Textile Chemistry

5 Natural fibres

Jakub Wiener

TEXTILE CHEMISTRY

Cellulose fibers

Vegatable wool

Cellulose is the structural component of the primary cell wall of green plants.

Cellulose is the most common organic compound on Earth.

About 33 percent of all plant matter is cellulose

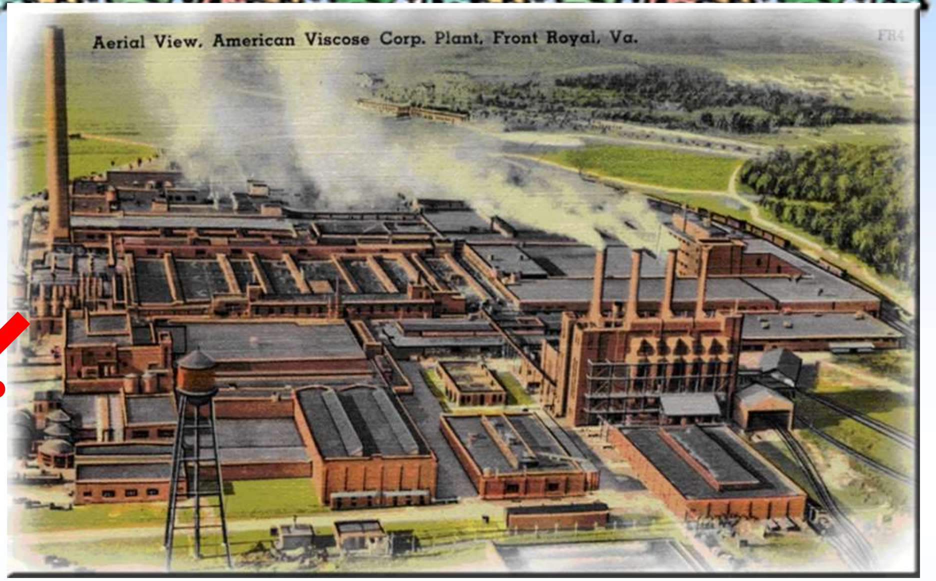
Natural cellulose fibers

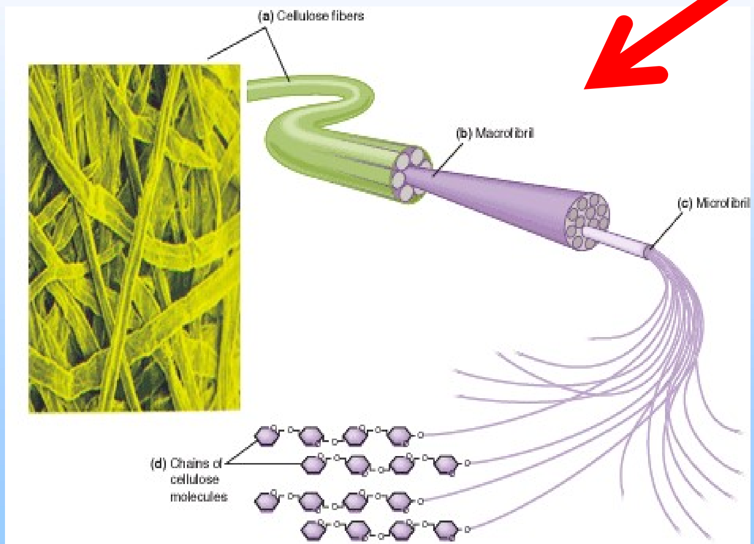
Natural cellulose fibers

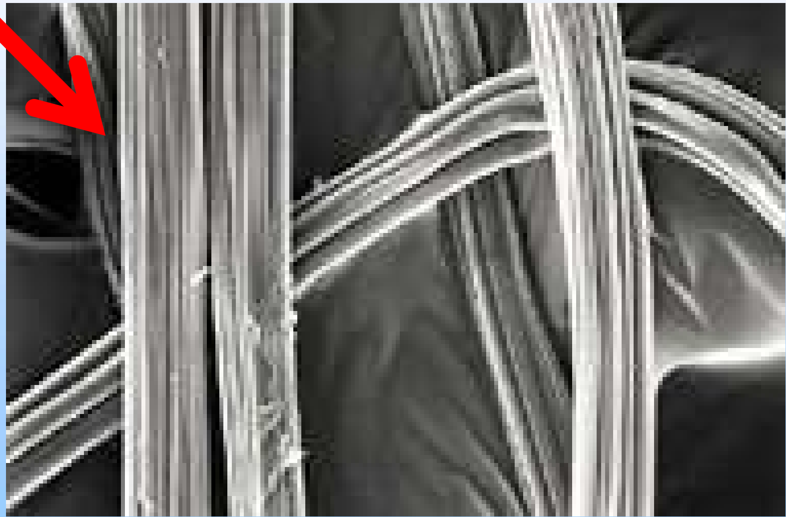
- -Cotton
- -Sisal
- -Hemp
- -Flax
- -Ramie
- -Jute

Different plants, but the same cellulose !!!

Viscose fibers – regenerated cell.

