NATURAL POLYMERS 4
POLYTERPENES

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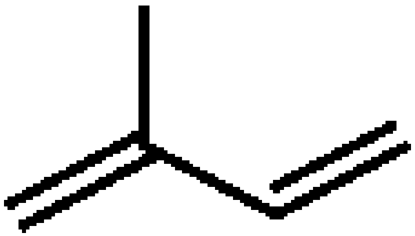
Time schedule

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 – celullosis
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

Isoprene – The basic molecular formula of terpenes



Systematic IUPAC name	2-methyl-buta-1,3-dien
The other name	2-methyl-1,3-butadien
Summary Formula	C_5H_8

Terpenes – the main component of RESINS

Nomenclature	Number of Carbon atoms	Physical State at Standard temperature (i.e. 23 °C)
Monoterpenoid	10	Liquid
SESQUITERPENOID	15	Liquid
Diterpenoid	20	Solid State
TRITERPENOID	30	Solid State

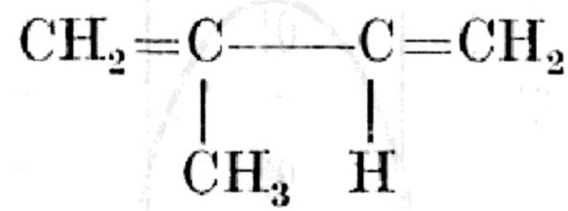
A bit of TERMINOLOGY is NECESSARY

POLYTERPENE = POLYISOPRENE

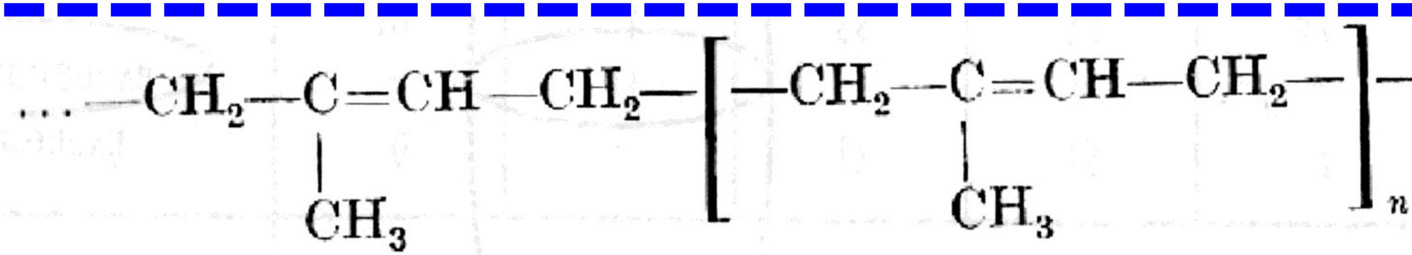
Rubber > Vulcanization > Vulcanized Rubber

Plant (vegetable) GUMS =
POLYSACCHARIDES = Mucilage (GUM)

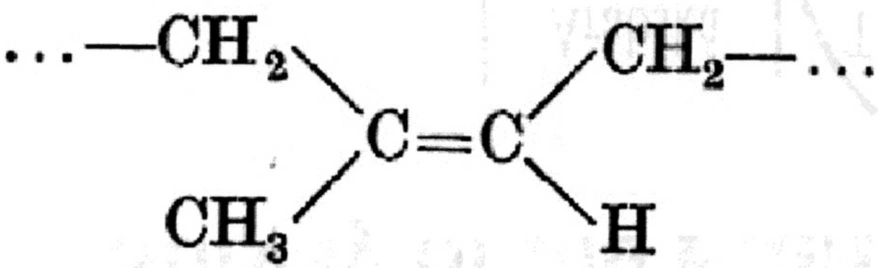
Composition of the NATURAL RUBBER – it is polymer made of ISOPRENE hydrocarbon (2-methyl-buta-1,3-dien)



Structure formula of the POLYISOPRENE

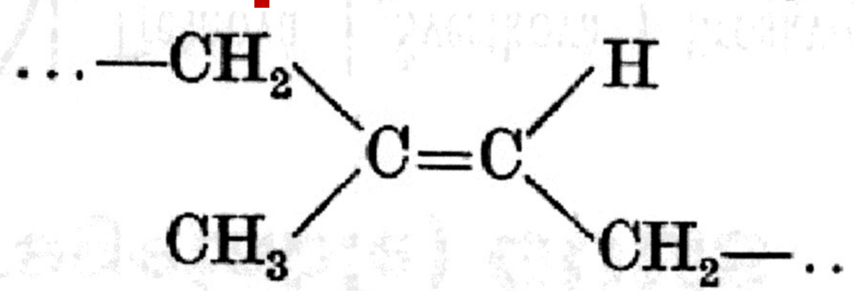


Cis-POLYISOPRENE
NATURAL RUBBER



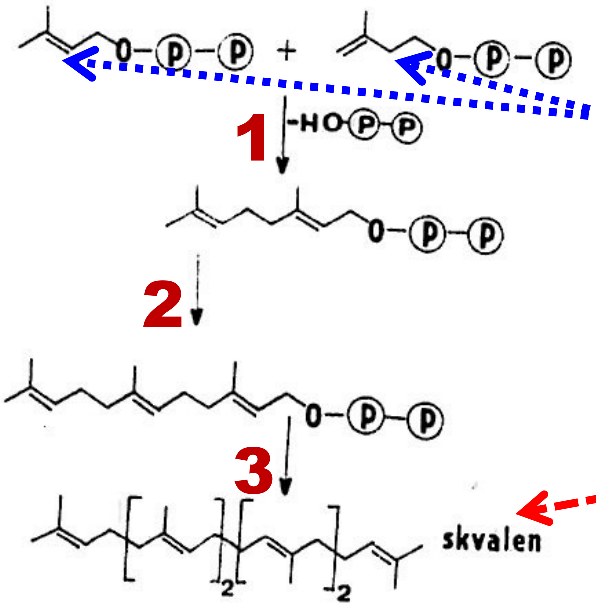
cis

trans-POLYISOPRENE
Gutta-percha

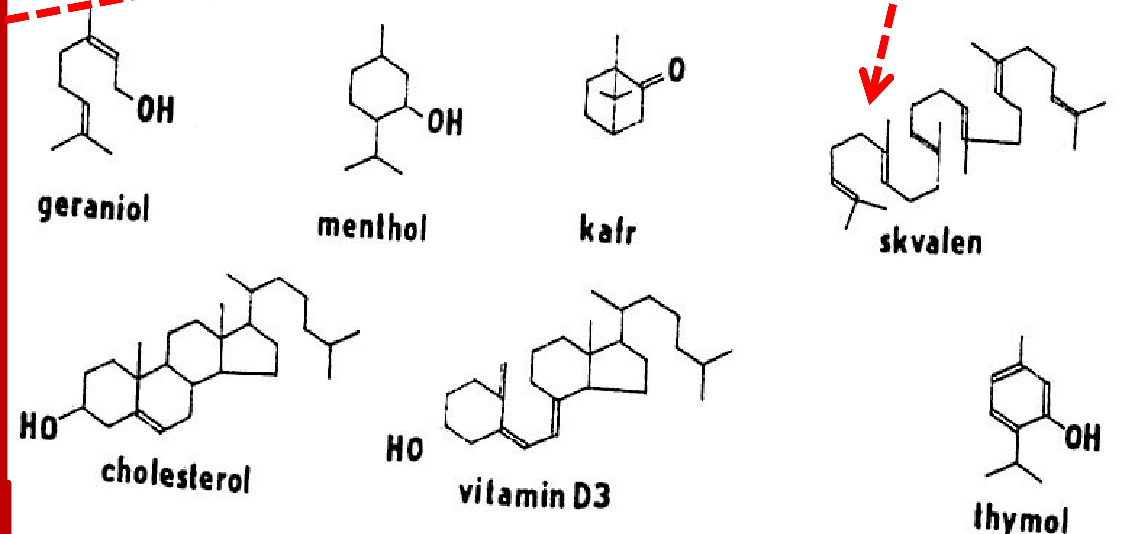


trans

Three step enzymatic synthesis of the TERPENOIDes



CONDENSATION „**HEAD – TAIL**“of two UNITS of so called „**ACTIVE ISOPRENE**“



TERPENOIDES

POLYTERPENE = POLYISOPRENE
Appearance in NATURE

- **POLYTERPENE -** are contained in approx. 2000 plants from various geographic regions
- Trees, Bush, Herbs
- The most important is the Tree: *Hevea brasiliensis*
- *HOPEFUL HERB: Taraxanum koksagyz*

Perhaps historical Pictures!

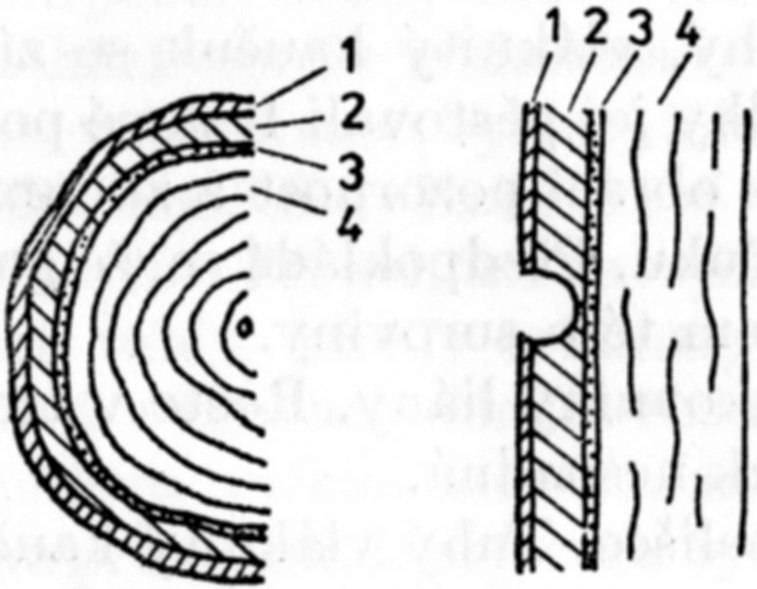
Obr. 2. Doprava přírodního latexu ke zpracování

Obr. 3. Srážení přírodního latexu

POLYTERPENE = POLYISOPRENE
Extracting in Nature > „Field latex"

