Cultural heritage as analysis object

Brief overview of some of the materials commonly encountered in cultural heritage objects

Prof. Ivo Leito

Cultural heritage materials

The flint insert with adhesive remains from Early Mesolithic Pulli settlement site (AI 4476: 1042)

(Photo: Aivar Kriiska)

The Bible (Estonia, 1899)

Photo: Liisa Eero

Cabinet decorated with intarsia

(19th c. or 20th c.)

Photo: Conservation and Digitization Centre Kanut

Ribbon from the Harju Risti memorial chaplet (1924)

Photo: Conservation and Digitization Centre Kanut

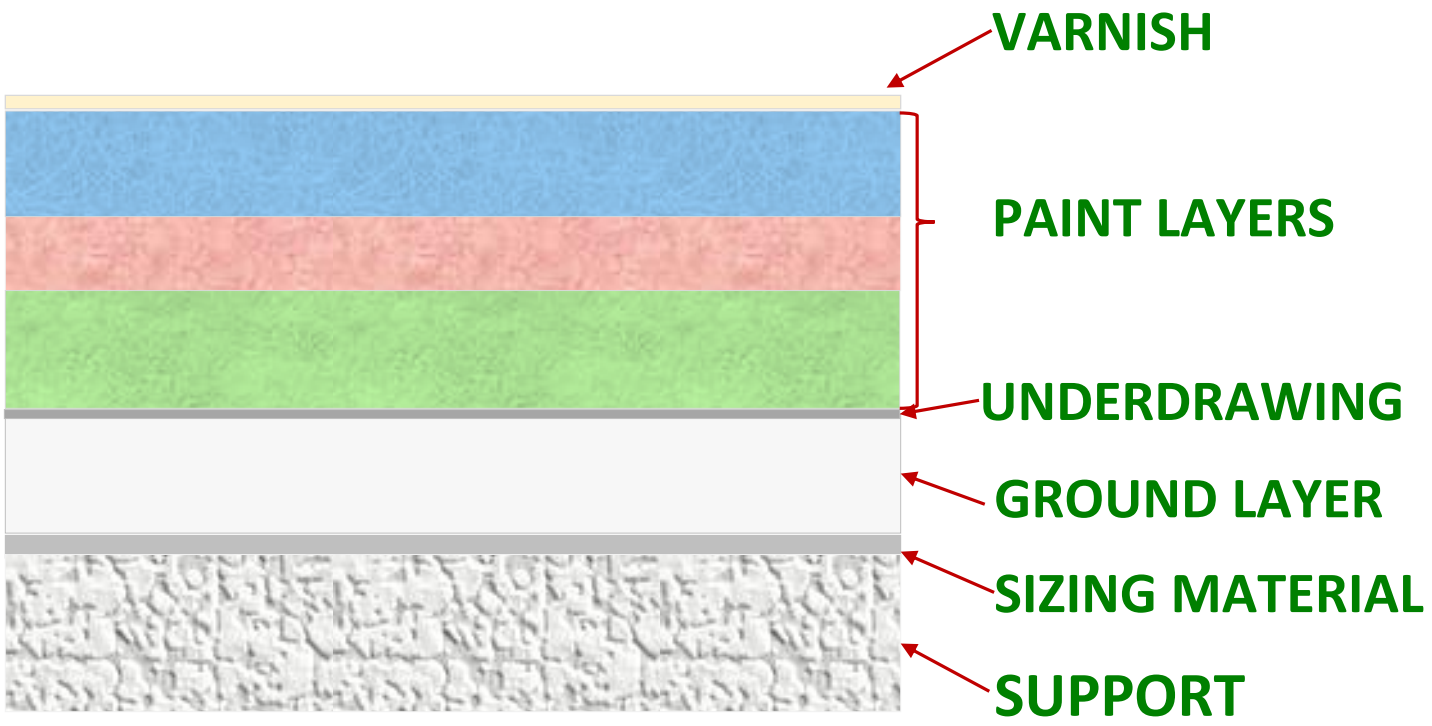
Coat of arms of C.J. Ekesparre from Saaremaa (18th c.)

