NATURAL POLYMERS

ACID'S DERIVATIVES, NATURAL RESINS, DRYING OILS, SHELACK ETC.

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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), Taraxacum_kok-saghyz
5	Polyphenol – lignin, humic acids
6	Polysaccharides I – starch
7	Polysaccharides II – cellulose
8	Protein fibres I
9	Protein fibres II
10	Casein, whey, protein of eggs
11	Identification of natural polymers
	Laboratory methods of natural polymers' evaluation

Products

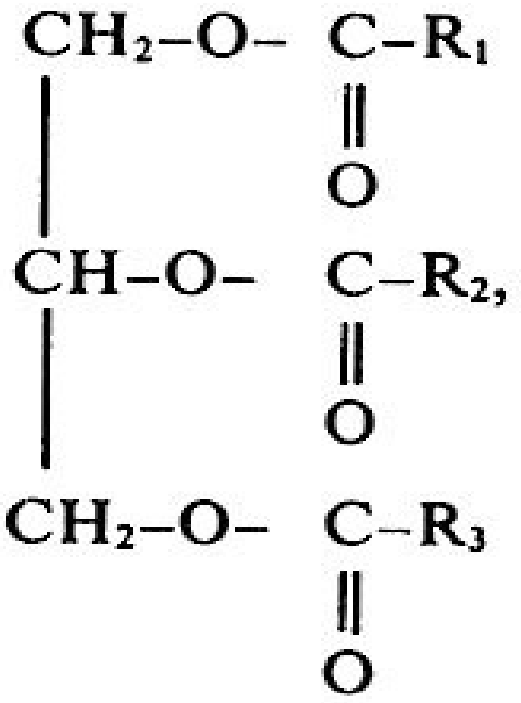
- Natural Products
  - Renewable Sources
  - UNRENEWABLE SOURCE
- Modified Natural Products
- Synthetic Products

Why do we put the Oils in the Natural Polymers ?

POLYMERS arising by radical Reaction from some of the Natural Oils

Fats & Oils

- **Vegetable Fats (Oils)**
  - **Glycerides**
  - **Higher Fatty acids (> 10 C Atoms)**
    - **Saturated**
    - **Unsaturated**
      - **One double Bond**
      - **More then one double l**
        - » **Isolated**
        - » **Conjugated**



OILS

Oil is a Liquid constituted (composed) of the Molecules, which comprise the hydrophobic hydrocarbon Chains. So they are not soluble (are INSOLUBLE) in the Water. They have lower Density then the Water has.

Food, edible Oils are the Vegetable liquid TRIGLYCERIDES. They can have one or more unsaturated Bonds between the Carbon Atoms. The more has the such Oil of the unsaturated Bonds between the Carbon Atoms, the less is its Viscosity.

Technical Grade Oils are mostly based on the utilisation of the so called MINERAL OILS, which are the Mixture of the HYRDOCARBONS manufactured by the Crude Oils Processing. The next Group of the Technical Grade Oils are the **SILICONE OILS,** which are manufactured by Synthesis (Polymerisation) from the Silicon based monomers.

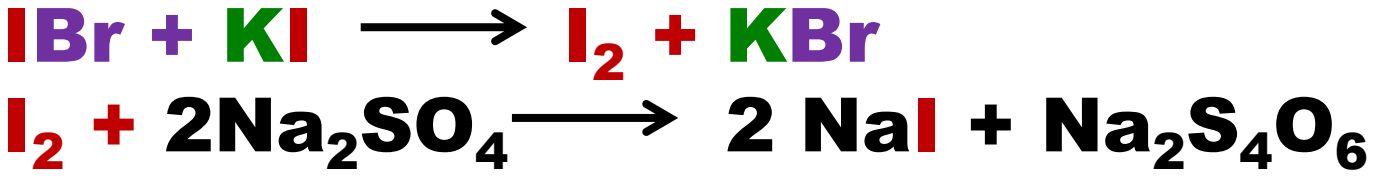
Glycerides of the Higher Fatty acids (> 10 C Atoms) 1

How to characterise in Practice the Unsaturation of the Higher Fatty acids

- **IodineVALUE – Determination according to prof. Hanush**

REACTION:

The **IODINE VALUE** (or **IODINE ADSORPTION VALUE** or **IODINE NUMBER** or **IODINE INDEX**)



Glycerides of the Higher Fatty acids (> 10 C Atoms) 2

The FATS are dividing the IODINE VALUE (IV) accordingly:

- **Drying Oils – IN > 120 % w/w**
- **Half Drying Oils – IN > 60 - 120 % w/w**
- **NON Drying Oils – IN < 60 % w/w**

Fat (Oil)	Iodine Value (% w/w)
Cow Butter	26 – 40
Beef Tallow melted	40 – 48
Pig Lard	53 – 77
Ricin Oil	81 – 90
Peanut/Groundnut Oil	84 – 100
Oilseed rape Oil	94 – 106
Soybean (Soy bean) Oil	114 – 138
Suflower Oil	127 – 136
Linseed/Flaxseed Oil	**170 - 204**

EN ISO STANDARDS

EN ISO 660

- Animal and vegetable fats and oils - Determination of acid value and acidity

EN ISO 3961

- Animal and vegetable fats and oils - Determination of iodine value

EN ISO 3657

- Animal and vegetable fats and oils - Determination of saponification value

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. 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.