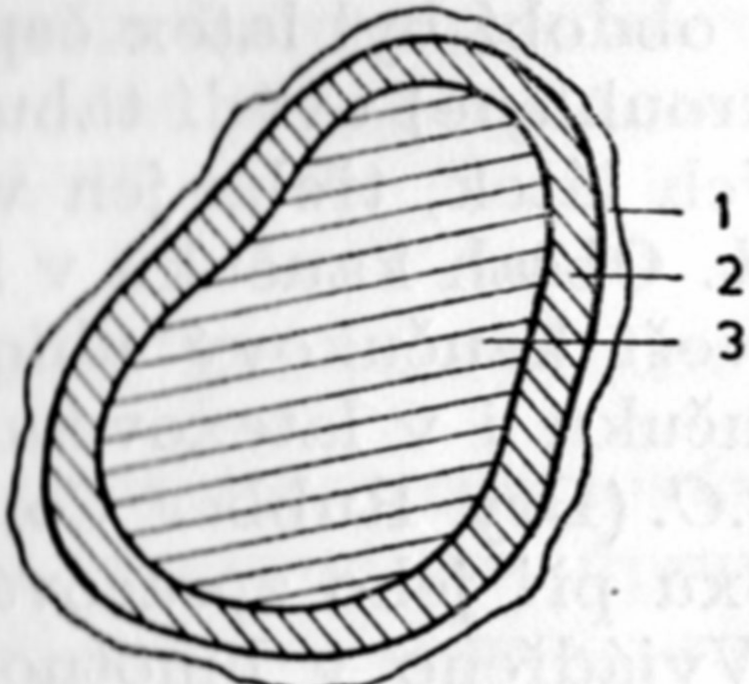
- **LATEX** (approx. 25 – 35 % w/w of Rubber)
- Coagulation by acids (formic, acetic) > **CREPE RUBBER**
- Drying & Preservation over a Fire> **Ribbed Smoke Sheet**
- Calendring and Stabilisation against oxidation and Microorganisms
- Expedition

Nature, over millions of years, evolved self-healing processes using elastomers (like latex). (Source: Jingdong)



The Layers in the Cross Section s of the *Hevea brasiliensis* tree stem:

1. ***The old dead Bark***
2. **The young Bark – the Rubber Latex source**
3. **The Cambium**
4. **WOOD**

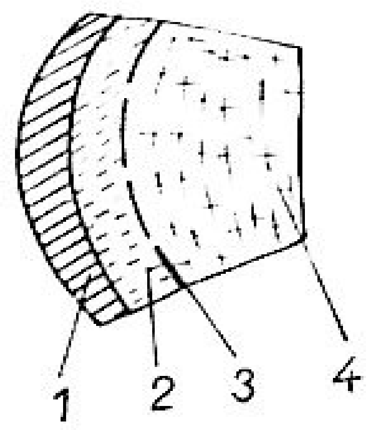


The Composition of the Rubber Latex Particle:

1. **Proteins and Resins**
2. **GEL of the Latex**
3. **SOL of the Latex**

LATEX (approx. 25 – 35 % w/w of Rubber)

- **Rubber (approx. 25 – 35 % w/w)**
- **Water (60 – 75 % w/w)**
- **Proteins (2 % w/w)**
- **Saccharides**
- **Inorganic Matter**
- **Resins**

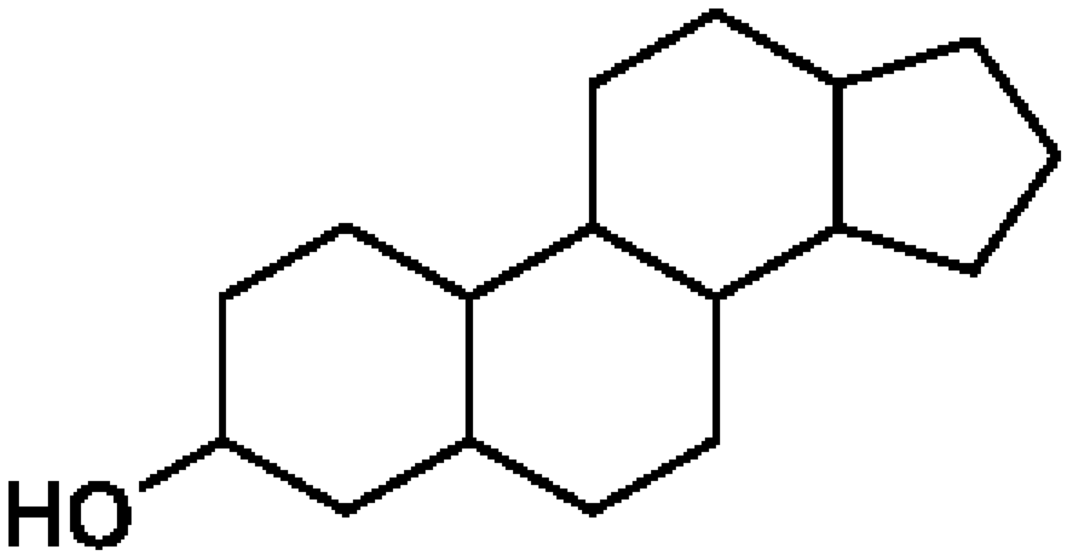


The Cross Section s of the *Hevea brasiliensis* tree stem:

1. ***The old dead Bark***
2. **The yongh Bark – the Rubber Latex source**
3. **The Cambium**
4. **WOOD**

Composition of the NATURAL RUBBER

	Values' Range	MEAN VALUES	
		Smoked Sheets	Crepes
Water (% w/w)	0,3 - 1,2	0,61	0,42
Acetone extract (% w/w)	2,5 – 3,2	2,9	2,7
Proteins (% w/w)	2,5 – 3,5	2,8	2,8
Ash content (% w/w)	0,15 – 0,90	0,38	0,30
RUBBER (% w/w)	92 – 94	93,8	93,6
Chlorides (% w/w)	0,002 – 0,010	0,006	0,003
Sulfates (% w/w)	0,02 – 0,05	0,03	0,04
Sterols (% w/w)	---	0,5	0,5
Higher fatty acids (% w/w)	---	1,4	1,1
Cuprum (ppm)	2 – 10	5	4
Manganese (ppm)	0,8 – 4,0	1,5	1



Sterols, also known as **steroid alcohols**, are a subgroup of the steroids and an important class of organic molecules. They occur naturally in plants, animals, and fungi, and can be also produced by some bacteria (however likely with different functions). [1] The most familiar type of animal sterol is cholesterol, which is vital to cell membrane structure, and functions as a precursor to fat-soluble vitamins and steroid hormones.

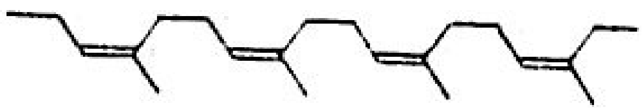
COMPOSITION of the NATURAL RUBBER	
Component	**Content (% w/w)**
Rubber hydrocarbon	35
Water	60
Resins & Fatta acids	2
Proteins	1,8
Inorganic substances & the other components	1,2

Dependance of the Density and Viscosity on the Content of the Rubber hydrocarbon		
Rubber hydrocarbon (% w/w)	**Density (kg/m^3)**	**Viscosity (m.Pa.s)**
20	996	2,5
30	983	4,0
40	972	5,5
50	959	7,5
60	948	27

POLYTERPENE = POLYISOPRENE

IZOMERs

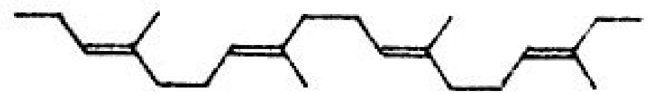
cis



NATURAL RUBBER

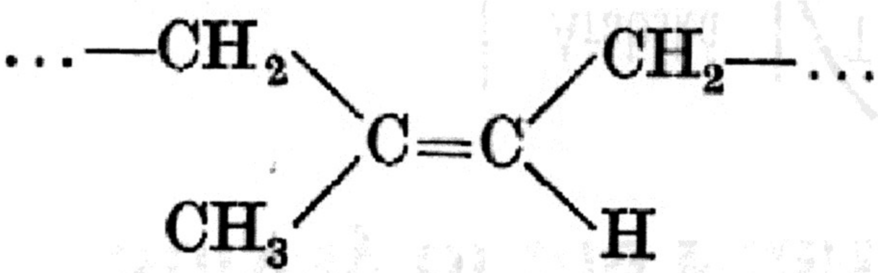
- **Vulcanization**
- **LOWER** resistance to oxidation (weathering)
- Elastic at normal temperature

trans



Gutta-percha

- **It does NOT vulcanize!**
- **BETTER** resistance to oxidation (weathering)
- **NOT** Elastic at normal temperature
- Soft and elastic at temperature over approx. 50 °C
- **TERMOPLAST**
- **It is gained from another plant then NATURAL RUBBER**