Photo: Conservation and Digitization Centre Kanut

Unknown artis's painting

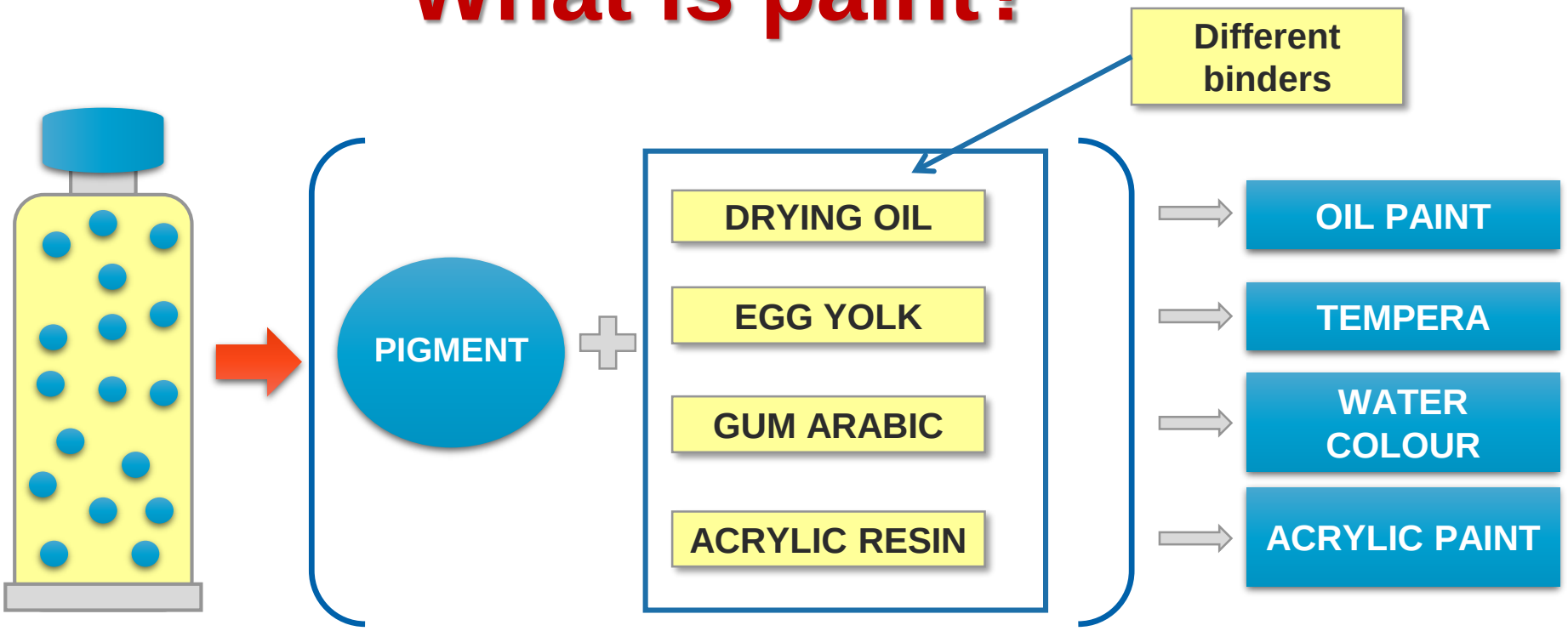
Photo: Anu Teearu-Ojakäär

Structure of the painting



- This structure is common for paintings on canvas and wooden support as well as for polychrome objects.