In a typical procedure, the fatty acid is treated with an excess of the Hanuš or Wijs solution, which are, respectively, solutions of iodine monobromide (IBr) and iodine monochloride (ICl) in glacial acetic acid. Unreacted iodine monobromide (or monochloride) is then allowed to react with potassium iodide, converting it to iodine, whose concentration can be determined by titration with sodium thiosulfate

The FATY ACIDS OF OUR INTEREST A WHY THEY ARE SO FOR US?

The common FATY ACIDS which are contained in the Vegetable Oils

FATY ACID'S name	Carbon Atoms Number	Double Bonds Number	Formulae	Iodine Value
Lauric	12	---	$CH_3(CH_2)_{10}COOH$	---
Myristic	14	---	$CH_3(CH_2)_{12}COOH$	---
Palmitic	16	---	$CH_3(CH_2)_{14}COOH$	---
Steraic	18	---	$CH_3(CH_2)_{16}COOH$	---
Oleic	18	1	$CH_3(CH_2)_7CH=CH-(CH_2)_7COOH$	90
Linolic	18	2	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH\ (CH_2)_7COOH$	181
Linolenic	18	3	$CH_3CH_2CH=CH-CH_2-CH=CH-CH_2-CH=CH\ (CH_2)_7COOH$	274

The FATY ACIDS - Sources and a Manufacturing Technology

Vegetable Oily Seeds

TECHNOLOGY

- **COLD PRESSING** (Analogue of the so called Virgin Olive Oil)
- **Hot PRESSING** (Analogue of the so called Olive Oil for Cooking)
- **Hydrocarbon's hot Extraction** (Analogue of the so called Olive Oil for Soap and Cosmetic)
- **WASTES, so called OIL CAKE > Animal's Feeding**

Boiled linseed Oil **: modified (treated) Linseed Oil**

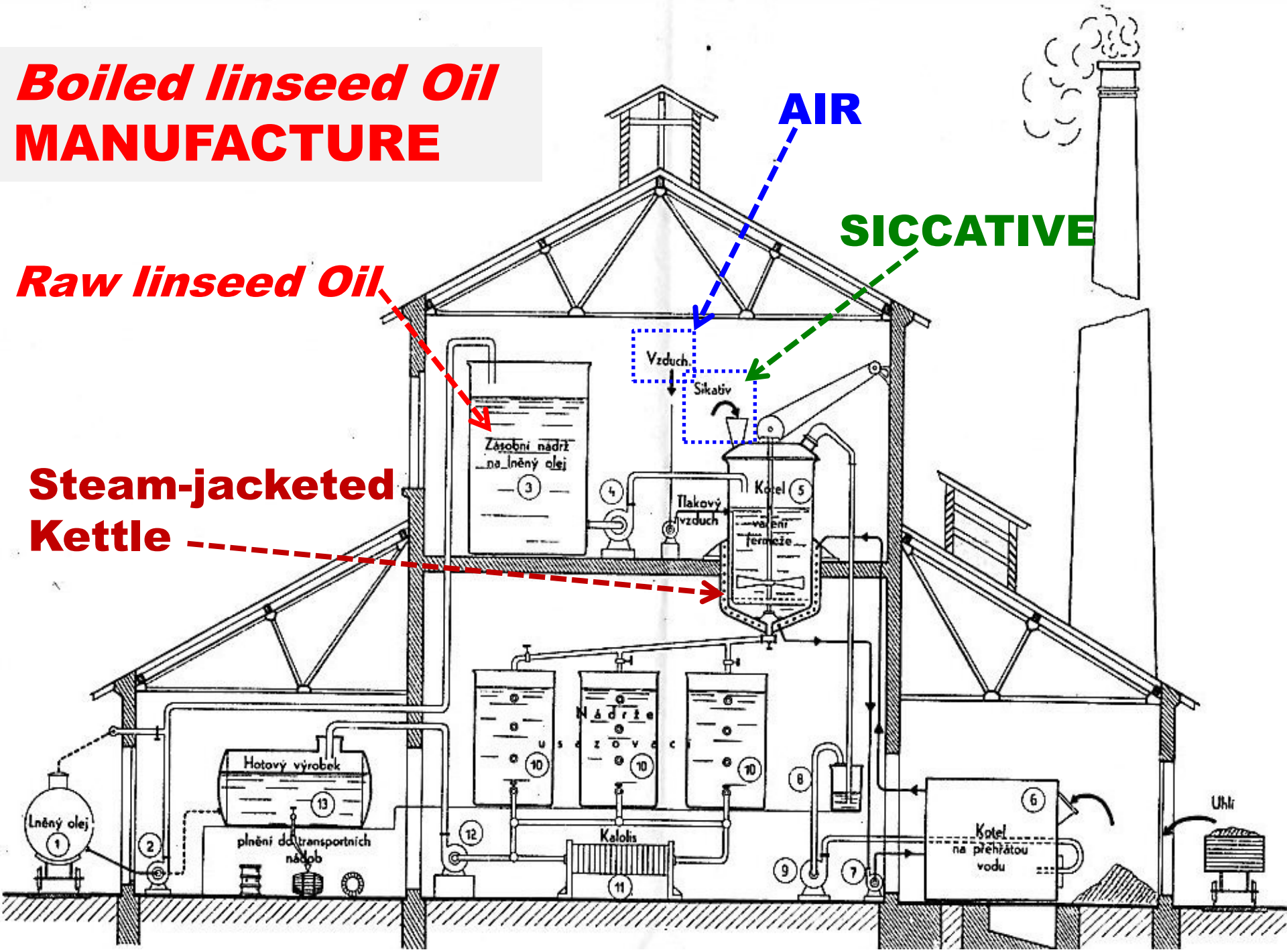
Boiled linseed Oil adjusted (mixed): **it contains some other Oils also, not the Linseed Oil only**