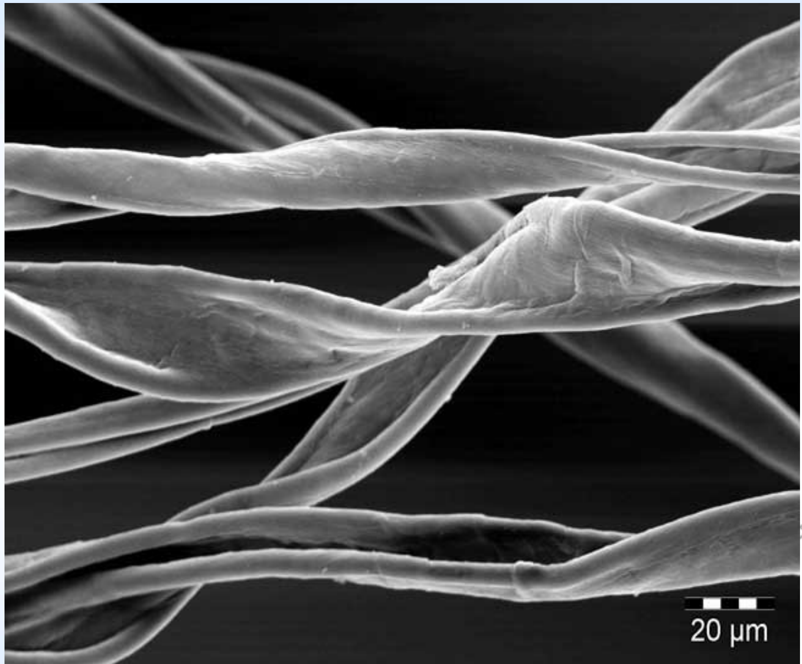


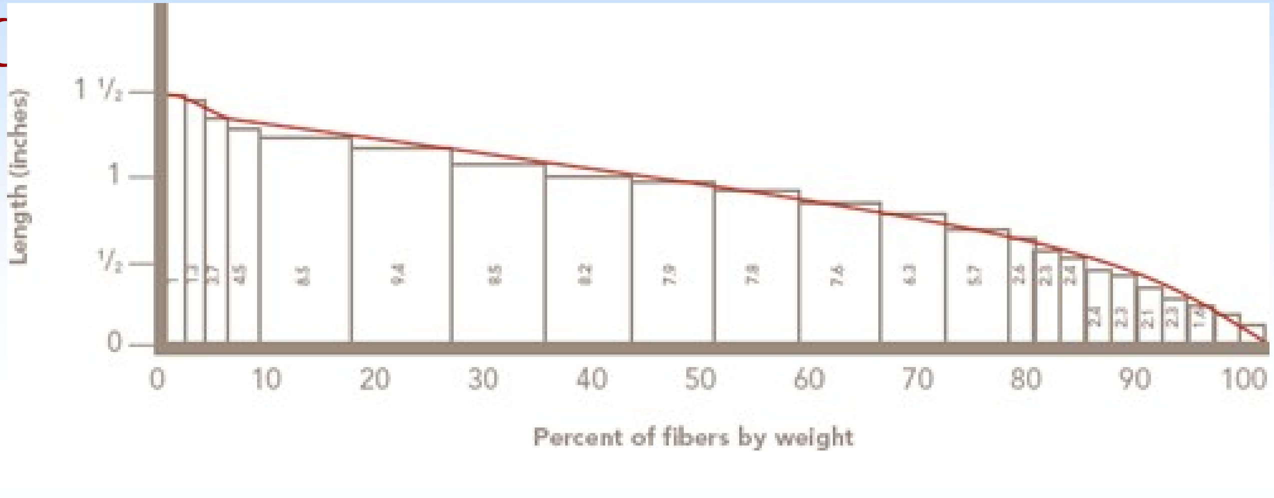


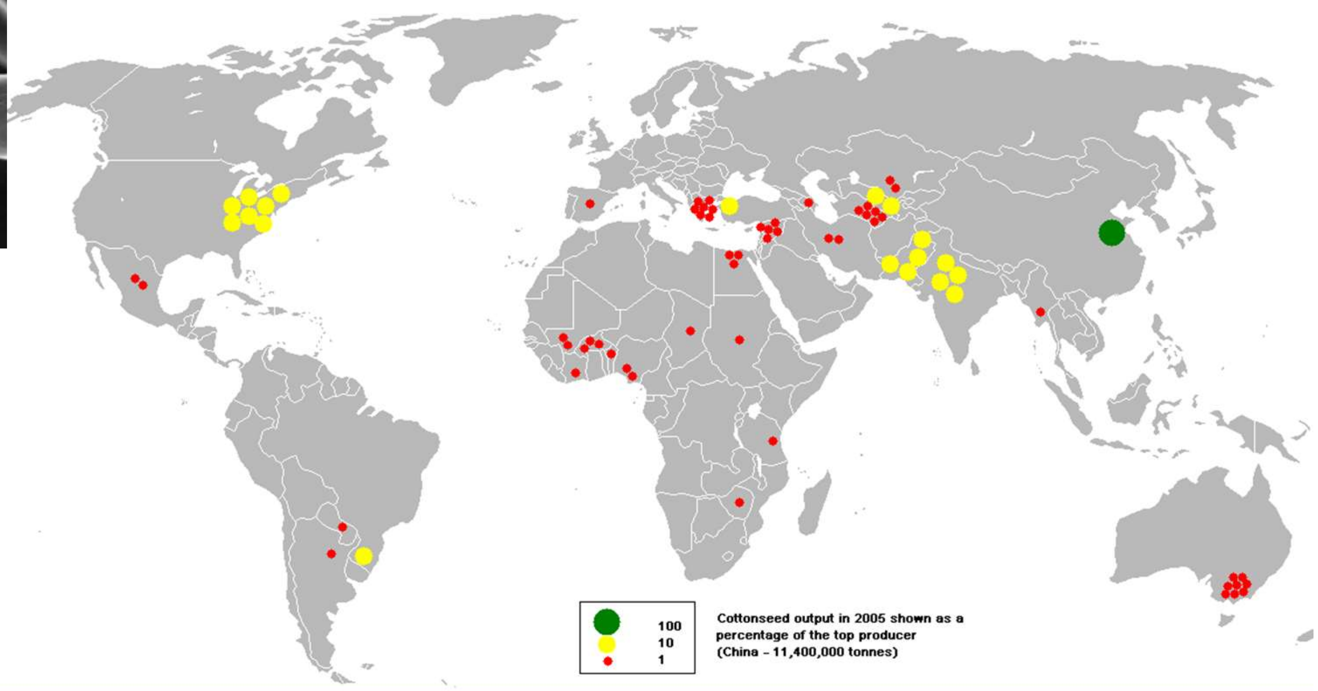


Natural cellulose fibers

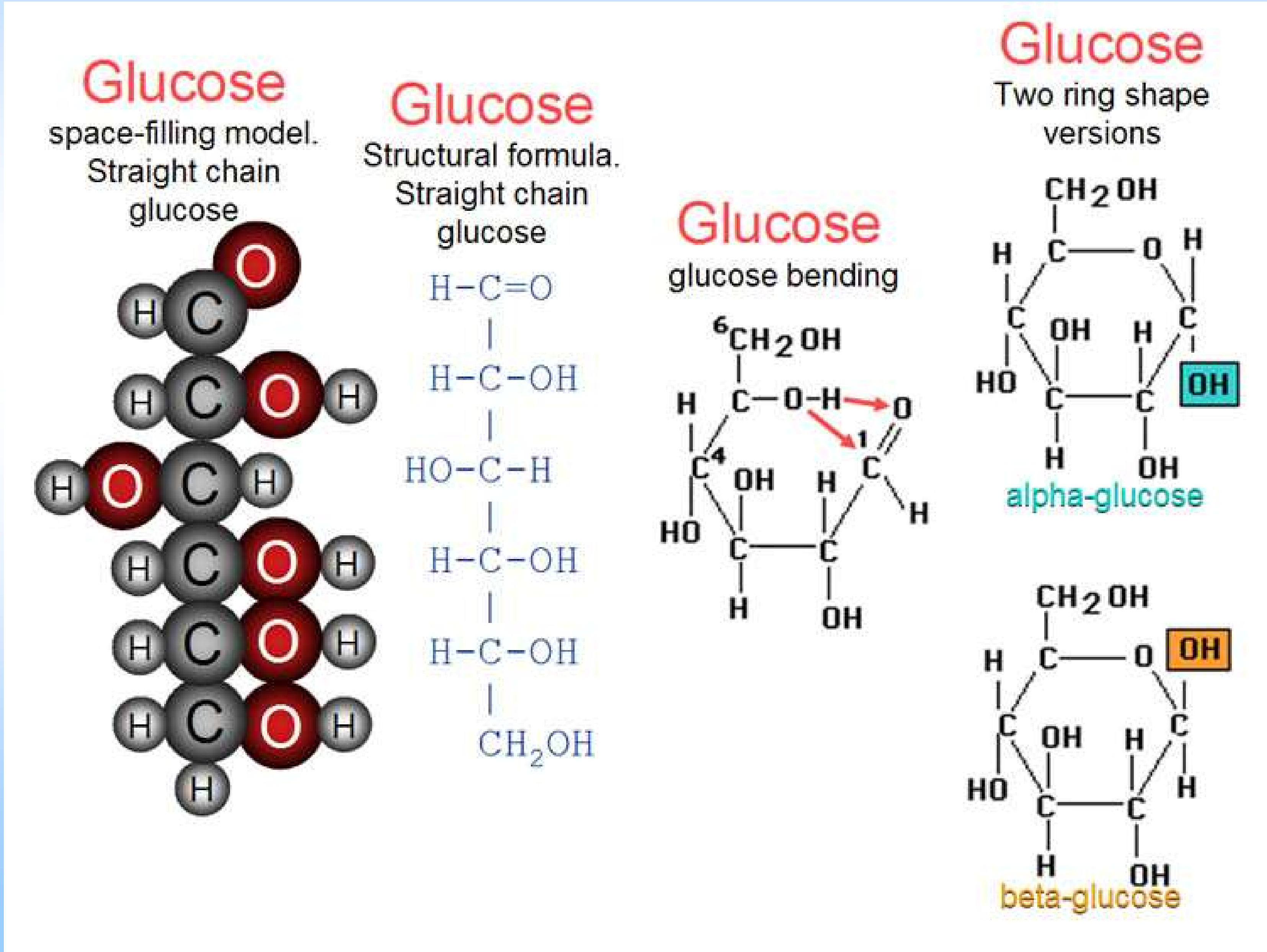
Natural cellulose fibers - C