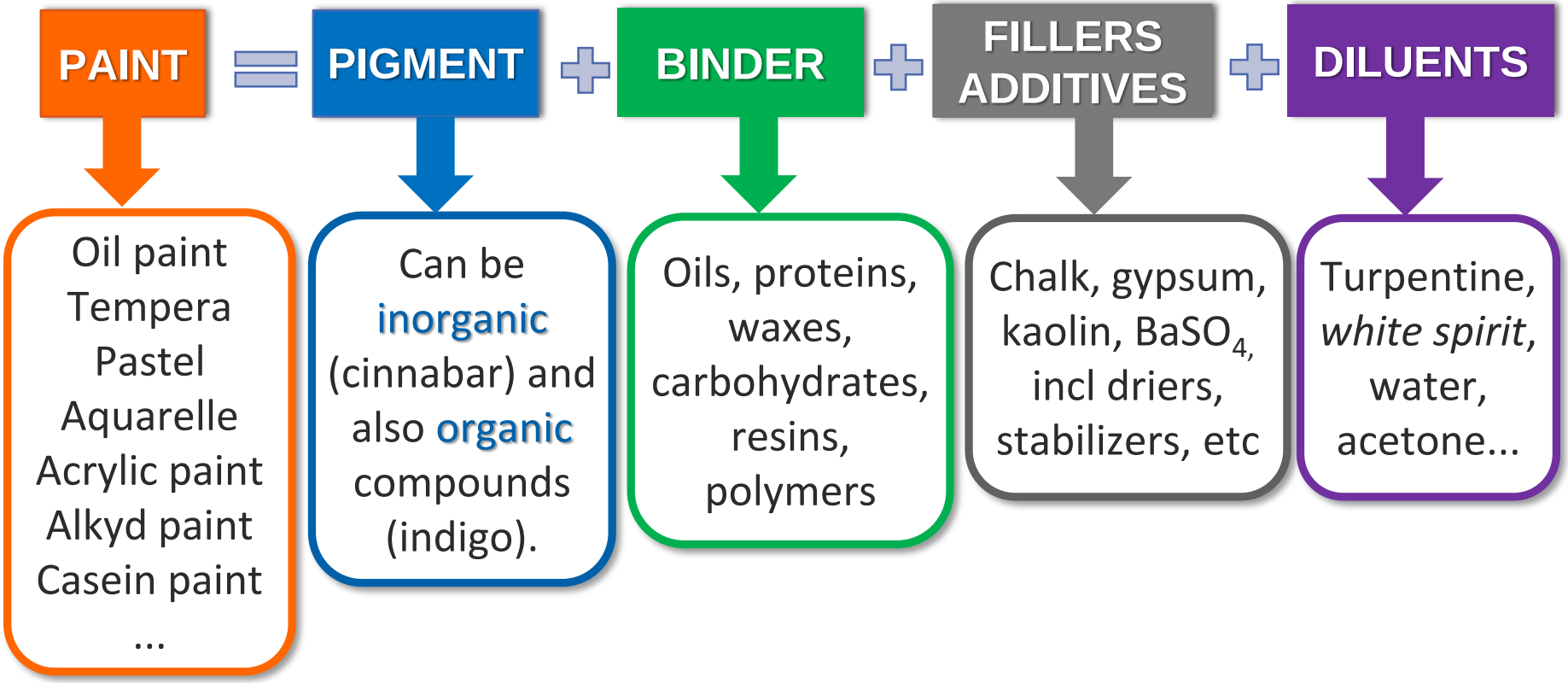
What is paint?



- Pigment is suspended in binder which forms a strong film of paint when it's dry.
  - Binder provides the adhesion and cohesion - keeps the pigment within the coating and ensures that the paint remains attached to the substrate.

http://www.cad-red.com/mt/b_basis.html

Paint composition



a) Inorganic pigments

Red lead (Pb_3O_4, n_D=2.42)
(BXXXD)

Chromium oxide
(Cr_2O_3, n_D=2.5)
(FK1954)

Natural Ultramarine blue
($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$, n_D=1.5)

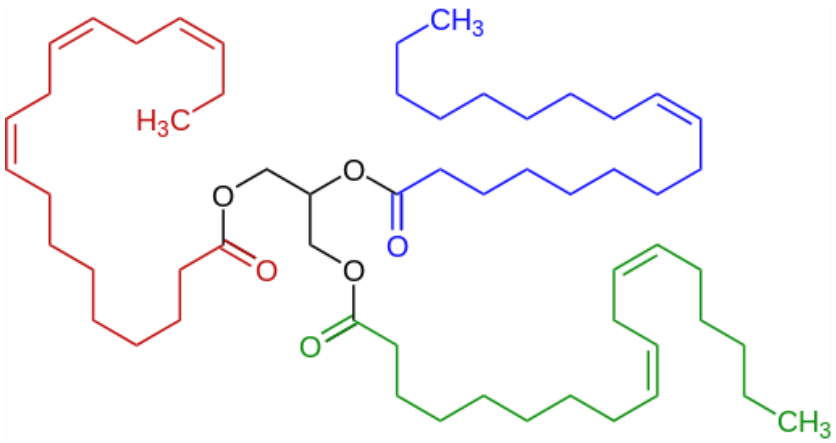
Asurite ($2CuCO_3{\cdot}Cu(OH)_2$)
(n_D=1.73–1.84)