CHEMICAL BASIS OF THE MODIFICATION (TREATMENT):

The –OOH Groups are arisen on the double Bonds of the higher fatty Acids

Impregnating Linseed Oil: diluted by the volatile organic Solvents to decrease the Viscosity and so increase the Infusion to the impregnated Material, usually the Wood

Boiled linseed Oil MANUFACTURE



The FATY ACIDS OF OUR INTEREST AND THEIR COMPOSITIONS

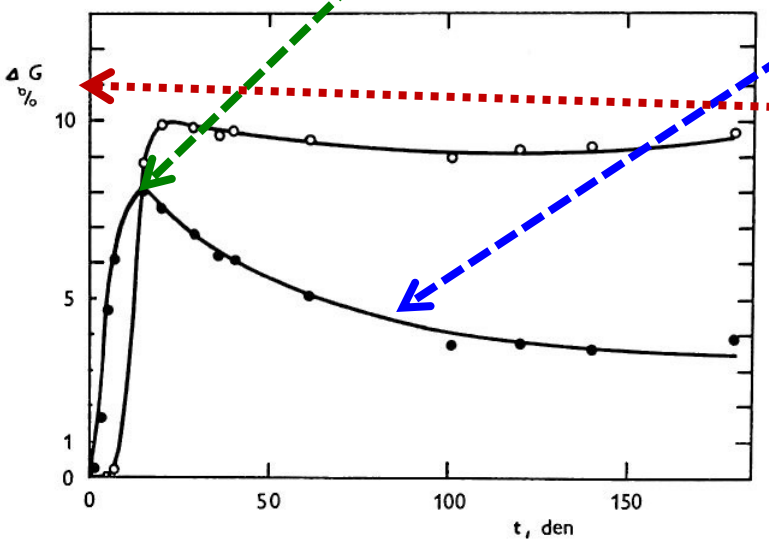
COMPOSITIONS OF THE TYPICAL VEGETABLE OILS			
ACID	Linseed Oil (% w/w)	Poppy/Poppy-seed Oil (% w/w)	Walnut oil (% w/w)
Palmitic	6	10	8
Stearic	4	2	3
Oleic	22	11	15
Linolic	15	76	61
Linolenic	52	---	12
OTHER	1	1	1
Ratio of the Palmitic to Stearic Acids	1,5	5,0	2,6

These Oils are used for the Oil based Paints and they are so called DRYING OILS

What is that of „OIL DRYING“

IT IS NOT REAL DRYING (Evaporation of the Solvent)!

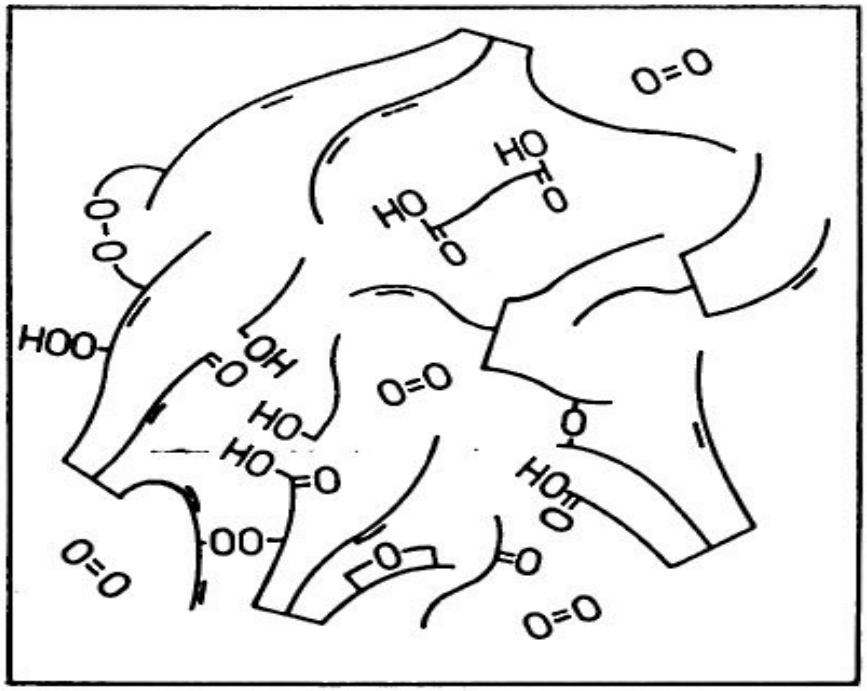
It is in Reality a Multistage Radical initiated Reaction, where the Group –OOH (Hydroperoxide) is arisen at first (**Mass is increasing**) , which then can initiate by its Decomposition a Crosslinking of the unsaturated Compounds (Fatty Acids in the Glycerides) and so the **Mass is decreasing** again



Obr. 15 Závislost přírůstku hmotnosti Δ *G* na době stárnutí *t* při 20 °C filmu z lněného (○) a makového oleje (●).