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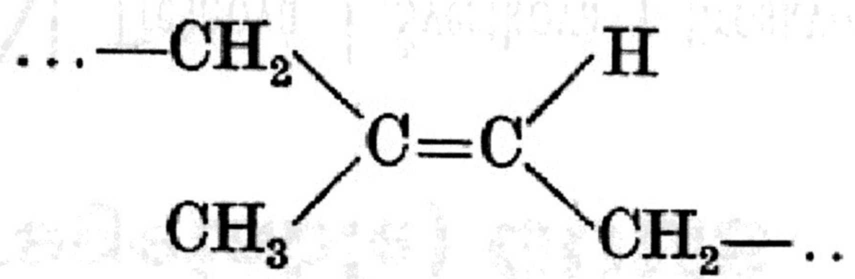
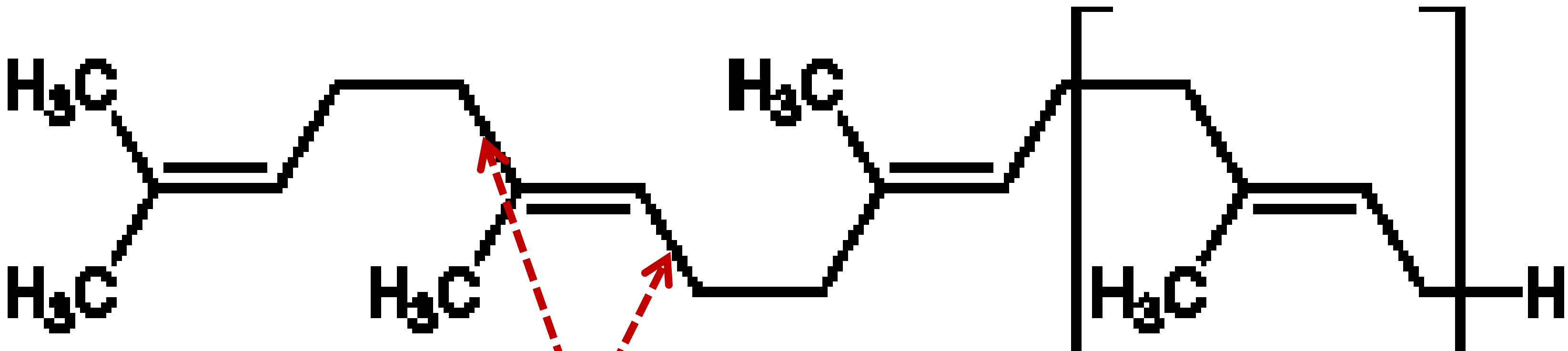
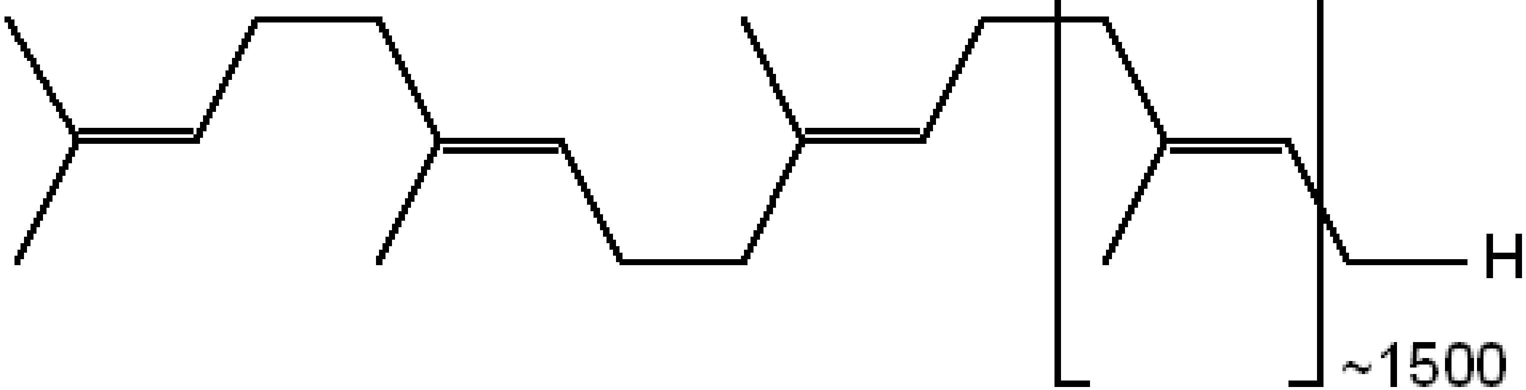


trans

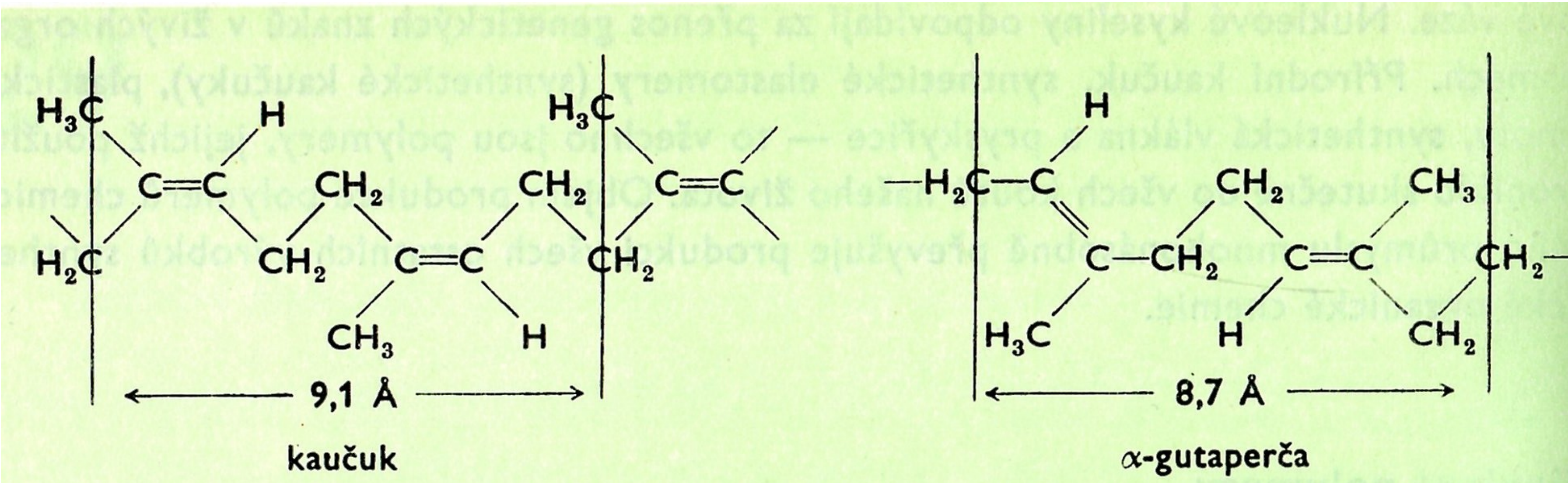
Gutta-percha - various presentations of the MAIN CHAIN in the Literature

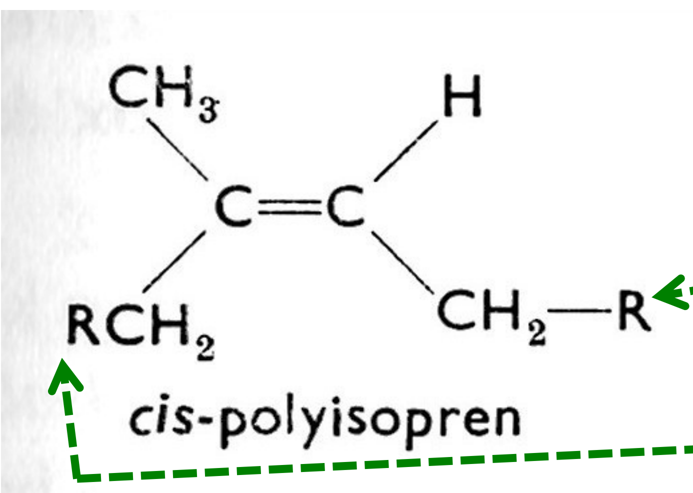


trans-1,4 polyisoprene designation is related to the MAIN CHAIN



Gutta-percha versus NATURAL RUBBER Various presentations of the MAIN CHAIN in the Literature





R is here the CONTINUATION of the MAIN CHAIN

Gutta-percha versus BALATA GUM

- **BALATA is very similar to Gutta-percha, but only as to the Physical Properties, not as to the chemical Point of view**
- **BALATA is more soft > it was used for Chewing Gums, but a synthetic food analogue is used now**
- **Its importance and use are marginal and decreasing now**

Manilkara bidentata is a species of *Manilkara* native to a large area of northern South America, Central America and the Caribbean. Common names include **bulletwood**, **balata**, **ausubo**, **massaranduba**, and (ambiguously) "cow-tree".

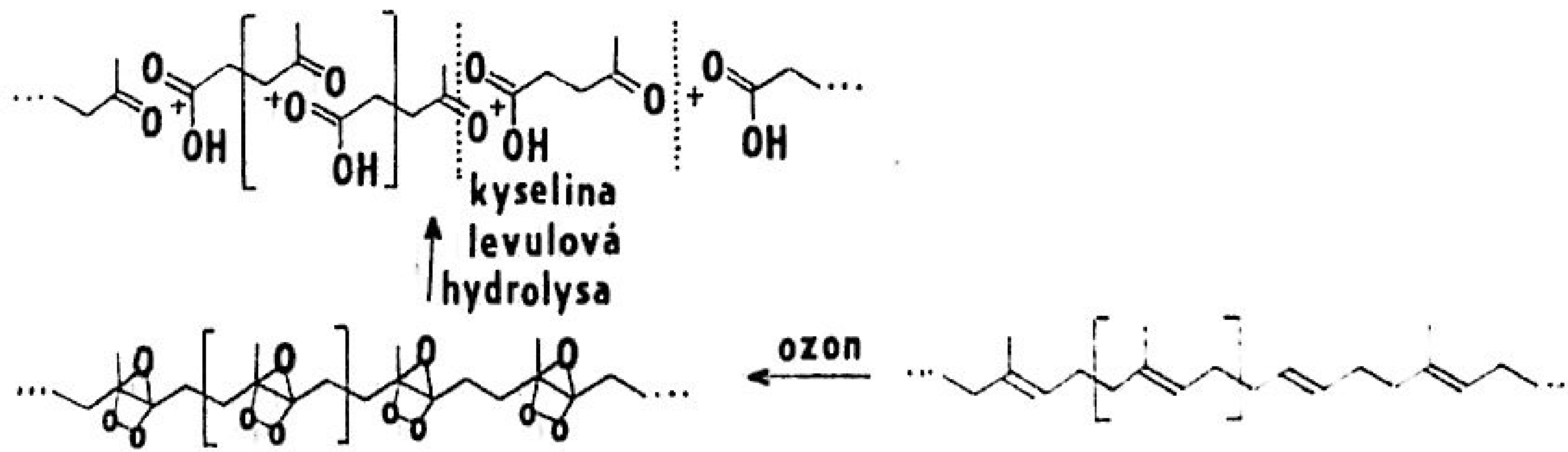
Balata is a large tree, growing to 30–45 m (98–148 ft) tall.

Its latex is used industrially for products such as chicle CHICLE is a natural gum >

POLYSACCCHARIDE, not POLYTERPENE!

POLYTERPENE = POLYISOPRENE

How was the Structure discovered



<u>It is demonstrated at</u> Gutta-percha here, but it is the Trans Structure!

Processing of the NATURAL RUBBER
Before Vulcanisation

- „Mastication “ –cleavage of the chains to shorter parts using mechanical energy and oxygen
- Addition of the other components and kneading (homogenisation of the mixture:
  - Fillers (mostly Carbon black, amorphous SiO_2, ……)
  - Plasticizers,
  - Pigments,
  - Antioxidants a antiozonants
  - Vulcanization agents (sulphur, accelerators, …)
  - Lubricants

Processing of the NATURAL RUBBER
One typical Mixture composition

Component	PARTS (not % w/w)	Function
NATURAL RUBBER	40	
Synthetic RUBBER 1	30	Modification of Properties
Synthetic RUBBER 2	30	Modification of Properties
ZnO	3 – 4	Vulcanization accelerator
Stearic acid	2	Lubricant
Carbon black stiffening	30	Modification of Properties
Plasticizers	4	
Sulphur	2 – 3	Vulcanization
Antioxidants and antiozonants	1,5	Protection against oxygen and ozone

People working with Rubber and PVC ussualy do not calculate % w/w, but using PARTS!