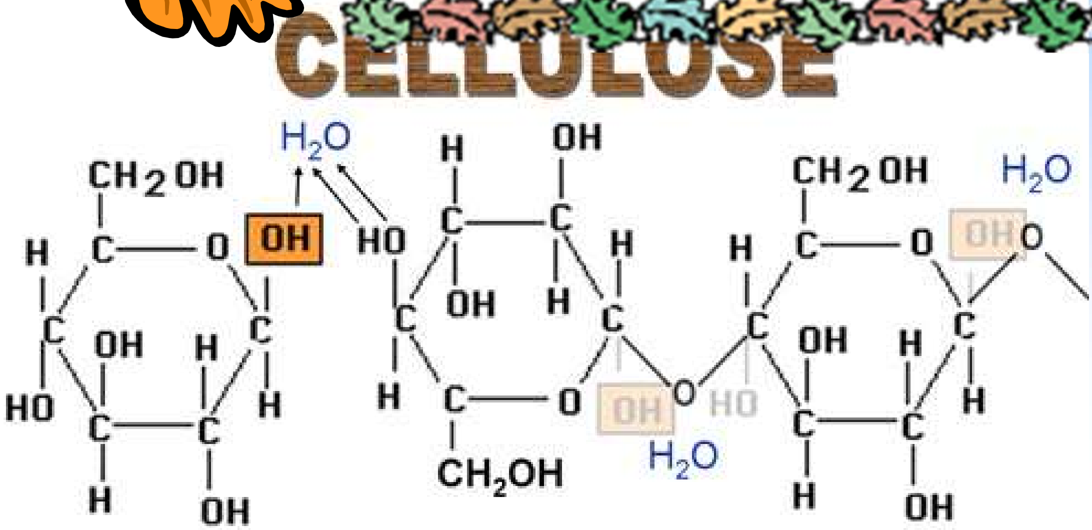


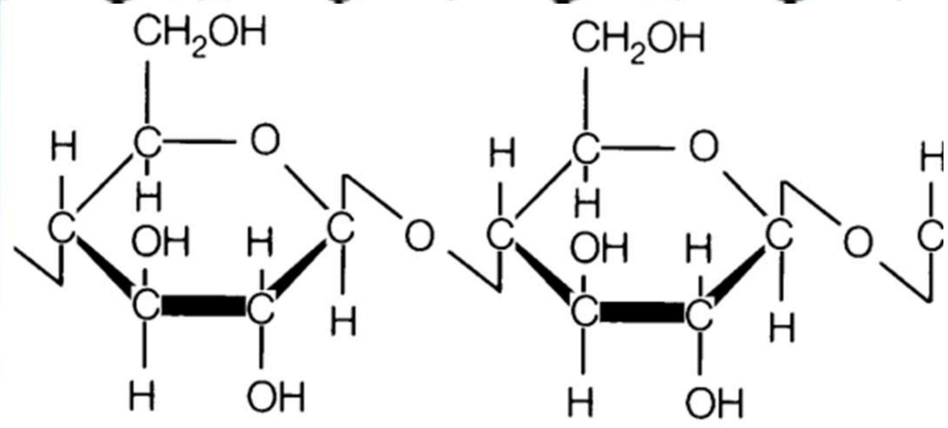


Glucose

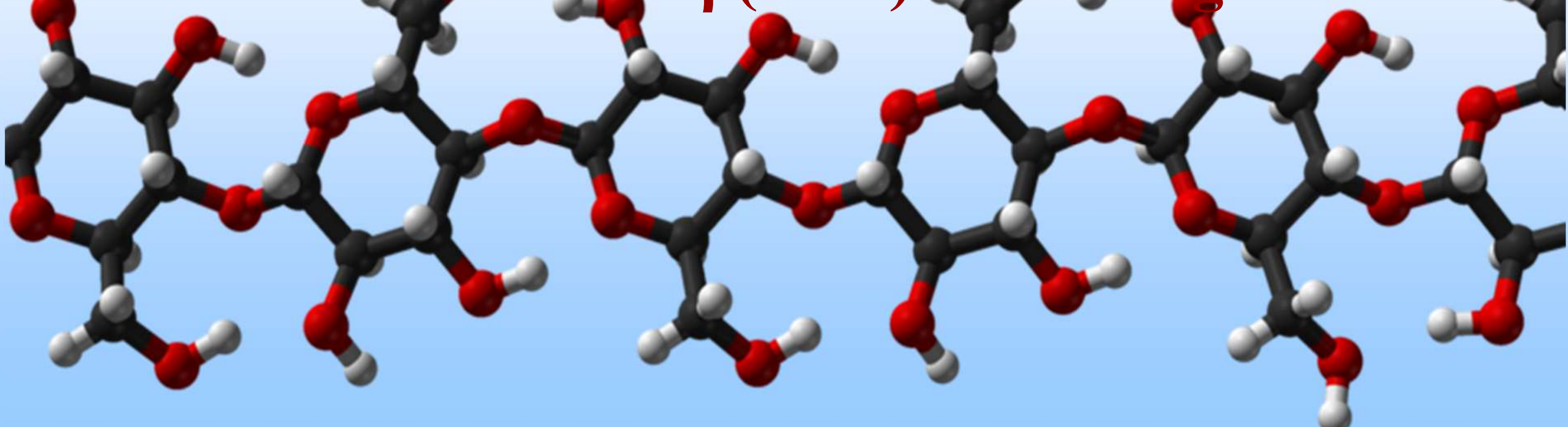

Glucose
space-filling model.
Straight chain
glucose
Glucose
Structural formula.
Straight chain
glucose
H−C=O
H−C−OH
HO−C−H
H−C−OH
H−C−OH
CH2OH
Glucose
glucose bending
Glucose
Two ring shape
versions
alpha-glucose
beta-glucose

Cellulose





Cellulose is an organic compound with the formula ($C_6H_{10}O_5$)$_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units.