Yellow ochre ($Fe_2O_3{\cdot}nH_2O$+clay)
(n_D=2.36 (average) - goethite)
(Marco Almbauer)

b) Binders

- Binders are liquid or semi-liquid substances in which the pigment is suspended.
- Binders can be divided: **oils, waxes**, **proteins**, **resins**, **carbohydrates** (gums, polysaccharides), **polymers**.

(http://www.seedguides.info/linseed-oil/) (licence CC-by -SA 3.0)



Linseed oil

Consist of different **fatty acid triglycerides**

https://en.wikipedia.org/wiki/Yolk (licence CC-by -SA 3.0)

Egg yolk: ~47 % **water**, ~17 % **proteins**, ~33 % **lipids** (triglycerides, phospholipids, cholesterol), ~3% **additives** (carbohydrates, inorganic compounds, etc.).

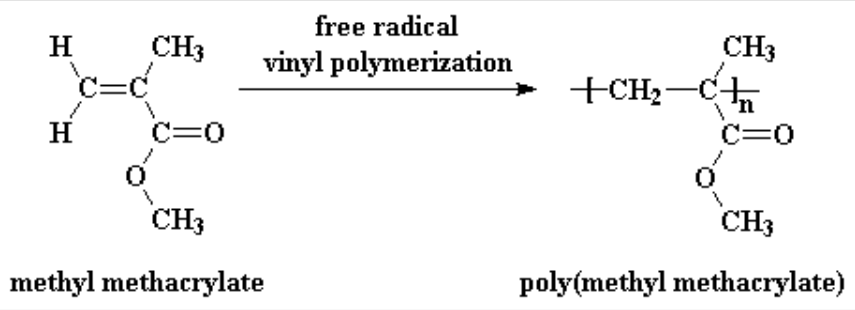
https://en.wikipedia.org/wiki/Linseed_oil, Neuroxic, licence CC-by -SA 3.0

Gum Arabic – natural gum consisting of the hardened sap of various species of the acacia tree.

- Mixture of **oligo-** and **polysaccharides** and **glycoproteins.**
  - The molecular mass of the macromolecules is between 250 000 to 300 000.

Acrylic resins - thermoplastic polymers.

- **Polymethyl acrylate (PMA)** and **polymethyl methacrylate (PMMA)**.