What interesting did I personally

DOCUMENTS FOR THE Court-appointed Expert

- **Black spot on the fairing of the Racer (motorcycle)**
- **Is it Spot the ASPHALT or Tyre rubber?**
- **SEM + EDX analysis of Elements in the Spot**
- **„What was my Target“**
  - **SULPHUR Vulcanization**
  - **ZINC Vulcanization accelerator**
- **RESULT: NO ZINC, NO SULPHUR, it MUST BE ASPHALT**

Two Roll Mill (Rubber, PVC, etc.)

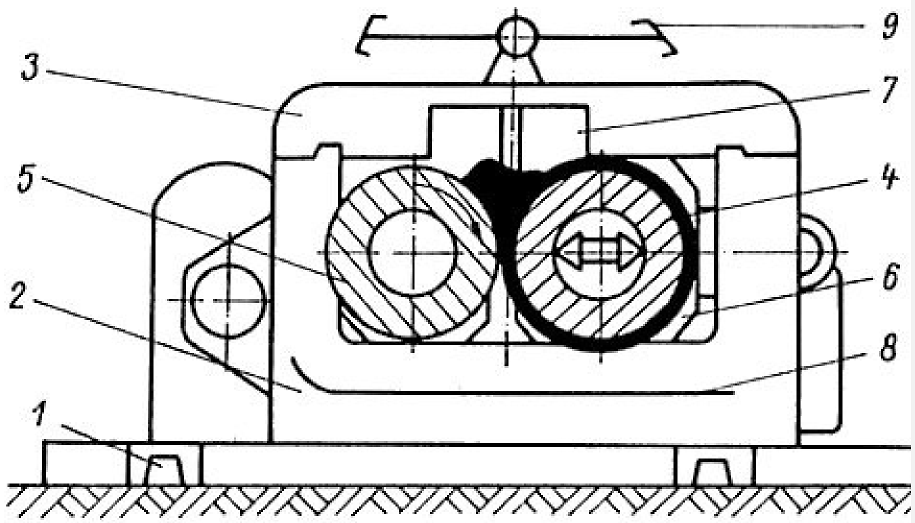
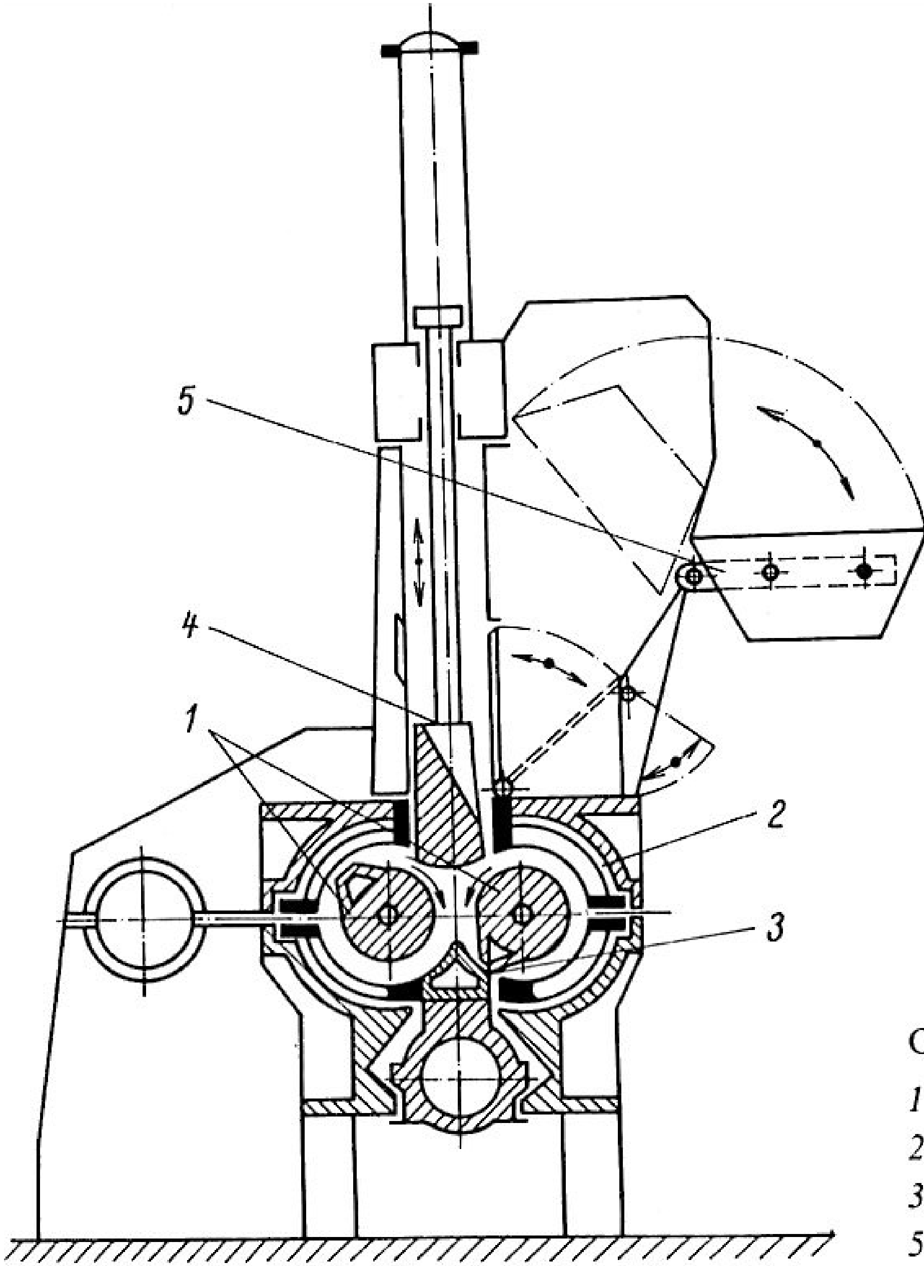


Diagram of the TWO ROLL MILL and Scheme of the Mixing and/or Mastication using it:

1. Main Frame
2. Side part of Frame
3. Shackle
4. Front adjustable Roll
5. Rare Roll with Drive
6. Bearing body
7. Doctor blade (scrubbing of the material covering the Roll)
8. Vessel
9. Emergency stop handle

BUNBARY Mixer (kneading machine) (The Inventor of this Machine was Mr. BUNBARY)



Kneading machine:

1. Mixing Blades
2. Mixing Chamber
3. Discharge stopper
4. Stopper
5. Hopper

Obr. 10. Hnětací stroj

1 – hnětadla,
2 – hnětací komora,
3 – uzávěr, *4* – beran,
5 – násypka

NATURAL RUBBER is for longest time used HYDROCARBON POLYMER!

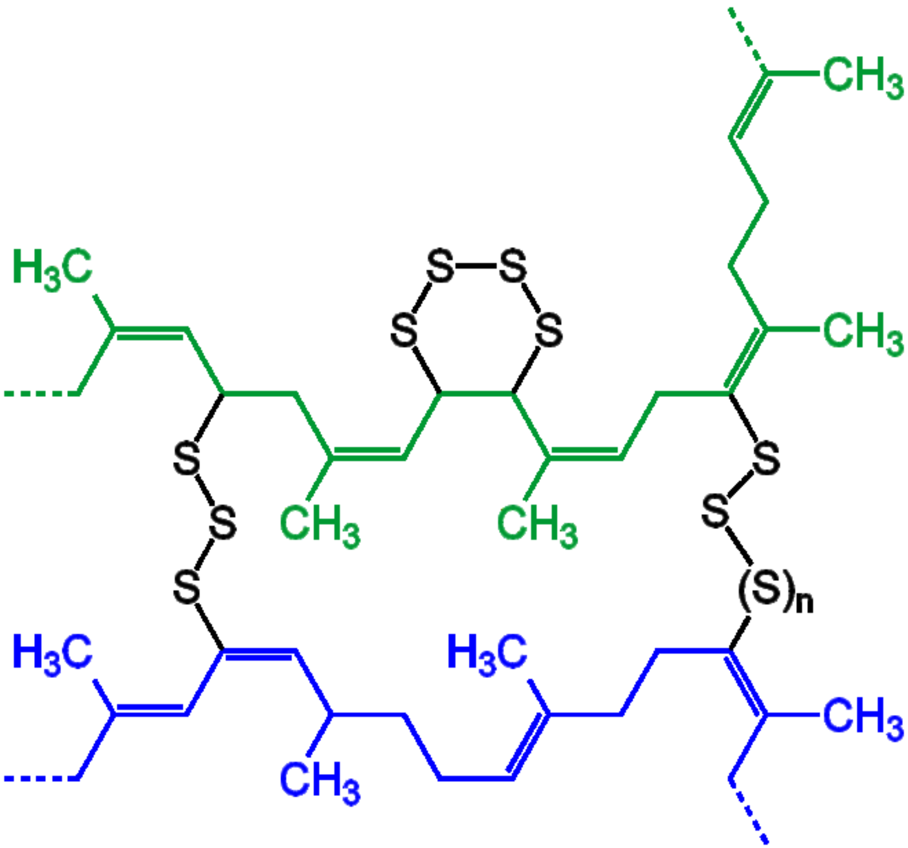
The first use of rubber was by the indigenous cultures of Mesoamerica. The earliest archeological evidence of the use of natural latex from the *Hevea* tree comes from the Olmec culture, in which rubber was first used for making balls for the Mesoamerican ballgame. Rubber was later used by the Maya and Aztec cultures - in addition to making balls Aztecs used rubber for other purposes such as making containers and to make textiles waterproof by impregnating them with the latex sap.