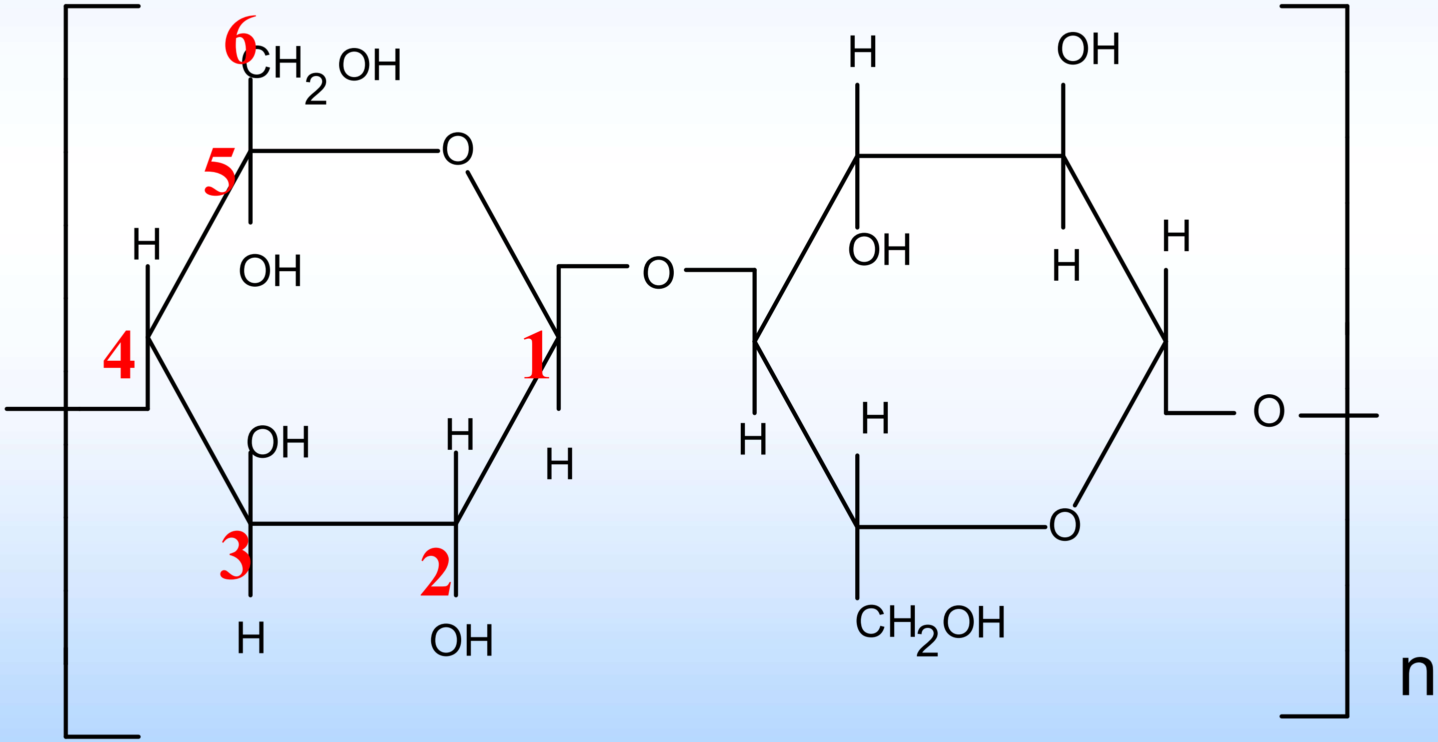


Cellulose

Cotton: n=2000

x

Viscose: n=500

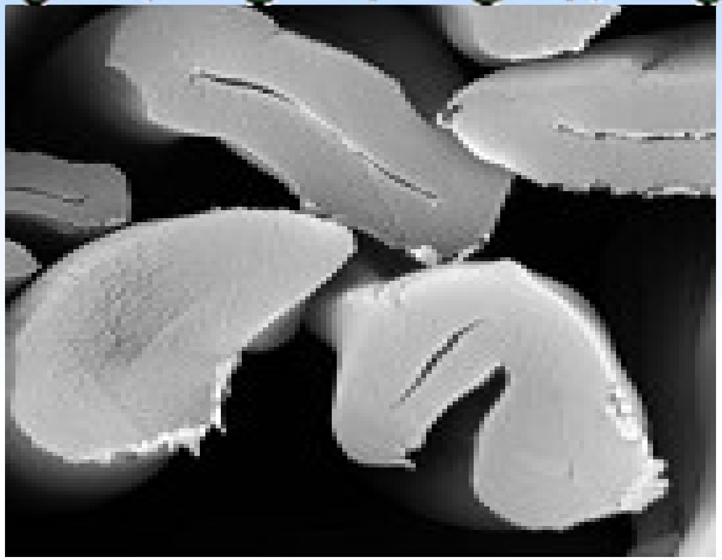


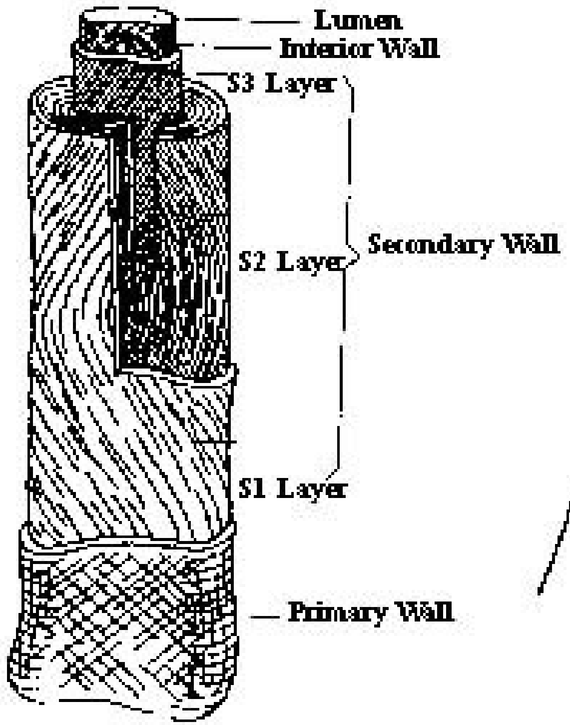
Carbon „6“ – primary hydroxyl group

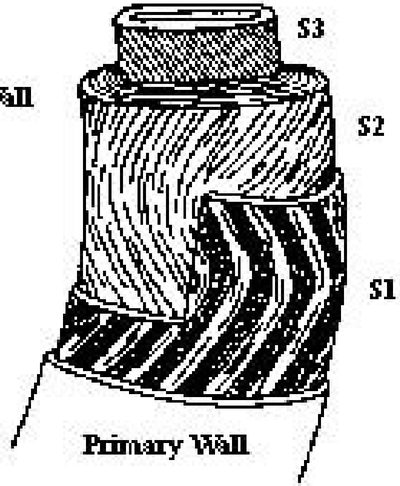
Carbon „2“ and „3“ – secondary hydroxyl group