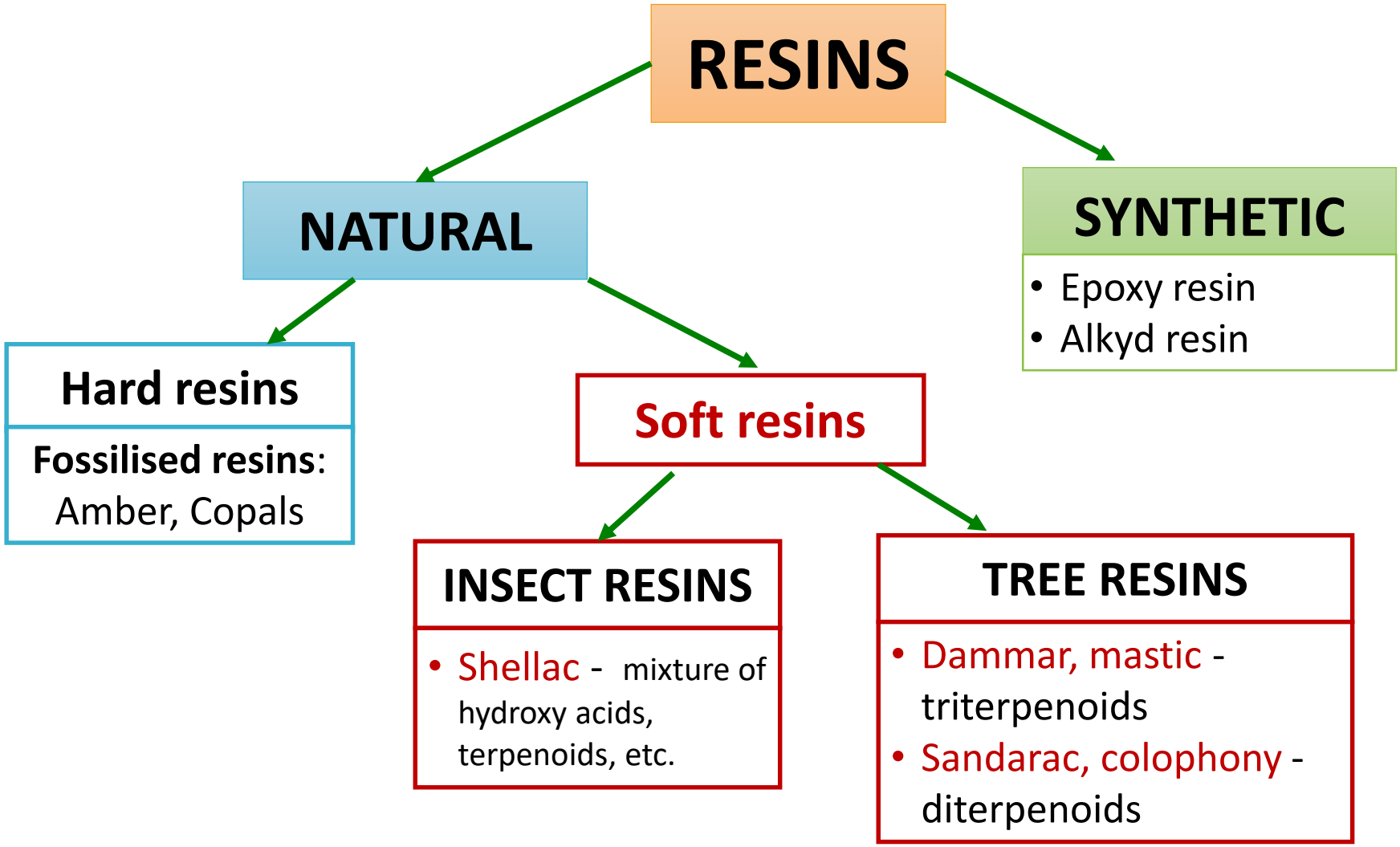


http://pslc.ws/mactest/level2.htm

- **Acrylic „latex“ paints** contain **PMMA** suspended in water.
  - PMMA doesn't dissolve in water, so dispersing PMMA in water requires another polymer (**poly(vinyl alcohol-co-vinyl acetate**) to make water and PMMA compatible with each other.