Δ G is here Δ of the Mass, not the Gibbs free Energy Change (Δ)!

What is that of „OIL DRYING“
Better said, it is Solidification



Schematic showing of the OXIDATION and DEGRADATION of the

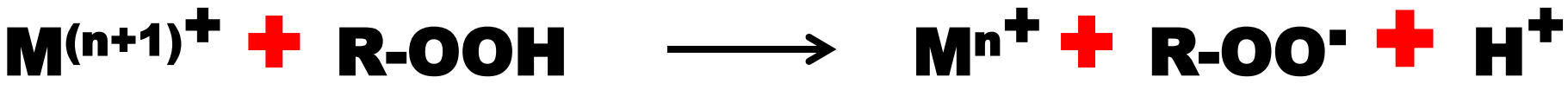
Linseed Oil Film

O=O ...Oxygen, -OOH ... Hydroperoxide, -OH ... Alcoholic Group, -COOH ... Carboxylic Group

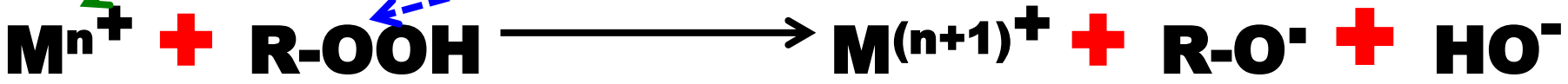
How to accelerate „OIL DRYING“?

Transition Valence Metals, e.g. Fe^{3+} , Co^{2+} , Mn^{2+} , Pb^{+2}

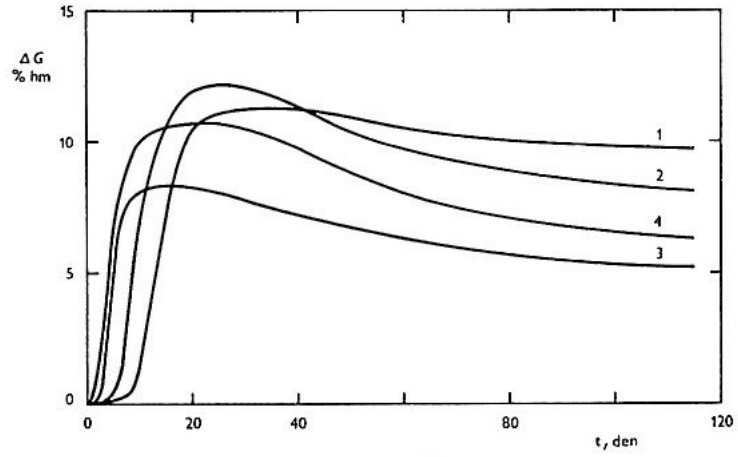
So called SICCATIVE



The Metal in the lower Oxidation State react with the Hydroperoxide decomposing it and increasing its Oxidation State back up. The Cycle is closed so.



Data from a Literature



ΔG as the Function of the Aging time t at 20 °C:

1. **Linseed Oil without any Pigments**
2. **Linseed Oil with the $ZnSO_4$ Pigment**
3. **Linseed Oil with the Cobalt Blue Pigment**
4. **Linseed Oil with the English Red Pigment**

Δ G is here Δ of the Mass, not the Gibbs free Energy Change (Δ)!

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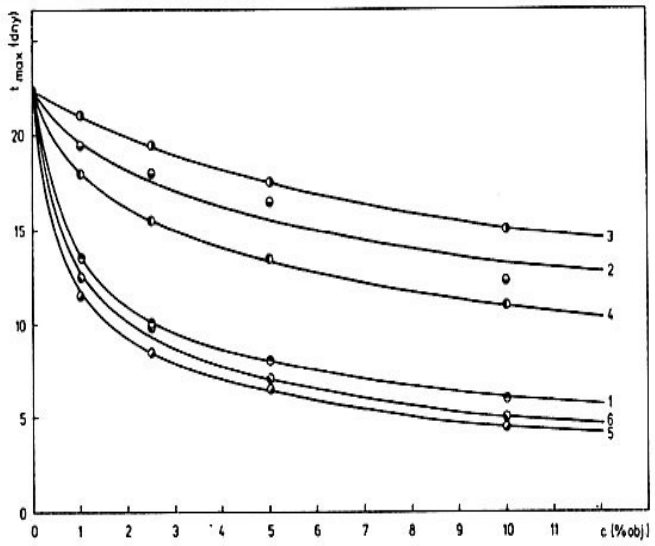
Ferric Pigments FEPREN

Ferric Red are the Iron oxides with the Red-brown Colour Shades



Time necessary to reach the Maximum on the „OIL DRYING“ Curve as the Function of the Ferric Red Pigment of the various Grades:

1. **English Red**
2. **Caput Mortuum**
3. **Puzuola**
4. **Ferric Red Lefrane**
5. **Bayferox**
6. **Windsor Newton**

How to *DECELERATE* „OIL DRYING“ and alternatively Protect the „Dry“ Film against undesirable Degradation?