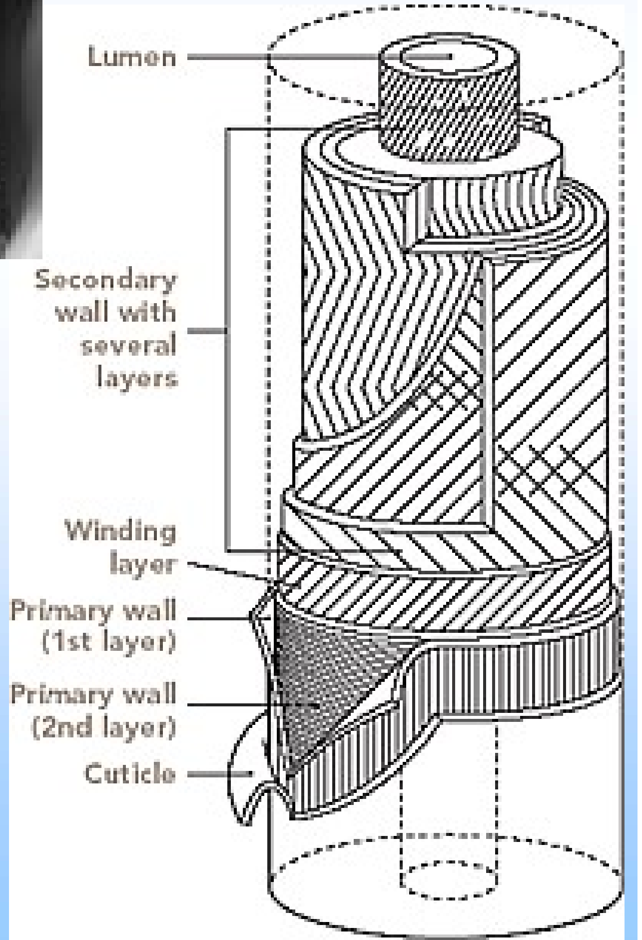
Structure of cotton fiber

- complicated structure – many layers
- hydrophobic surface (raw cotton)









Structure of cotton fiber

The „Wax layer“ is a hydrophobil protection of fiber. Noncellulosic chemiclas: waxes, fats, proteins, pectins… Will be removed by scouring.

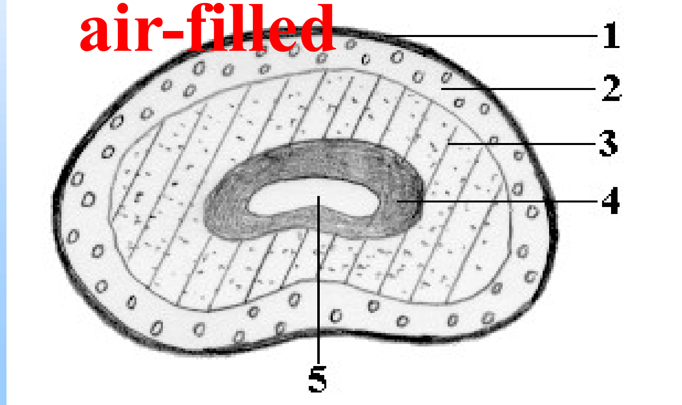
The “Primary wall” is the original thin cell wall - cellulose

The “Secondary wall” consists of concentric layers of cellulose, which constitute the main portion of the cotton fiber. After the fiber has attained its maximum diameter, new layers of cellulose are added to form the secondary wall.

The “Lumen wall” separates the secondary wall from the lumen and appears to be more

Bean-shaped cross section through a cotton fiber

1 - Wax layer
2 - Primary wall
3 - Secondary wall
4 - Lumen wall
5 - Lumen (cavity), air-filled



Chemical composition

<u>Average cotton composition:</u>

86 – 96% cellulose,
2-3% peptides,
0,4 - 1,2% pectin,
0,4 – 0,8% fats and waxes,
1 – 1,8% minerals,
6 – 8,5% water (humidity),
pigments

Depends on the origin of fibers (place of growing, weather, maternity of fibers...)

Depends on the pretreatment of cotton (bleaching, scouring...)