Charles Goodyear developed vulcanization in 1839, although Mesoamericans used stabilized rubber for balls and other objects as early as 1600 BC

Various Descriptions of VULKANISATION

See the following three slides

VULKANISATION NATURAL RUBBER
By elementary Sulphur 1

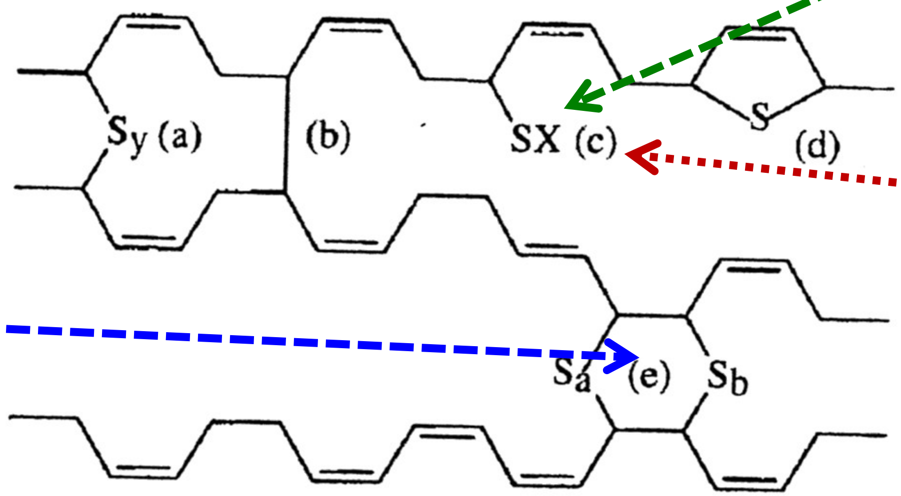


- Mixtures with **NATURAL RUBBER VULKANISE** at Temperatures approx. 150 – 180 °C.
- Synthetic Rubbers VULKANISE at Temperatures approx. 180 –220 °C.

VULKANISATION USSUALY DOES NOT GO BY REACTION OF THE DOUBLE BONDS, THEY ARE USSUALY MAINTAINED > SENSITIVITY TO OZONE

VULKANISATION NATURAL RUBBER
By elementary Sulphur 2

Accelerator



It is possible to VULKANISE by Sulphur Compounds also (here SX)!

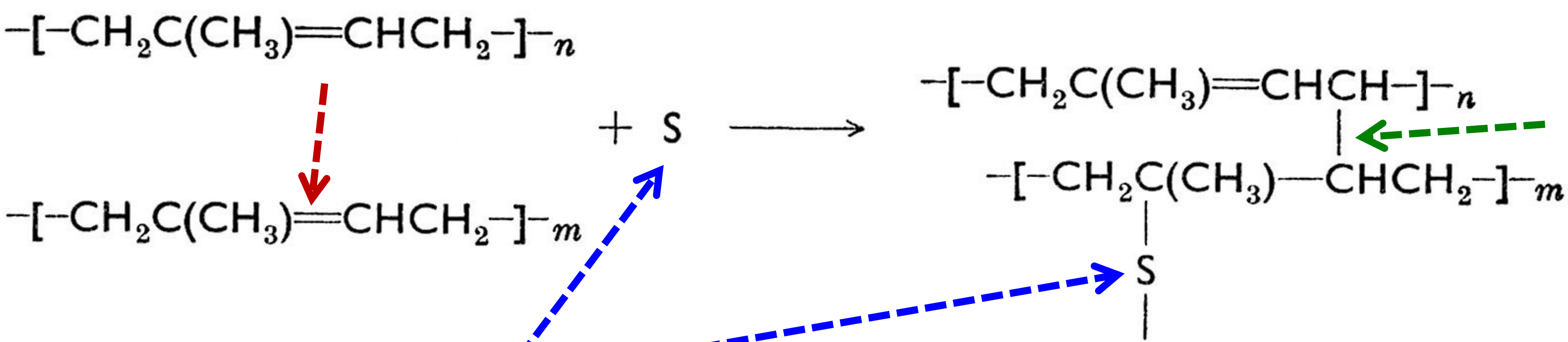
Vicinal crosslinks = CROSSLINKING at neighbouring Carbons

FIG. 2. — Various chemical structures encountered in accelerated sulfur vulcanization. (a) sulfur crosslinks (y = 1 mono, y = 2 di and y >2 polysulfide crosslinks); (b) carbon-carbon crosslink; (c) pendant accelerator sulfide where X is the accelerator moiety; (d) cyclic sulfide; and (e) vicinal crosslinks that have junction points at common olefin chains and constitute only *one* elastically effective crosslink. Figure adapted from Nieuwenhuizen *et al.*[3]

THE ONLY THIS CROSSLINKING FORMS THE ELASTIC BEHAVIOUR

VULKANISATION NATURAL RUBBER
By elementary Sulphur 3

It is considered also the Bond C-C, on which one Double bond „was employed“, but it is NOT USSUAL!



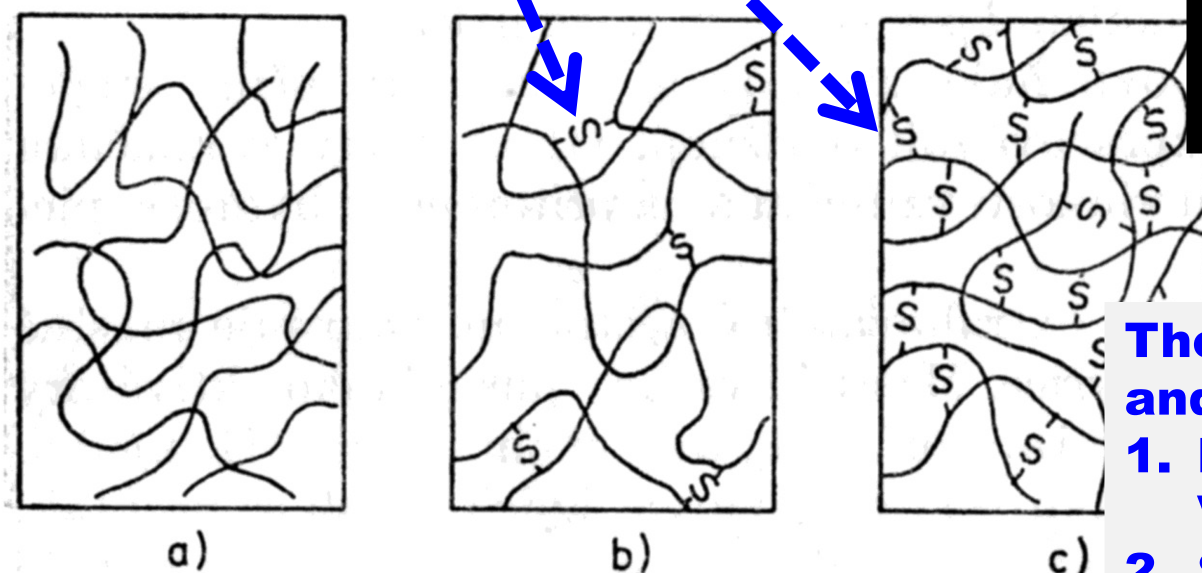
SULPHUR as the Atom is written as a Simplification only!

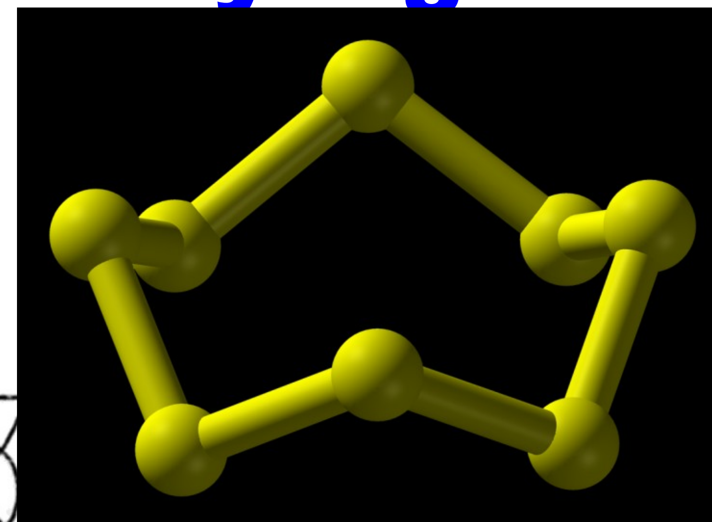
You can meet so many various Schemes of the **VULKANIZATION .** *, The Schemes 2 and 3 are PROBABLY the most realistic.*

VULKANISATION NATURAL RUBBER

By elementary Sulphur 4

Sulphur is not one Atom, but CHAIN OF ATOMS, usually eight



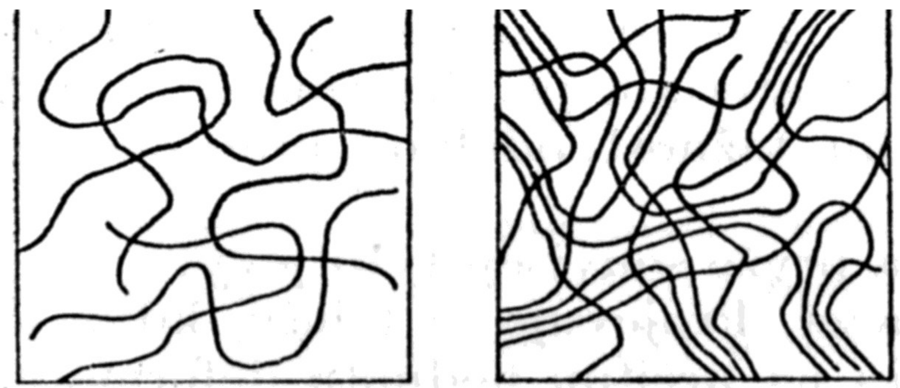


The Structure of the Rubber and Vulcanise Rubber:

1. Rubber before Vulcanisation
2. Soft Vulcanised Rubber
3. Hard Vulcanised Rubber

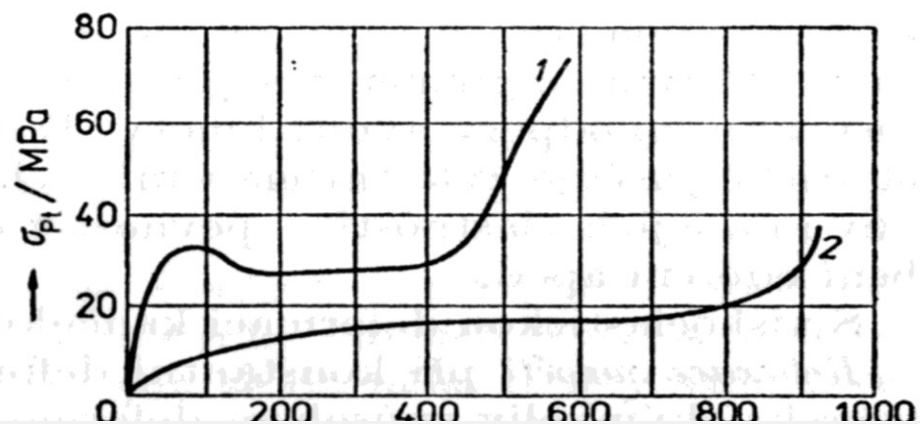
CRYSTALLISATION OF NATURAL RUBBER

- The Macromolecules having the Long Chains, e.g. **NATURAL RUBBER**, have good possibility to be extended by hundreds percent.
- The Development of the Crystallisation is clearly shown at the Stress – Strain Curves.
- The Molecules are self-aligning after initial Deformation and in this Stage of the Deformation Curve is the only low Load sufficient to do high Deformation.
- This Deformation and also Crystallinity is lost after Breakage of the Sample or Releasing the Mechanical Stress.