- **UV Stabilisers – against the Light Degradation**
  - **HALS,**
  - **UV Absorbers,**
  - **Excited States Scavengers**
  - **……..**
- **Inhibitors of the Radical Reactions acting against the „OIL DRYING“?**

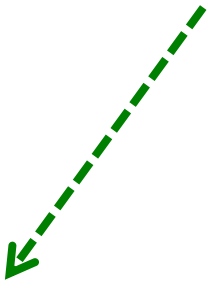
Natural RESINS

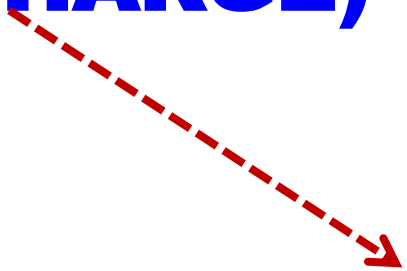
- **They are gained by Bleeding (Resin Tapping) from the Tree Injury or the purposely done Cuts of the Tree's, mainly the Fir Trees (e.g. Pine Tree)**
- **They are MIXTURES of the mainly Terpenoid's Compounds *(the only Exception is SHELACK)* and Essential/Ethereal Oils**
- **They are the Viscous Liquids, called also as BALSAMS or DISCHARGES (THIS MIXTURES)**
- **These BALSAMS are divided to RESINS & Essential/Ethereal Oils by Distillation to the SOLID MATERIAL (SOLIDS) & LIQUIDS**

Natural RESINS

Bleeding (Resin Tapping)

BALSAM (DISCHARGE)





Terpenoid (SOLID MATERIAL)

Essential/Ethereal Oils (LIQUID)

Natural RESINS versus Essential/Ethereal Oils

Natural RESINS are the **oligomeric**, viscous, low Volatile Materials (Mixture of the Compounds)

Essential/Ethereal Oils are the Volatile, even at low Temperature. They are Water insoluble, oily Substances of their Mixtures, frequently aromatic and having the acrid/pungent Taste.

They are TERPENOIDE in both cases

Shellac

- **Shellac is NOT the Vegetable Product!**
- **Shellac is the Animal Product, Insect's Secrete**
- **Shellac doesn't contain** Terpenoide Acids, but the Polyhydroxy Acids, mainly (up to 50 % w/w) of the Aleuritic Acid and its Oligomers

$$HOCH_2(CH_2)_5CH(OH)CH(OH)(CH_2)_7COOH$$

- **Shellac** is highly polar Substance > Solubility in the **EtOH** and in the other Alcohols and Glycols
- **Shellac is** Water insoluble, but it is soluble in the alkali Solutions > the Binder for the China Ink

Shellac – various Grades

Shellac - Use

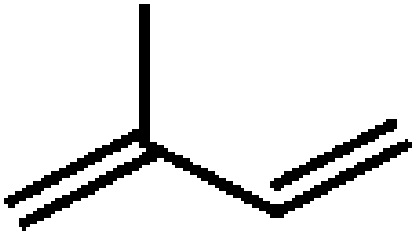
HISTORICAL USE

- **GRAMOPHONE RECORDS**, even before the Use of the PVC Copolymers!
- **IT WAS FILLED BY THE VERY FINE GROUND SLATE!**

CURRENT USE

- Manufacture of the musical Instrument – the by Hand Varnishing of the Violin and also for some by Hand Vvarnishing of the woodwind Instruments made of the light Wood.
- Surface Treatment of Wood by Shellac Polish at Restoration Work, what give the Wood excellent Gloss.
- Furnace polishing (in the 18.–19. Centuries).
- Food Additive E904, e.g. Impregnation of the Fruit and Vegetable Surface to keep the Freshness.