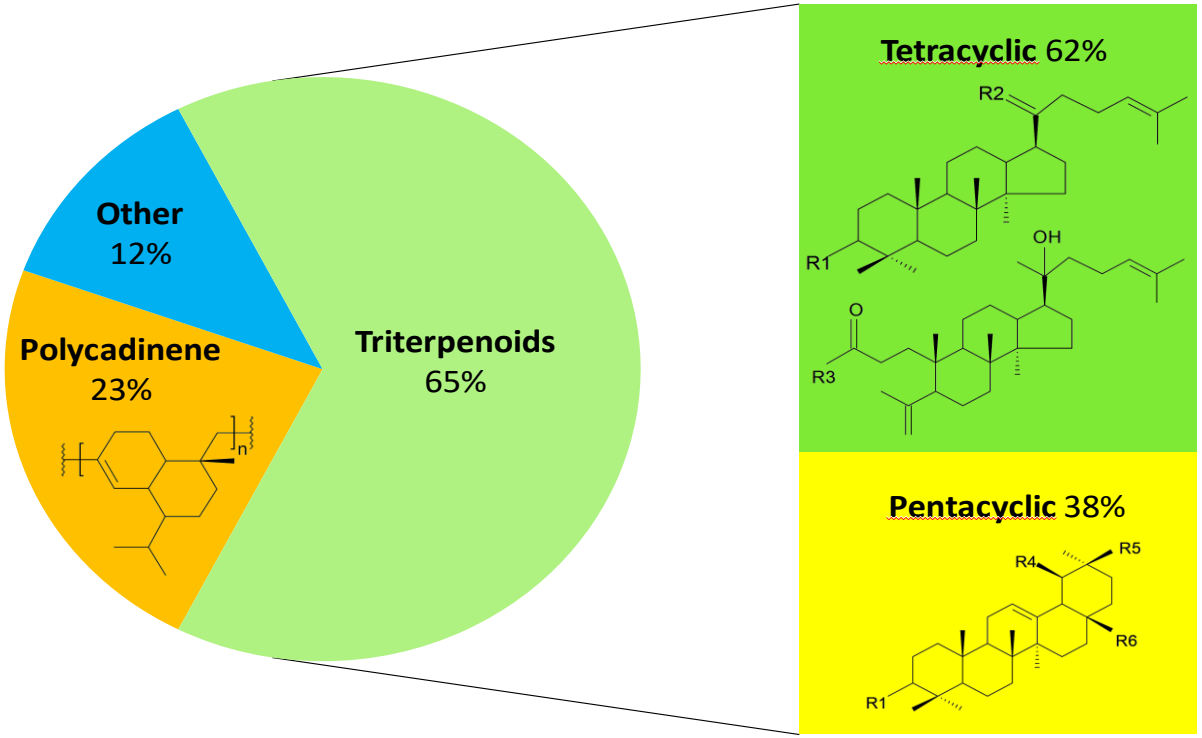
Varnishes

Composed of a **resin dissolved** in a **liquid** (linseed oil, turpentine etc) which upon drying form a hard transparent film.



Dammar resin

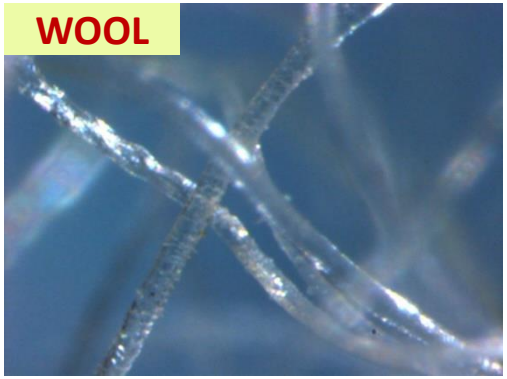
Is obtained from various species of trees belonging to the *Dipterocarpaceae* family



R1: O/ OH, H; **R2**: OH, H/ CH2; **R3**: OH/ OMe;
R4 ja R5: CH3/ H; **R6**: COOH, H/ CHO, H

Vahur, S.; Teearu, A.; Haljasorg, T.; Burk, P.; Leito, I.; Kaljurand, I. *Journal of Mass Spectrometry*, **2012**, *47*(3), 392 - 409.

Textiles



- Textiles are flexible woven materials consisting of mainly natural or synthetic fibres.

- **Natural fibres**:
  - **Vegetable fibres** (cotton, linen, hemp, jute etc.) - mainly composed of cellulose
  - **Animal fibres** (wool, silk, mohair, angora etc.) - proteinaceous materials
- **Modified natural fibres**:
  - Viscose, lyocell (i.e. Tenzel), cellulose acetate,
- **Synthetic fibres**:
  - polyamide (nylon), polyester, polyacrylic, elastane, etc.

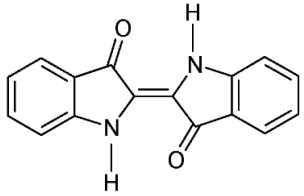
Dyes

Organic molecules that give intense color in small quantities. These are divided into groups like **anthraquinones**, **flavonoids**, **tannins**.