a) b)

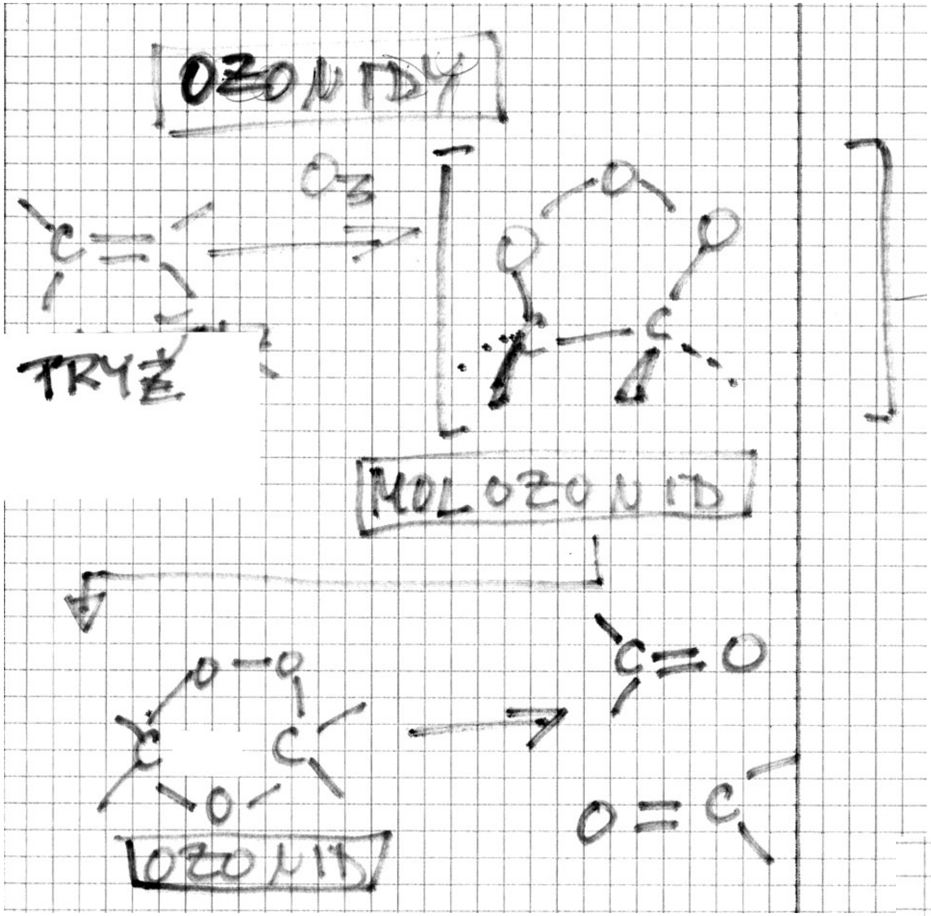
a) Unoriented amorphous Structure
b) ORIENTED semi-crystalline Structure



Deformation Curves
1. Polyamide
2. NATURAL RUBBER

σ_{Pt} – stress, ε – relative deformation

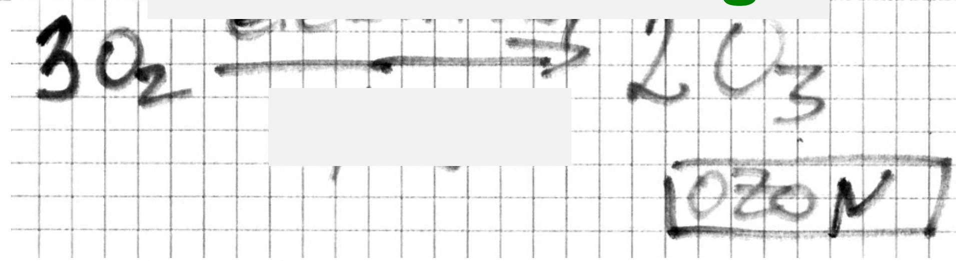
Degradation of Rubber by Ozone



Ozone is the Natural part the atmosphere and is formed e.g. at Lighting (electric discharge in the atmosphere)

It formed also by artificial procedure

electric discharge



VULKANISATION NATURAL RUBBER
By Sulphur Compounds

Charles GOODYEAR (1839) – the INVENTOR

SULPHUR CONTENT IS:

- **1 – 5 % w/w (soft Vulcanized RUBBER)**
- **Up to 15 – 30 % w/w (HARD Vulcanized RUBBER, e.g. Ebonite)**

Product	Content of RUBBER (% w/w)
Transparent Vulcanized Rubber, Dipped rubber, Rubber thread	Over 80
Mixtures for Tires and Tubes (both Tread and Casing) – Car,Bike, Motocycle…. Foamed Rubber, Cables electro	50 – 80
Rubber shoes, Conveyor belts, Mechanical Rubber Goods (e..g. Holes, Waveguide, Rubber bush	30 – 50
Accumulator (Battery) casing, Flooring, Sealing (Gasket)	< 30

The other % w/w up to 100 % w/w are Additives!

Sulphur Content more than 30 % w/w and more

EBONITE

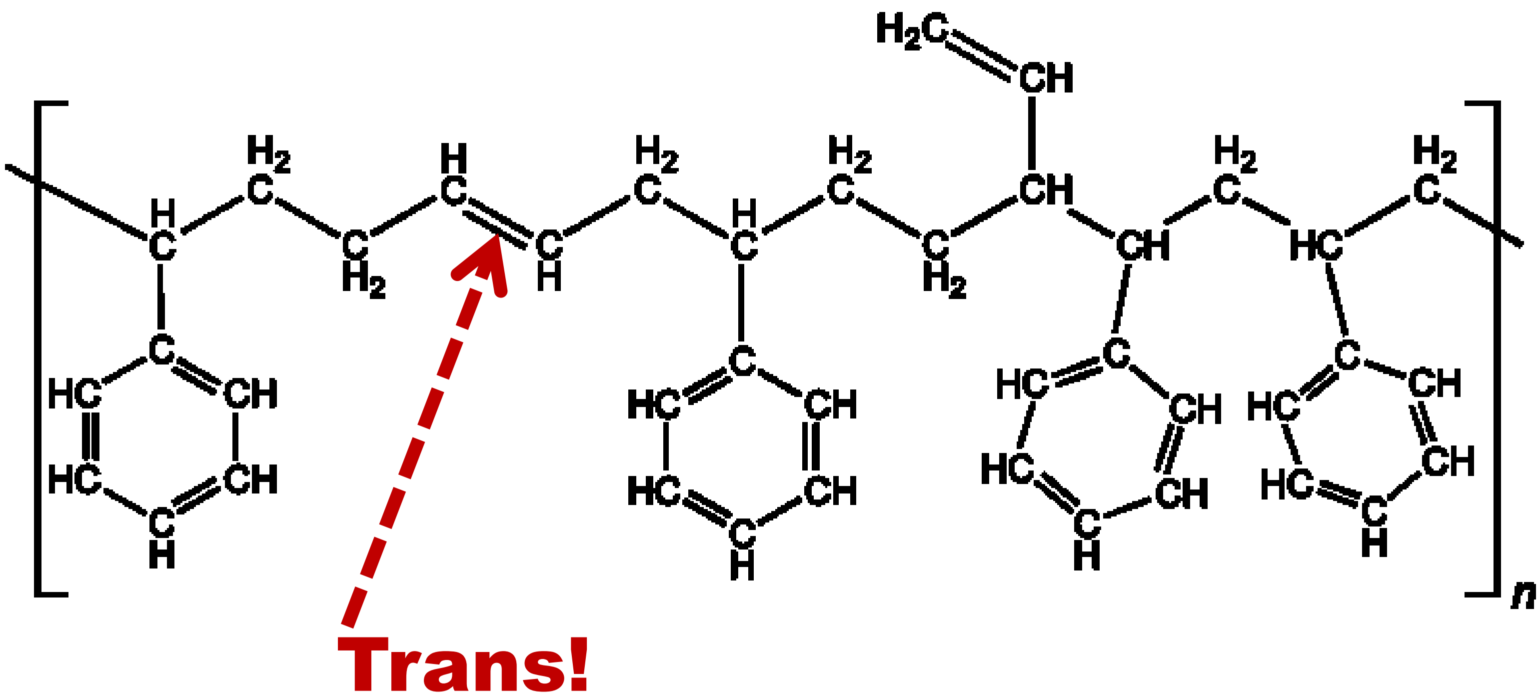
Hard rubber was used in the cases of automobile batteries for years, thus establishing black as their traditional colour even long after stronger modern plastics like polypropylene were substituted.

It is also commonly used in physics classrooms to demonstrate static electricity because it is at or near the negative end of the triboelectric series.

NATURAL RUBBER versus SYNTHETIC RUBBER

- The Effort to develop various types of the Synthetic Rubber takes more than 100 already and are successful.
- Butadiene-styrene Rubber is probably the most widespread synthetic Rubber type
- **NATURAL RUBBER is the Irreplaceable up to now**
- POLYMERISATION of isoprene is not giving the cis-isomer only > it can NOT replace the **NATURAL RUBBER**
- The Mixtures **NATURAL** & **SYNTHETIC RUBBER** enable the Optimisation of the desired Properties

Butadiene – styrene Rubber



KRALEX® 1500

is a standard grade of styrene butadiene rubber. It is produced by a technology of cold emulsion polymerization based on soaps of rosin acids and contains 23.5% of chemically bonded styrene. It is coagulated by a system of acid and organic coagulant, does not contain extender oil and is stabilized by staining antioxidant. KRALEX® 1500 is appropriate for rubber compounds used in the production of car tires and inner tubes, conveyor belts, footwear, cables, hosepipes and various technical rubber articles.

It is not approved for production of rubber articles coming into contact with foods or drinking water.