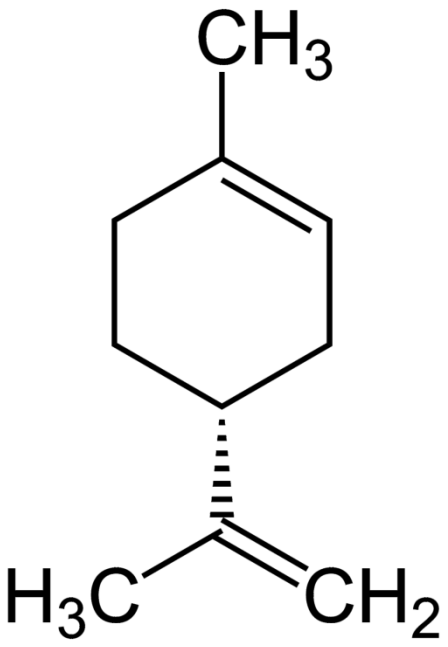
ISOPRENE – basic Unit of the TERPENOIDS

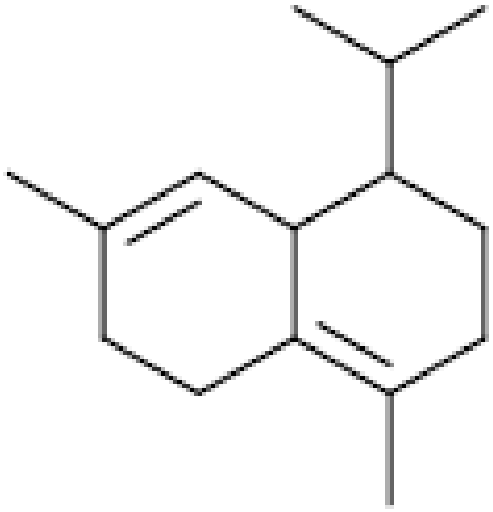


Systematic Name	2-methyl-buta-1,3-dien
Other names	2-methyl-1,3-butadien
Summary Formula	C_5H_8

TERPENOIDS – the main Components of the NATURAL RESIN

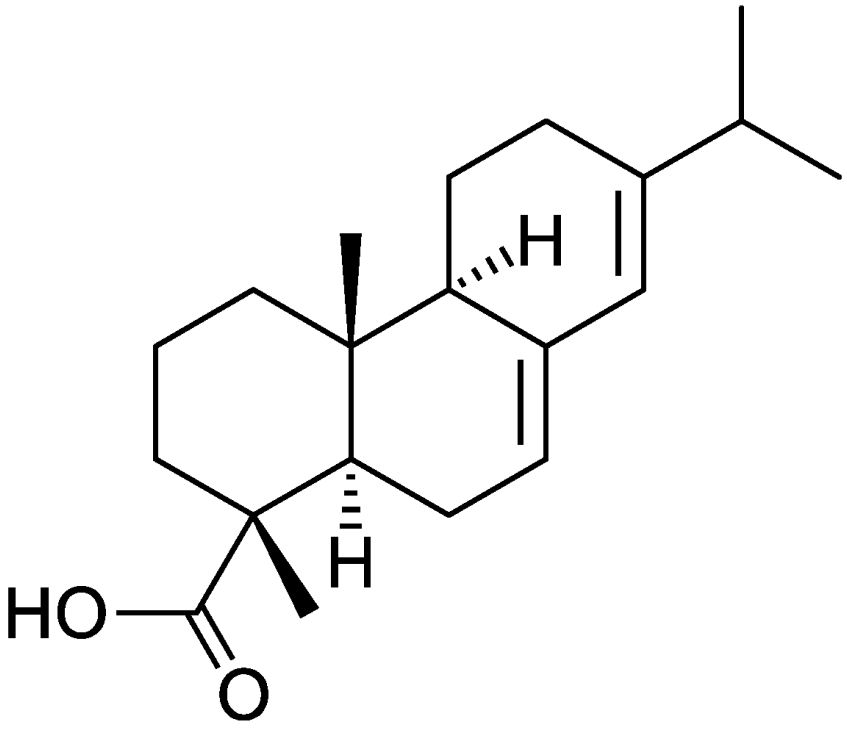
DENOMINATION	CARBON ATOMS NUMBER	State of Matter at normal Temperature (23 °C)
MONOTERPENOID	**10**	**Liquid**
SESQUITERPENOID	**15**	**Liquid**
DITERPENOID	**20**	**Solid State**
TRITERPENOID	**30**	**Solid State**





MONOTERPENE
LIMOLENE
(in the Orange Peel)

SESQUITERPENE
δ KADILENE



DITERPENE
Abietic Acid

The most important natural Resins

Physical and Chemical Properties of the natural Resins

Resin	Acid Number (mg KOH/g)	Saponification Number (mg KOH/g)	Iodine Value (% I_2/g)	Softening Temperature (°C)
Colophone	140 – 180	147 – 195	200 - 225	73 – 79
Venice Turpentine	75 - 95	105 - 120	120 - 145	136 – 138
Sandarac	130 - 150	180 - 200	70 - 100	110 - 120
Copal Mannila	130 - 150	180 - 200	70 - 100	110 - 120
Damara	25 - 40	35 - 40	55 - 65	84 – 86
Mastix	60 - 65	85 - 100	70 - 85	73 – 74
Shellac	40 - 60	200 - 250	4 - 10	82 - 88

Natural Resins – an Example

- **Fir Trees** > **PINE**
- > **Turpentine BALSAM (DISCHARGE)**
- > **DESTILATION of the Essential/Ethereal Oils** > **Turpentine** > Thinner (Diluent) of the Boiled linseed Oil and Oil's based Paint
- > The Rest after DESTILATION (Bottoms) is the **RESIN = COLOPHONE**