Indigo

Indigofera tinctoria

(Kurt Stüber, CC-by-SA 3.0)

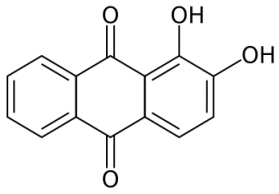


Madder

Main component: alizarin

Rubia tinctorum

(H. Zell, CC-by-SA 3.0)

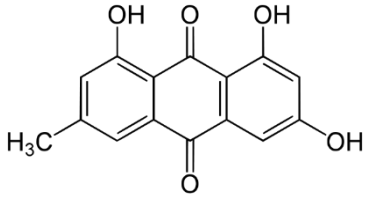


Bloodred webcap

Contains emodin, dermorubin, dermocybin, etc

Cortinarius sanguineus

(Jerzy Opioła, CC-by-SA 4.0)

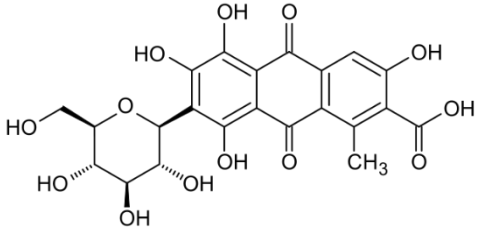


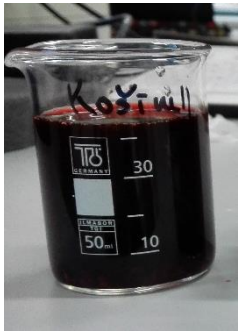
Cochineal

Main component: carminic acid

Dactylopius coccus

(www.webexhibits.org/causesofcolor/7.html)



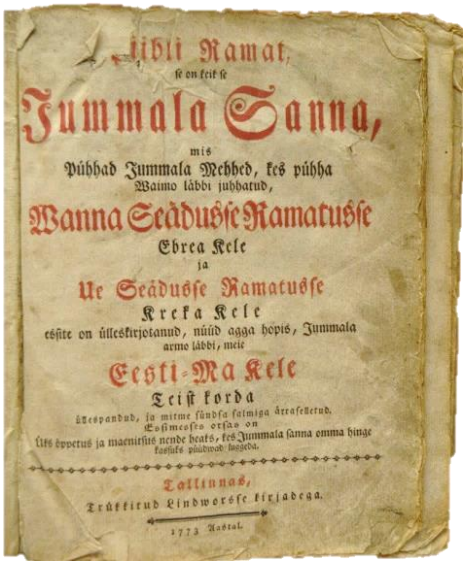


Cochineal

https://en.wikipedia.org/wiki/Dye, licence CC-by-SA 3.0

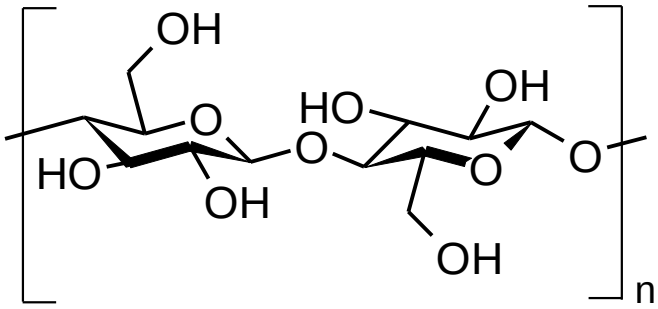
Paper

- **Main components**:
  - **Fibrous matter** (hemp, linen, cotton, wood) – cellulose based materials
    - additives in the wood cellulose pulp - hemicellulose and lignin
  - **Sizing materials** – gelatine, starch, alum, colophony, etc
  - **Fillers** and **pigments** – kaolin, chalk, gypsum, talc, $BaSO_4$, - TiO_2, ZnO, etc
  - **Coating materials** – pigments, fillers, binders