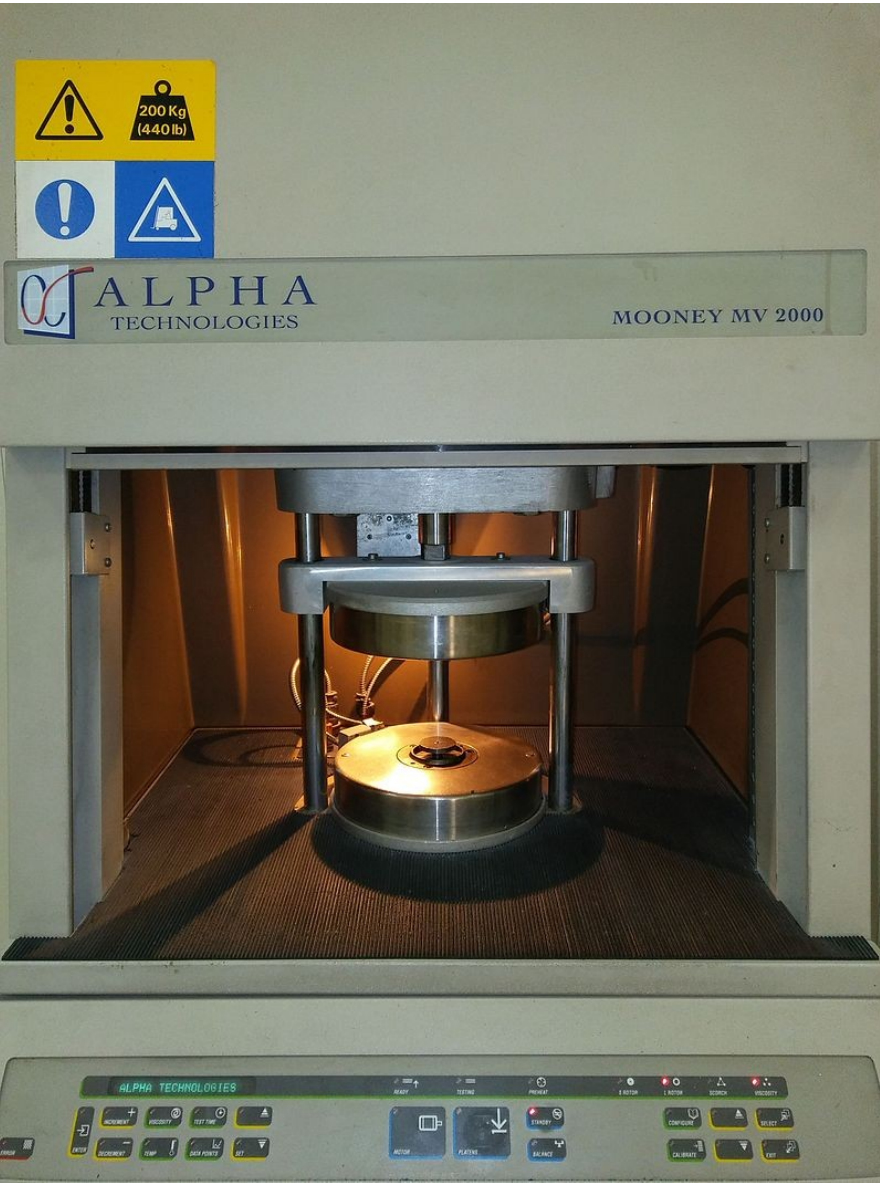
Physical Properties	Metric	English	Comments
Volatiles	<= 0.75 %	<= 0.75 %	ASTM D5668
Mooney Viscosity	44 - 54 @Temperature 100 °C	44 - 54 @Temperature 212 °F	(1+4); ASTM D1646
Ash	<= 0.40 %	<= 0.40 %	ASTM D5667

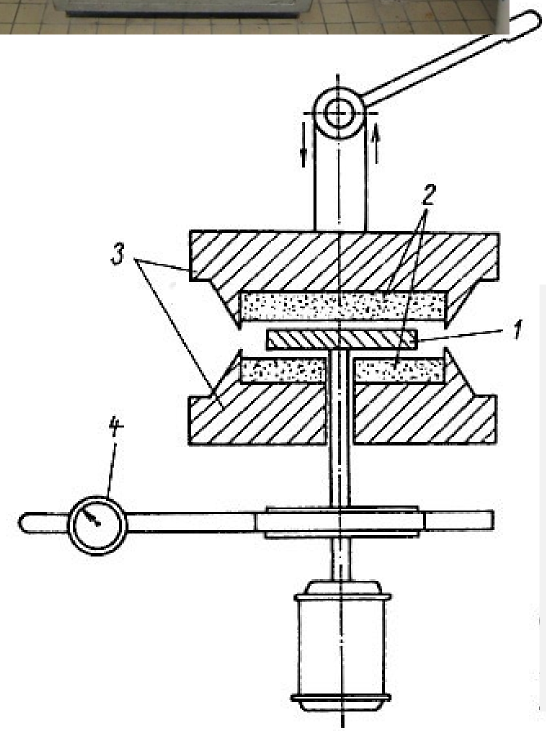
Chemical Properties	Metric	English	Comments
Acid Value	5.0 - 7.5	5.0 - 7.5	ASTM D5774
Styrene Content	23.5 %	23.5 %	ASTM D5775

Mechanical Properties	Metric	English	Comments
Tensile Strength, Ultimate	23.0 MPa	3340 psi	35'/145°C; ASTM D412
Elongation at Break	400 %	400 %	35'/145°C; ASTM D412
300% Modulus	13.0 - 19.0 MPa	1890 - 2760 psi	35'/145°C; ASTM D412

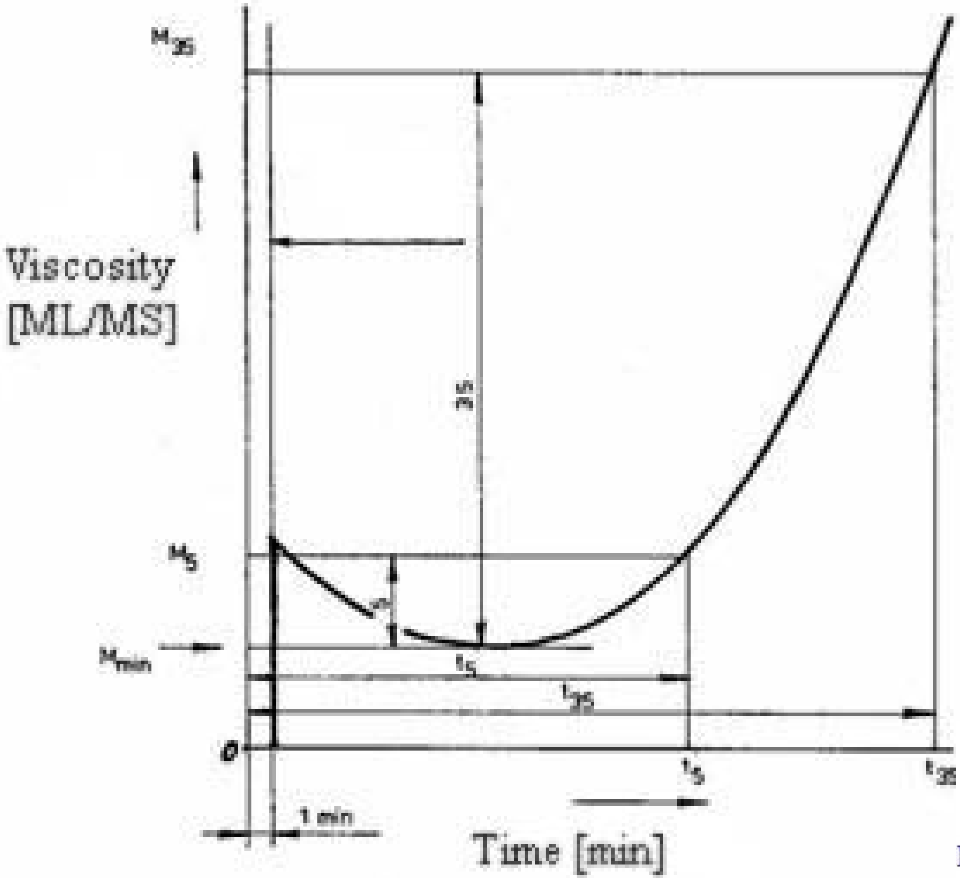
Descriptive Properties			
50% of Vulcanization t' 50 (min.)	6.5-10.5		ASTM D5289
Antioxidant Grade	Staining		
Compound Safety ts 1 (min.)	2.2-4.0		ASTM D5289
Maximal Moment (dNm)	19-22		ASTM D5289
Minimal Moment (dNm)	2.1-2.8		ASTM D5289
Optimal Vulcanization t' 90 (min.)	12-17		ASTM D5289
Soaps content (%)	<= 0.3		

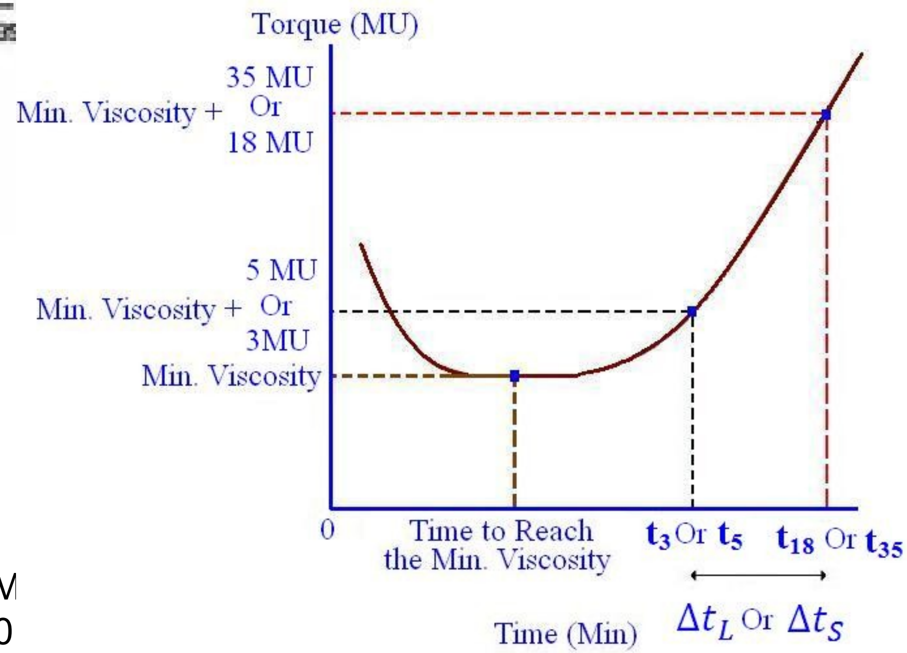
Viscosity Mooney – Explanation and Measurement