COLOPHONE

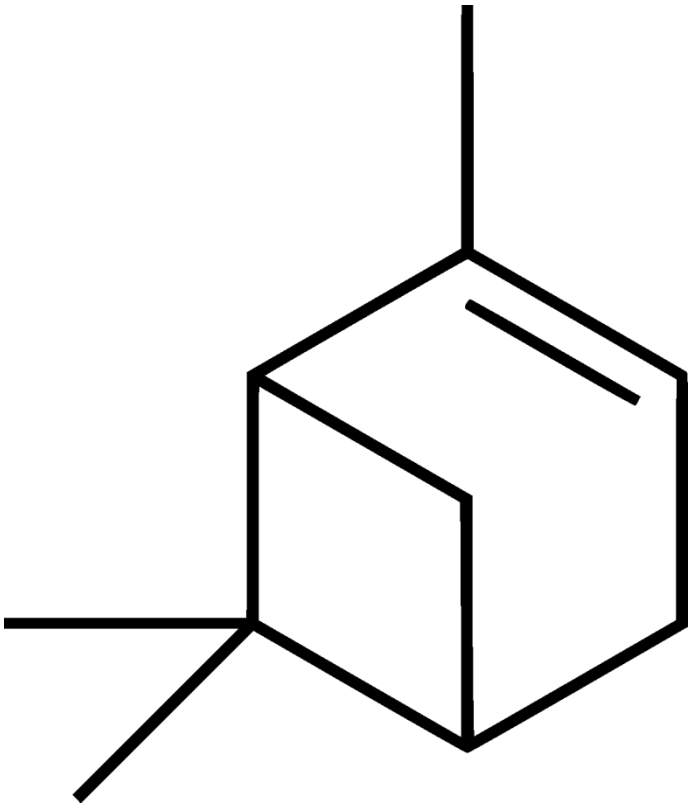
- **Hard and Brittle at Room Temperature**
- **It is changing Hard to Soft at approx. 70 °C**
- **It melts at approx. 120 °C**
- **It is soluble in the Alcohols, Esters, Aromatics, Chlorine substituted Solvents, Ketones, Turpentine etc.**
- **It contains mostly Abietic acid > its Oxidation results as the Brittleness, Reduction of the Solubility etc.**
- **It is soluble in the Alkali > RESIN'S SOAPS**
- **Co^{+2} Salts > SICCATIVE**
- **Cu+2 Salts > Pigment & SICCATIVE**
- **Hot Melts**
- **Soldering > it destroys the Oxide's Layers**

COLOPHONE (*eng. Rosin or Colophony or Greek Pitch, Yellow Rosin*)

- Colophony or Greek Pitch > it is derived fro the Old Greek Town Colophon, fames for the export of the **COLOPHONE**
- Other uses:
  - Surface Treatment of the Violin Bow to increase the Friction with the Strings
  - If mixed with some Waxes is used for Iron on the old paintings to the new under laid Canvas (Textile) > **RENTOALAGE**
  - Pharmacy
  - Food Industry
  - ……

COLOPHONE (*eng. Rosin or Colophony or Greek Pitch*)

Essential/Ethereal Oils Example - Turpentine

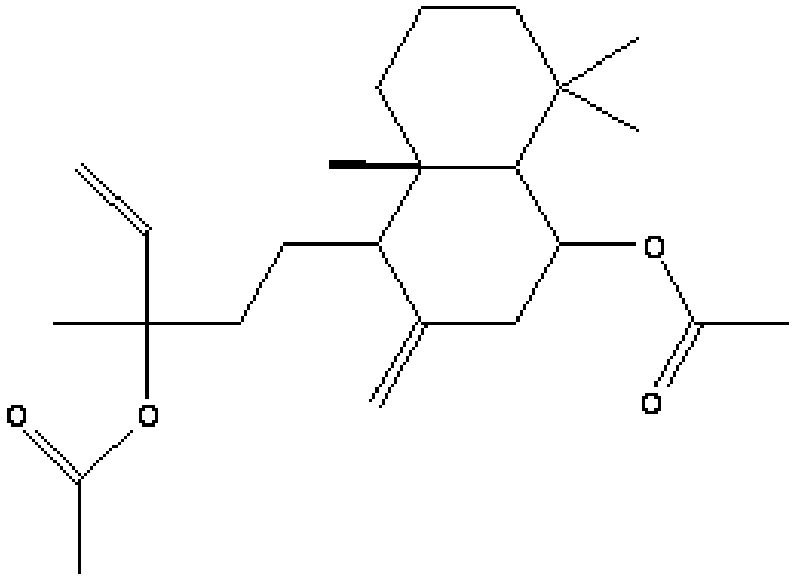


The main Components are PINENE (α, β)

- Solvent for the Oils based Paints
- As the Mixture with the Beeswax or the Carnauba Wax is used as the Furnace Polishing Agent
- Synthesis of the fragrant Substances, e.g. Camphor

Venic (Venetian) Turpentine

Add to oil paints, mediums and varnishes for an exquisite jewel-like quality and tough, enamel-like surface. Derived from European larch trees, this resin has the CONSISTENCY OF HONEY and is offered in its pure, undiluted state. Dilute with 20% turpentine and use sparingly to a 5% maximum of the total paint mixture.



