent, and not only of metals
- WAX PASTES for making of models etc.
- Substitution of the **BEESWAX** or its dilution

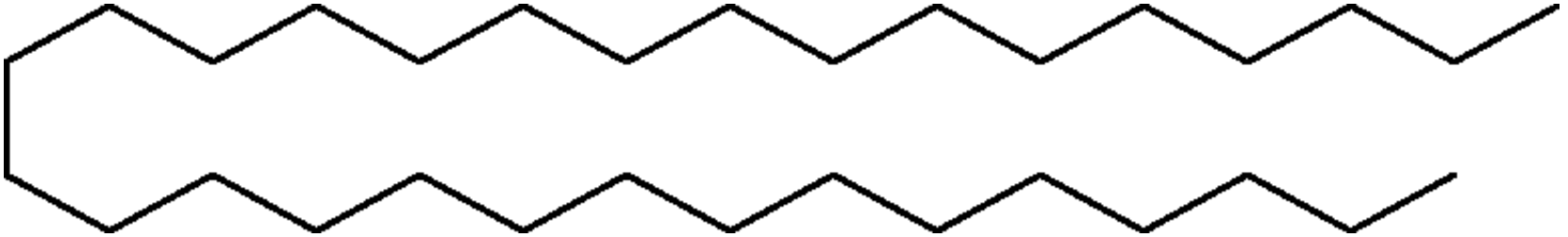
CERESIN 3 - použití

- Konzervování (tukování) usní
- Všeobecně jako prostředek povrchové ochrany, a to nejen kovů
- Voskové pasty na modelování atd.
- Náhrada včelího vosku nebo jeho ředění

PARAFFIN 1

HDPE and LDPE look like! WHY?

The hydrocarbon C31H64 is a typical component of paraffin wax.



PARAFFIN 2

- It contains mostly LINEAR STRUCTURES
- PARAFFIN = HIGHER alkane, approx. > C_{26}
- Melting point approx. 45 – 70 °C
- Boiling point 300 °C > vacuum distillation of the Crude oil products > crystallisation from the Mixture with oils
- Density approx. 900 kg/m_3, similar to HDPE >**WHY**?
- Excellent ELECTROISOLATION PROPERTIES
- Excellent chemical resistance, also for HF acid > preparation of the glass bottles for HF acid

PARAFFIN 3

- Excellent resistance to Weathering (UV, oxygen etc.)
- Waterproof surface treatments > paper cups for beer, beverages and milk products in the past (now plastics)
- Dilution of the more expensive Waxes (e.g. Beeswax), but there is danger of the Phases Separation
- Polishing pastes, Candles, Ski waxes, …
- The Part of the old painting Removers > it inhibits the fast Evaporisation of a Solvent

PARAFÍN 4 - another use

- Component of the poisoned bait for rodents – a bait is flowing on water surface
- Cosmetics – creams, medicine in the form of ointment or cream, lipsticks, makeup, greasepaint
- Healing - body wrap
- Waterproofing treatments, slip waxes, car and shoe polishing waxes, ……
- Precise casting of metals or other materials
- Impregnation of the Wood
- Civil engineering – injection to the brickwork (dampf proofing), Impregnation of the building parts
- **Preservation** of the Amuniation against humidity, e.g. dynamite charge
- **Potting** of tissues in histology for cutting (TEM)

PARAFFIN 5 – How is it supplied

- **Paraffin is supplied either in the form off lakes or pellets or blocks**
- **Current price (Wholesale) is for STANDARD GRADE approx. 2 EUR/kg (2006 - 2008). HDPE and LDPE available now at price approx. 3 EUR/kg**
- **Coding od Paraffines:** e.g. **60/62** or **50/52**) gives the **Temperature of congealing pour point a revolving thermometer**, not the Melting Point!

ISO 2207 (ČSN 65 7115) Petroleum waxes - Determination of congealing pour point a revolving thermometer

Microcrystalline Wax

It is again Product obtained by Distillation of the Crude Oil

PARAFFIN

- It contains mostly LINEAR STRUCTURES
- Colourless
- C_{26} and more
- Almost transparent

CERESIN

- It contains LINEAR & BRANCHED & CYCLIC STRUCTURES
- Colourless
- C_{26} and more
- Almost transparent

Microcrystalline Wax

- It contains MOSTLY LINEAR & BRANCHED & CYCLIC STRUCTURES
- MOSTLY yellow like to brown, Colourless after Purification only
- C_{50} and more
- Opalescent

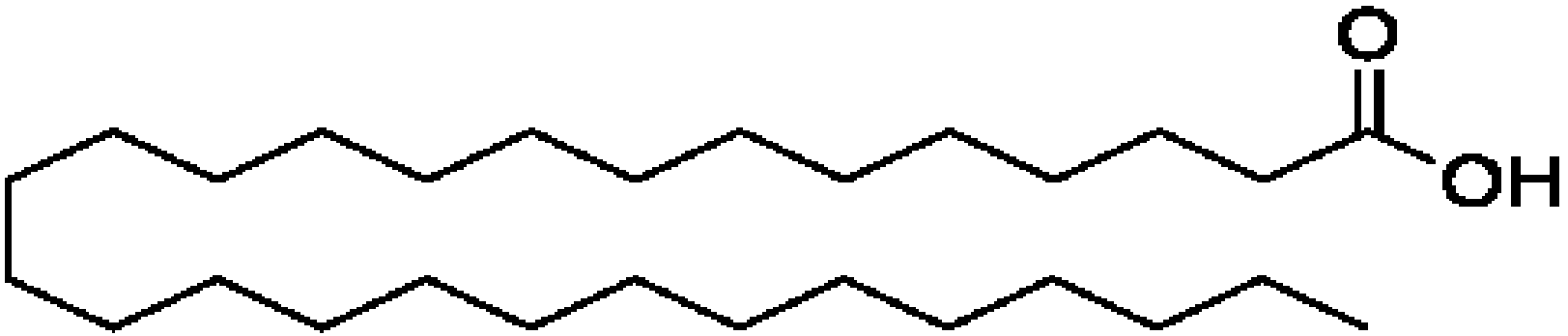
Microcrystalline Wax Use – similar to Paraffin