Basic chemical properties of cellulose

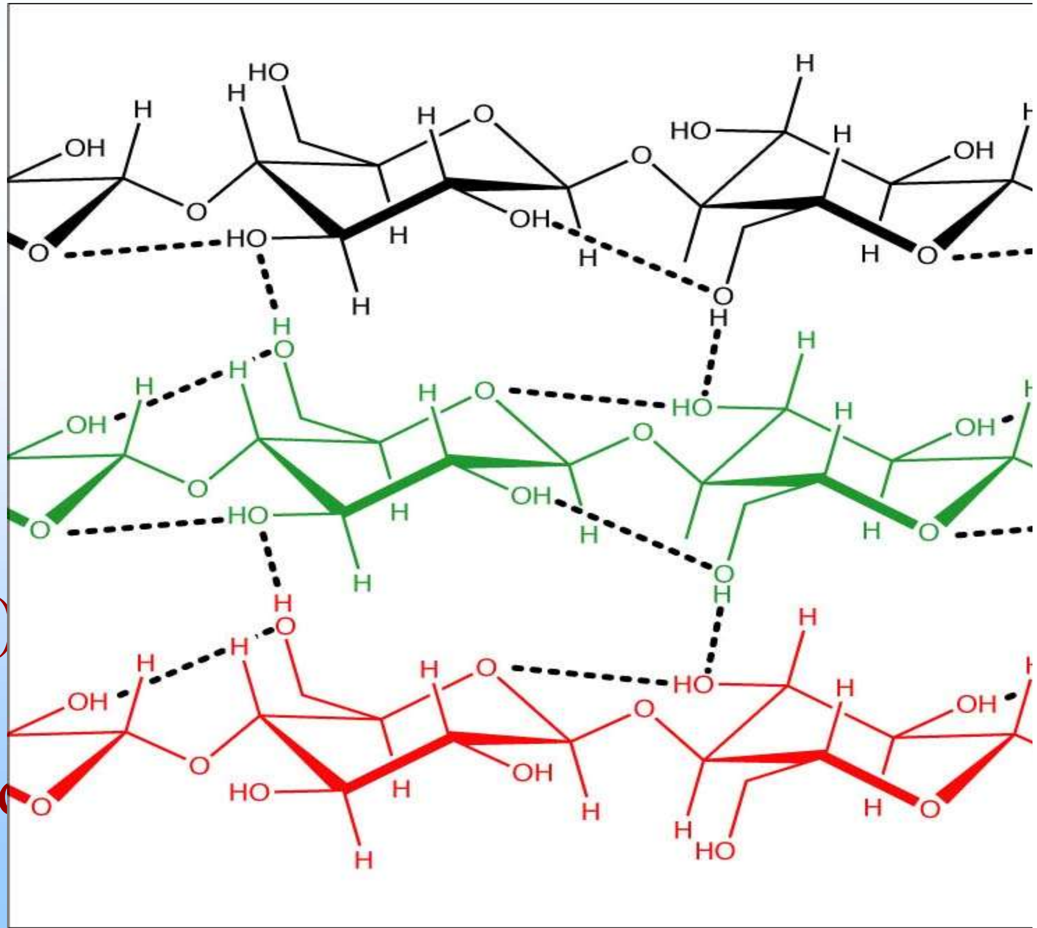
Between –OH groups are Hydrogen bond = intramolecular (between OH groups of one molecule) and itermolecular (between to molecules) forces ... Crystalisation of cellulose

Intermolecular ... Low solubility of celulose in solvents

Reactivity of cellulose is low.

Potential problem: lenght of macromolecule (polymeration degree)

Damage is easy if are the fiber swelled – the structure is open for chemicals.



Cellulose – basic properties

Cellulose fibers can be damaged by:

Acids

Oxidative chemicals

+Alkali solutions **(only at high temperature and together with air oxygen)**

All these chemicals degradate cellulose polymer – the function groups in cellulose are changed and the polymerarization degree is reduced – mechanical effects: reduction of mechanical properties (low strength) and the fibers are more sensitive to future damage

Acid damage

<u>Damage by (sensitive to):</u>

- **<u>Acides</u>**

<u>Strong – HCl, H2SO4</u>

<u>Weak – CH3COOH</u>

$$K_a = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$$

The stronger of two acids will have a higher K_a than the weaker acid; the ratio of hydrogen ions to acid will be higher for the stronger acid as the stronger acid has a greater tendency to lose its proton.

<u>+ acid salts</u> (NH_4Cl, $MgCl_2$) (created by weak alkali and strong acid)

– acid solution, hydrolyses

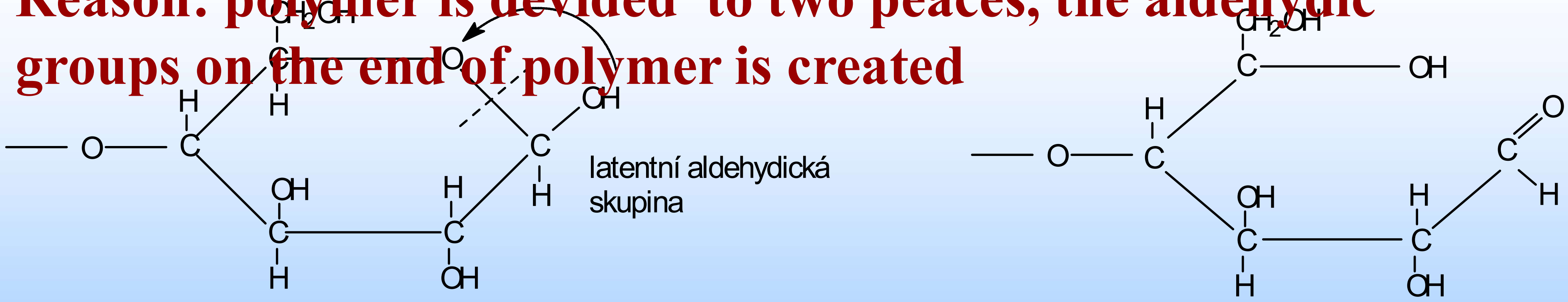
Acid damage

Hydrocellulose

by acid treatment … depolymerization = hydrolitic reaction

Result: new aldehydic groups in cellulose = new reduction properties of cellulose

Reason: polymer is devided to two peaces, the aldehydic groups on the end of polymer is created



Testing of hydrolitical (acid) damage: by testing of reductive properties of cellulose - tipicall by Fehling method

Hydrolitic damage of cotton accorging Fehlings method

Fehling's solution
(copper (II) sulfate pentahydrate CuSO4.5H2O, **distilled water, potassium sodium tartrate and Sodium hydroxide NaOH)**

Procedure:

cotton and Fehling solution – boiling !!!