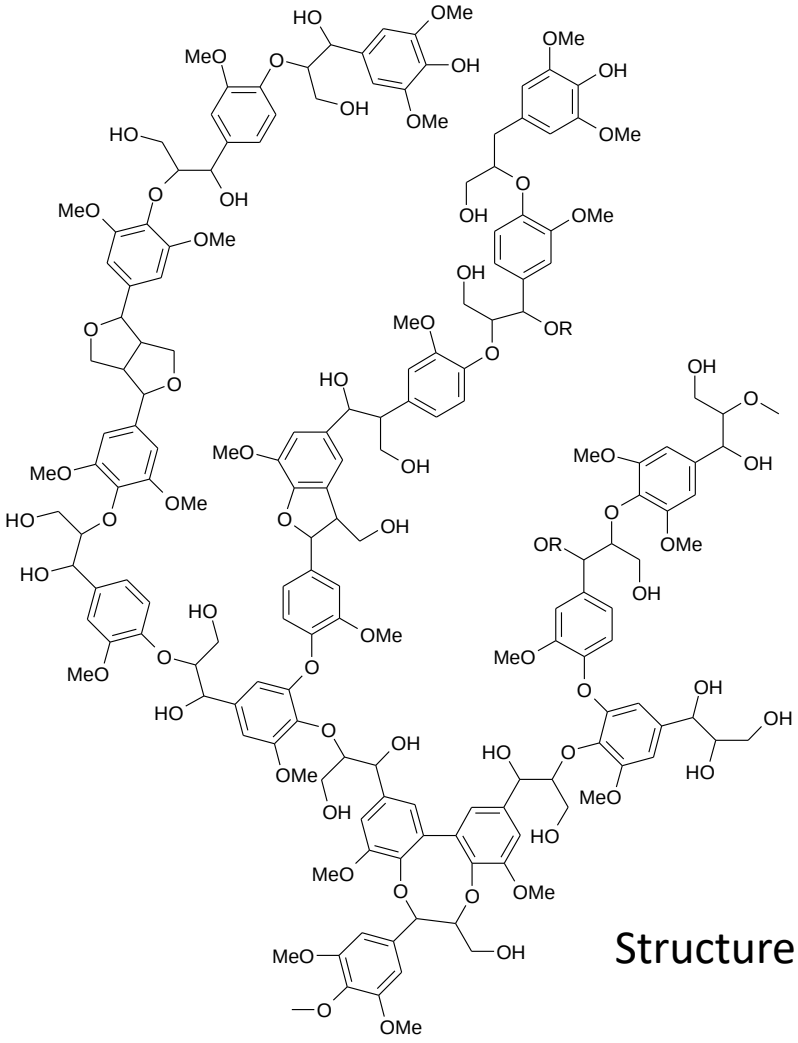


The Bible
(Estonia, 1773)
Photo: Liisa Eero

Cellulose and Lignin



Structure of cellulose



Structure of lignin

- **Cellulose** is the main fibrous material in paper
- **Lignin** is largely responsible for the low stability of papers made of wood

Ceramic materials

- Ceramic objects are typically made of clay
- **Clay** is a diverse material that can be composed of different minerals, e.g. **Kaolin, illite, calcite**, etc.

- The mineral composition of clay is strongly dependent on its origin

Archaeological pot from Kukruse cemetery
(12th to 13th c. female burial no. XXII)
Photo: Ester Oras (TÜ 1777: XXII)

Example: archaeological finds

- Such finds can contain multiple objects, composed in turn of multiple materials:
  - Ceramic objects from clays
  - Food residues from the ceramic pots
  - Textile fibres
  - Metal objects
  - Adhesives
  - Animal and human bones
  - Stone objects

Archaeological pot from Kukruse cemetery

(12th to 13th c. female burial no. XXII)

Photo: Ester Oras (TÜ 1777: XXII)

Ageing

- **Due to the ageing the composition is in fact much more complex**
- Material composition has undergone different changes (degradation, hydrolysis, oxidation, polymerization, etc)
- Ageing is irreversible

- As a result:
  - In the mixture can be different degraded, polymerized, oxidized by-products
  - Occasionally there can be only traces of original compounds left

Summary

- CH materials are **complex multicomponent and multi-layered** mixtures
  - Ageing adds to the complexity
- Analysed sample amount is usually **very small**
- If some component from the sample has **degraded**, **leached**, **evaporated**, then this component (in general) can not be determined
- Results often remain **probabilistic**

- **More information is on the web:**

https://sisu.ut.ee/heritage-analysis/