1. **Rotor**
2. **Tested Material**
3. **Mould**
4. **Registration Device**

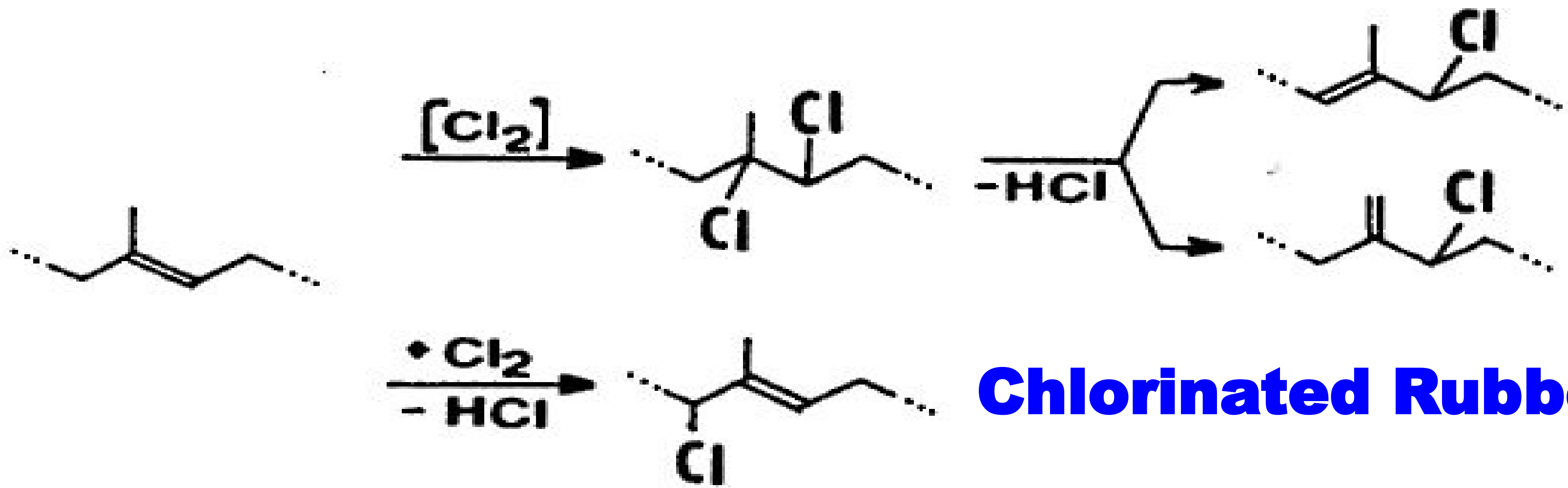

Viscosity
[ML/MS]
M_{35}
M_5
M_{min}
35
5
t_5
t_{35}
0
1 min
Time [min]


Torque (MU)
35 MU
Min. Viscosity + Or
18 MU
5 MU
Min. Viscosity + Or
3MU
Min. Viscosity
0
Time to Reach
the Min. Viscosity
t_3 Or t_5
t_{18} Or t_{35}
Δt_L Or Δt_S
Time (Min)

The rubber compound, including the vulcanizing system, is shaped on the mill as 6–8 mm thick sheets. Round-shaped samples with 45 mm diameter are cut from the sheets. The samples are pierced in the middle in order to allow the rotor shaft to pass. Before the beginning of the measurement, the instrument is heated up to 118 degree C. After the sample is introduced, it takes a minute for the sample to reach the thermal equilibrium, and then the rotor is started.
The value of Mooney viscosity decreases at the beginning, due to the decrease of the compound viscosity as temperature rises. After about 4 min, a minimum value is reached, which stays constant for a while. This value is indicated as MV. After a certain period of time, vulcanization starts and the Mooney viscosity increases.
The following values are indicated on the obtained curve:
minimum viscosity MV; scorch time (t5) - the time interval (measured from rotor start) corresponding to a viscosity increase of 5 Mooney units over MV, measured at rotor start. The t5 value indicates the prevulcanization tendency of the compound. The larger t5 is, the lower the prevulcanization tendency, and, therefore, the rubber compound can be more reliably processed on mill, calender or extruder. [3] vulcanization time (t35) - the time interval (measured from rotor start) corresponding to a viscosity increase of 35 units over the MV value. vulcanization index - Dt30 = t35 - t5 - provides indications about the vulcanizing ability of a rubber compound. A compound with a low vulcanization index, cures more rapidly than a compound with a higher vulcanization index. optimum vulcanization time at the experimental temperature employed (top).

Modification of the NATURAL RUBBER 1

The MOST COMMON IS CHLORINATION by elementary Chlorine



Chlorinated Rubber

<u>It is here Demonstrated at:</u>

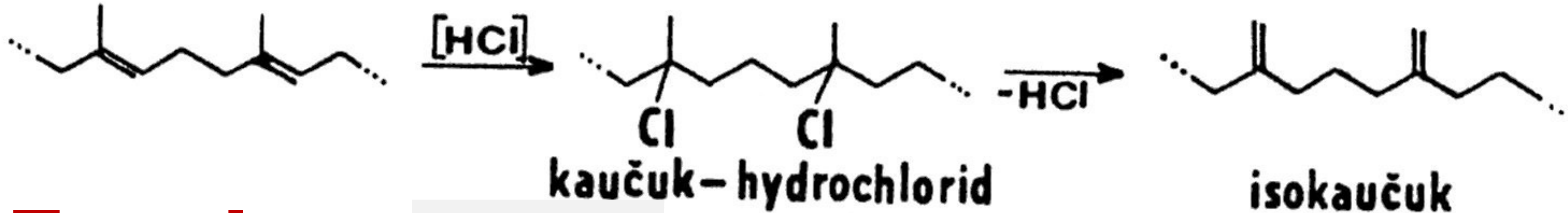
Trans isomer = Gutta-percha

The double Bonds are here maintained > Kept the Possibility of the Vulcanisation

Modification of the NATURAL RUBBER 2 & 3

The LESS COMMON PPROCEDURES

2

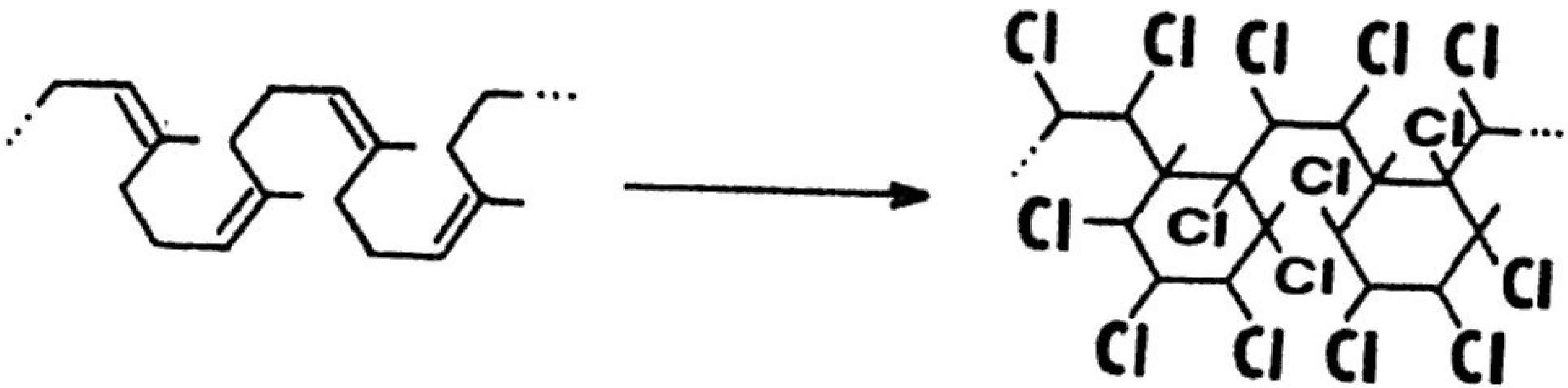


Trans!

RUBBER

iso-RUBBER

3



Acid catalyzed addition of H^+ on the DOUBLE BONDS, isomerisation and cyclization > CYCLORUBBER

Modification of the NATURAL RUBBER (NOT VULCANIZED RUBBER)

Type	Properties	Use
Chlorinated Rubber (chlorine content up to 60 % w/w)	Film forming, better chemical stability than **NATURAL RUBBER** , decreased flammability, SOLUBILITY IN ORGANIC SOLVENTS	**Coating compositions (chemical works, e.g.** Starch factory, Sugar factory etc.**)**, Glues
Rubber hydrochloride (modification by gaseous HCl) (chlorine content up to 35 % w/w)	Film forming, better chemical stability than **NATURAL RUBBER**, bur worse than **Chlorinated Rubber,** decreased flammability, SOLUBILITY IN ORGANIC SOLVENTS	Films, Sizing for Textile industry

Chlorinated Rubber is probably the most important
MODIFIED **NATURAL RUBBER**

Modification of the NATURAL RUBBER (NOT VULCANIZED RUBBER)

Type	Properties	Use
CYCLORUBBER	Film forming, SOLUBILITY IN ORGANIC SOLVENTS	Films, Sizing for Textile industry, paper, lacquers, glues, printing inks

Modification of the NATURAL RUBBER
(NOT VULCANIZED RUBBER)
What interesting did I personally

Coating compositions (Starch factory in Brno town)

I have worked in the Maintenance department, getting ready for the Starch season (Beginning of the Potato processing to Starch). I have painted the processing devices inside.

EXPERIENCE: Hygiene problems, Vapours of Solvent, Shortage of fresh Air

Vulcanized Rubber and Antiques conservator - restorer

- **The response need also the Subjects made of Rubber already!**
- **My former Student turned to me for Help in his Task in the Technical Museum in Brno**
- **PROBLEM:**
- **Gas mask restoration dated in the 1. World war**
- **Gas mask restoration dated in the last 30^{rd} years**

POLYTERPENES and
Antiques conservator - restorer

- **Gutta-percha** ***> isolation of the electric conductor > The first submarine TELEPHONE CABLE EUROPE - AMERICA***
- ***BALATA > another interesting Plant,*** a similar and cheaper natural material called *balatá* is often used in gutta-percha's place. The two materials are almost identical, and *balatá* is often called *gutta-balatá*.