Venic (Venetian) Turpentine

European Larch

Some Remarks more

1. **The Trivial Names are most common in the Chemistry of the Natural Substances, frequently related to the place of the Occurrence of the Substance in Question**
2. **There are also the other Substances besides the main Natural Substances (Polymers) in the common Natural Substances Samples (Materials)**
3. **The Composition and the Amount of the accompanying Substances are related to the Substance's Source and Place of the Origin, the harvesting Season etc.**

Let's go to the other RESINS and BALSAMS (DISCHARGES)

DITERPENOIDE RESINS

Let's go to the other Resins & Balsams (DISCHARGES)!

Canada Balsam (Balsam of Fir)

- It is taken from the Canadian Fir
- It is used for the Assembling of the Optical Devices, because having very suitable refractive Index, very close to that of the optical Glass

Venic (Venetian) Balsam

- It is taken from the **European Larch**
- It forms the Glossy not yellowing Film
- It was used in Painting (Oil Painting) in the time of Rubens already, mixed with the Nuts Oil and Mastix

Copal

Copal is a name given to tree resin, particularly the aromatic resins from the copal tree *Protium copal* (Burseraceae) used by the cultures of pre-Columbian Mesoamerica as ceremonially burned incense and for other purposes. More generally, the term *copal* describes resinous substances in an intermediate stage of polymerization and hardening between "gummier" resins and amber.

Copal is highly soluble in the EtOH and is (was) valuable ingredient in making a good wood varnish. It became widely used in the manufacture of furniture and carriages.

COPAL versus Novolacs
Novolacs = Synthetic Condensate of Phenol + Formaldehyde

- **NOVOLACS are good soluble in the EtOH,**
- **NOVOLACS resulting in the glossy and hard Paints (Coatings),**
- **NOVOLACS can be used as the COPAL in the alcohol Varnishes, which were formerly called (*in a simple Slang*) only as „COPALS“,**
- **NOVOLACS were sometimes used for the falsification of the genuine COPAL in the alcohol Varnishes**

Sandarac

It is taken from the **Coniferous Tree** which is growing in the Nord Africa

It is used for the protective Coating on the Pictures and Antiquities

It is the Components of the Oil Varnishes, being soluble in the:

- Turpentine,
- Aromatics,
- Amyl alcohol.

Let's go to the other RESINS and BALSAMS (DISCHARGES)

TRITERPENOIDE RESINS

Mastic (Mastix)

Mastic (Mastix) is the Resin, which is taken from the little Bush MASTIC TREE (*Pistacia lentiscus)* **growing on the Greek Island Chios.**

Mastic is used in some varnishes. Mastic varnish was used to protect and preserve photographic negatives. Mastic is also used in perfumes, cosmetics, soap, body oils, and body lotion.

Chios **Mastic** is a known spice in the Eastern Mediterranean. It is commonly used for baking and cooking, adding its aroma to foodstuffs such as brioches, ice-cream and other desserts. It is especially known to the Arabian cuisine, but recently mastic is also increasingly used in Japanese cooking.

One of the earliest uses of **Mastic** was as chewing gum; hence, the name. Mastic-flavored chewing gum is sold in Syria, Lebanon, Turkey, and Greece. Mastic is used in ice cream, sauces, and seasoning in Lebanon. In Egypt, mastic is used in vegetable preserves, in jams that have a gummy consistency, in soups, and in the preparation of meats. In Morocco, mastic is used in the preparation of smoked foods.

Mastic has been used as a medicine since antiquity and is still used in traditional folk medicine of the Middle East.

Mastic contains antioxidants and also has antibacterial and antifungal properties.

Mastic is the Components of the Oil Varnishes, being soluble in the:

- **Turpentine,**
- **Aromatics,**
- **Amyl alcohol.**

Dammar gum

- **DAMMAR GUM has a low IODINE VALUE > low Tendency to Yellowing and Polymerization**
- **Dammar gum as the Component of the Varnishes gives them high Gloss**

DAMMAR GUM is soluble in the: Turpentine, Alcohols, Ketones, Esters, ...

DAMMAR, also called **DAMMAR GUM**, or **DAMAR GUM**, is a resin obtained from the trees in India and East Asia. Most is produced by **TAPPING TREES**, however, some is collected in fossilised form from the ground. The gum varies in colour from clear to pale yellow, while the fossilised form is grey-brown. **DAMMAR GUM** is a triterpenoid resin, containing a large number of triterpenes and their oxidation products. Many of them are low molecular weight compounds (dammarane, dammarenolic acid, oleanane, oleanonic acid, etc.), but dammar also contains a polymeric fraction, composed of polycadinene.

DAMMAR GUM is used in foods, as a clouding or glazing agent, and in incense, varnish and other products. *Dammar varnish*, made from dammar gum mixed with turpentine, was introduced as a picture varnish in 1826; commonly used in oil painting, both during the painting process and after the painting is finished.

Dammar crystals are also dissolved in molten paraffin wax to make batik, to prevent the wax from cracking when it is drawn onto silk or rayon.

Dammar crystals are dissolved into beeswax with pigment added to harden it in order to make encaustic paints.

Dammar resins were often used in the past to caulk ships, frequently together with pitch or bitumen.