- **It is more sticky > it is better for the coverings**
- **It gives them, if mixed with the other waxes, better mould ability**
- **The other properties are like the paraffin**

My favourite WAX
MONTAN WAX 1

- **NATURAL PRODUCTS > UNRENEWABLE SOURCES > EXTCTION FROM THE WOODY LIGNITE OR YOUNG BROWN COAL**
- Montane Resins
- **Montan Wax**
- Asphalt

MONTAN WAX 2



Montane acid ($C_{28}H_{56}O_2$)> esters > Montan Wax
It is stated C_{24} – C_{30} pro „Montane acids“

It is contained in the following Waxes:

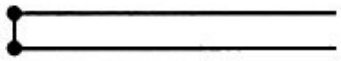
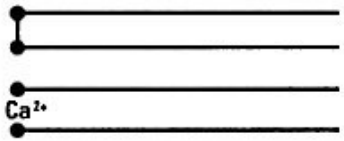
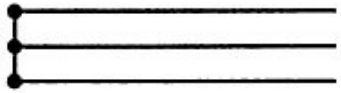
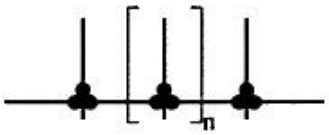
- **Montan Wax**
- **Chinese Wax**
- **Beeswax Wax**

MONTAN WAX 3

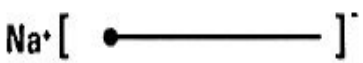
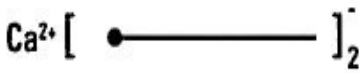
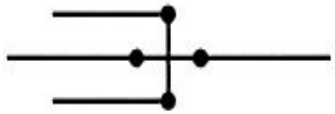
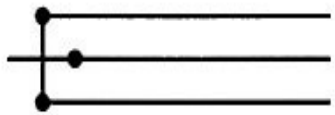
Possibilities of the MODIFIED PRODUCTS preparation

- Esters –SAPONIFICATION, also partly
- Pure (Free) montane acid – formation of Salts Me^{+} či Me^{+2}
- Pure (Free) montane acid– esterification with diols (e.g. ethylenglykol) and triols (e.g. glycerine)
- Many Waxes LICOWAX made by Clariant Company

MONTANE WAX - CLARIANT 4

Name	Chemical profile	Physical and chemical properties of the product				
		Drop point [°C]	Acid value [mg KOH/g]	Density 23 °C [g/cm³]	Viscosity [mPa·s]	Color
Licowax E	Esterwax on the basis of montanic acids 	~ 81 [1]	~ 18	~ 1.02	~30'	pale yellowish
Licowax OP	Partly saponified ester wax on the basis of montanic acids 	~ 99 [1]	~ 12	~ 1.02	~ 300**	yellowish
Licolub WE 4	Ester wax on the basis of montanic acids 	~ 80 [1]	~ 26	~ 1.01	~ 60*	yellowish
Licolub WE 40	Complex ester of the montanic acids 	~ 76 [1]	~ 20	1.02	~ 150*	yellowish

MONTANE WAX - CLARIANT 5

Name	Chemical profile	Physical and chemical properties of the product				
		Acid value [mg KOH/g]	Alkali content	Drop point [°C]	Density (23 °C) [g/cm³]	Color
Licomont NaV 101	Na salt of the montanic acids 	~ 3	~ 5.5 % Na	–	–	yellowish
Licomont CaV 102	Ca salt of the montanic acids 	~ 10	~ 4 % Ca	–	–	pale yellow
Licomont ET 141	Ester wax of the montanic acids 	~ 25	–	~ 79 °C	~ 1.01	pale yellowish
Licomont ET 132	Ester wax of the montanic acids 	~ 18	–	~ 78 °C	~ 1.00	yellowish

MONTANE WAX – Main use 6

- **GENERALLY**: There, where is necessary , glossy and hard coating (surface)
  - **Car polish** – approx. one third of the world consumption
  - **Shoe polish**
  - **Lubricant for plastics processing**
  - **The Substitution or modification of the BEESWAX**
  - ……

Carnauba Wax & Palm Tree

BACK TO THE PLANTS ! Carnauba Wax 1

- **Natural products > RENEWABLE SOURCES > WAXY COATING on the Leafs of the Carnauba palm, growing in Brazil**
- **Air-dried Leafs > mechanical separation >cleaning by Melting & Filtration**
- **Myricilcerotate – main Component (approx. 80 % w/w)**
- **$C_{30}H_{61}OOC_{25}H_{51}O$ *(in the BEESWAX is stated boththis Acid and this Alcohol)***
-

Carnauba Wax 2

- High Melting Point, approx. 81 – 86 °C
- The Addition of this Wax increases the Melting Point and the Hardness of other Waxes (e.g. Beeswax), like the Montane Wax
- It is soluble at room temperature in diisopropylether and chloroform, at high temperature also in EtOH, turpentine, ketones, …
- Polishing agents
- Coating of medicines
- Separation agent for plastic processing

The other Substances classified as WAXES

- **Lanoline – from the Waste after a Wool cleaning**
- **Japanese wax** – from the tree Fruits
- **Chinese wax – insect secret**
- **Esparto wax** – protective cover on the Esparto Grass
- ……