Cu_2O is produced by reaction in stoichiometric ratio to glucose (aldehyd groups)

$$R\text{-}CHO + 2\,Cu^{++} + 5\,OH^{-} \longrightarrow R\text{-}COO^{-} + Cu_2O + 3\,H_2O$$

Quantity of produced Cu2O is equal to quantity of

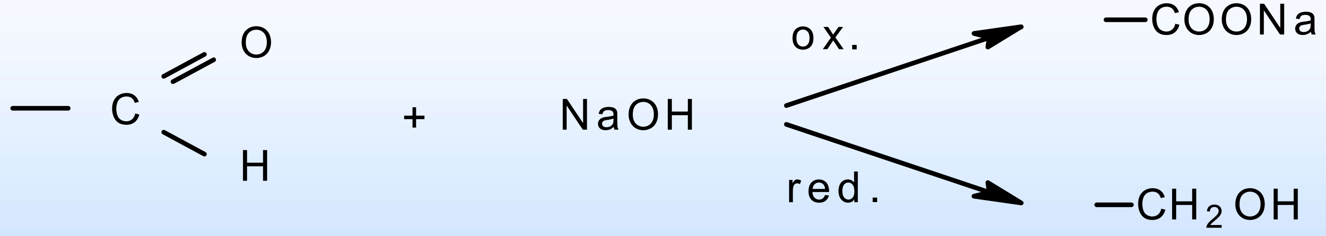
Hydrocellulose

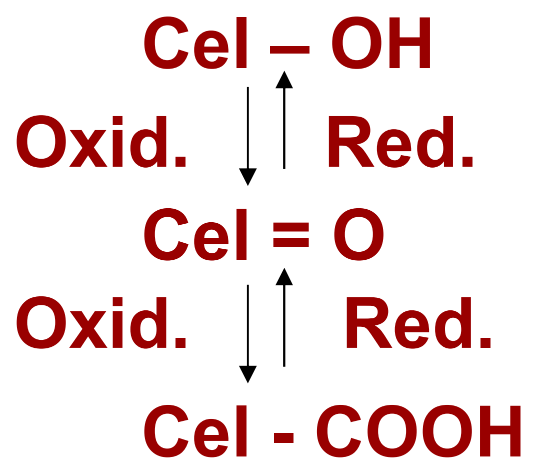
<u>**Hydrocellulose can lost the reductive properties by the treatment in alkali solution at high temperature**</u>

Disproportionation of aldehydic group (Cannizar´s reaction)

- Aldehydic group is unstable in alkali solution – will by oxidized to carboxylic croup easily or reducted

group





Carboxylic and hydroxy groups has not any reductive properties – Fehling test will be not positive !!!

<u>**The aldehydic groups can be oxidized to carboxylic groups by air oxygen in alkali solution at high temperature**</u>

Oxidative damage

Oxidation create on fibers aldehydic and carboxylic groups

- **<u>Oxycellulose</u>**
- **According the strength of oxidation, time, temperature and pH – aldehydic or carboxylic groups**
- **Dividing of polymer in position between carbons 1 and 4 – reduce of polymerization degree**

Cel – OH

Oxid. ↓ ↑ Red.

Cel = O

Oxid. ↓ ↑ Red.

Cel - COOH

Reason: NaClO, O2, H2O2... (bleaching and alkali scouring)

Testing:

1) Fehling method – testing of aldehydic groups

2) Testing of sorption properties of COOH – sorption of dyes or metal ions – problems by dyeing – damaged places have different affinity of dye

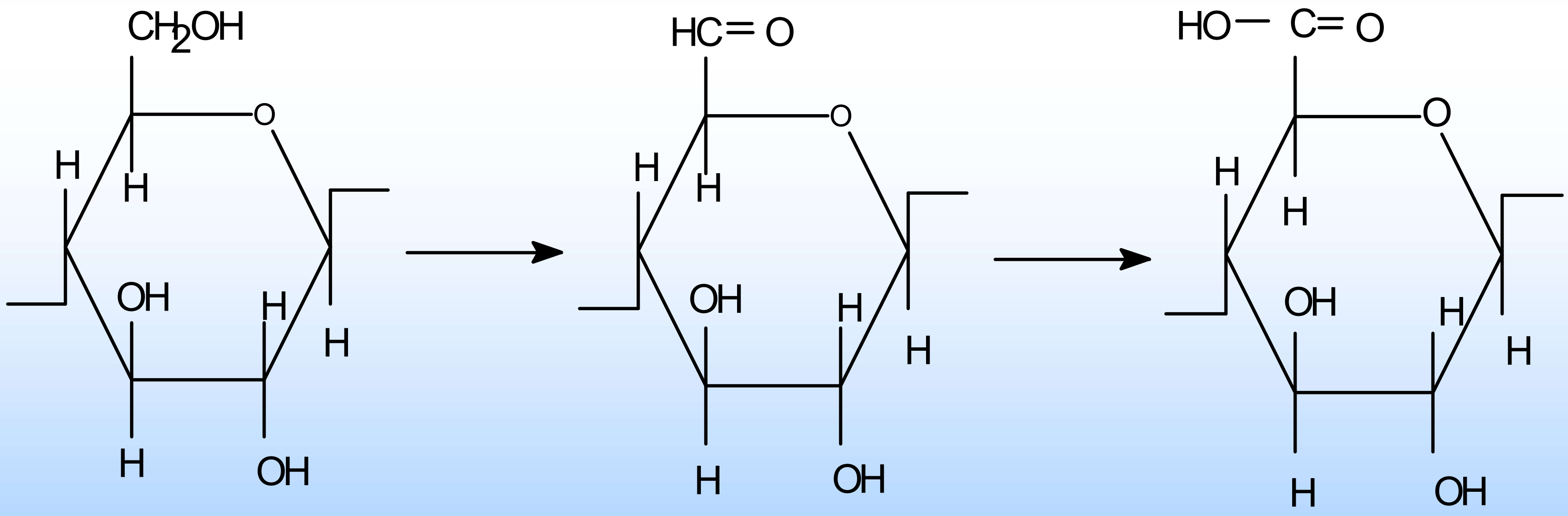
3) Solubility in solvents – damaged cotton is more soluble – more chemical groups, shorter polymer chains

Every Bleaching is a source of oxicellulose (chemical damage of fibers)

Oxidative damage of cellulose

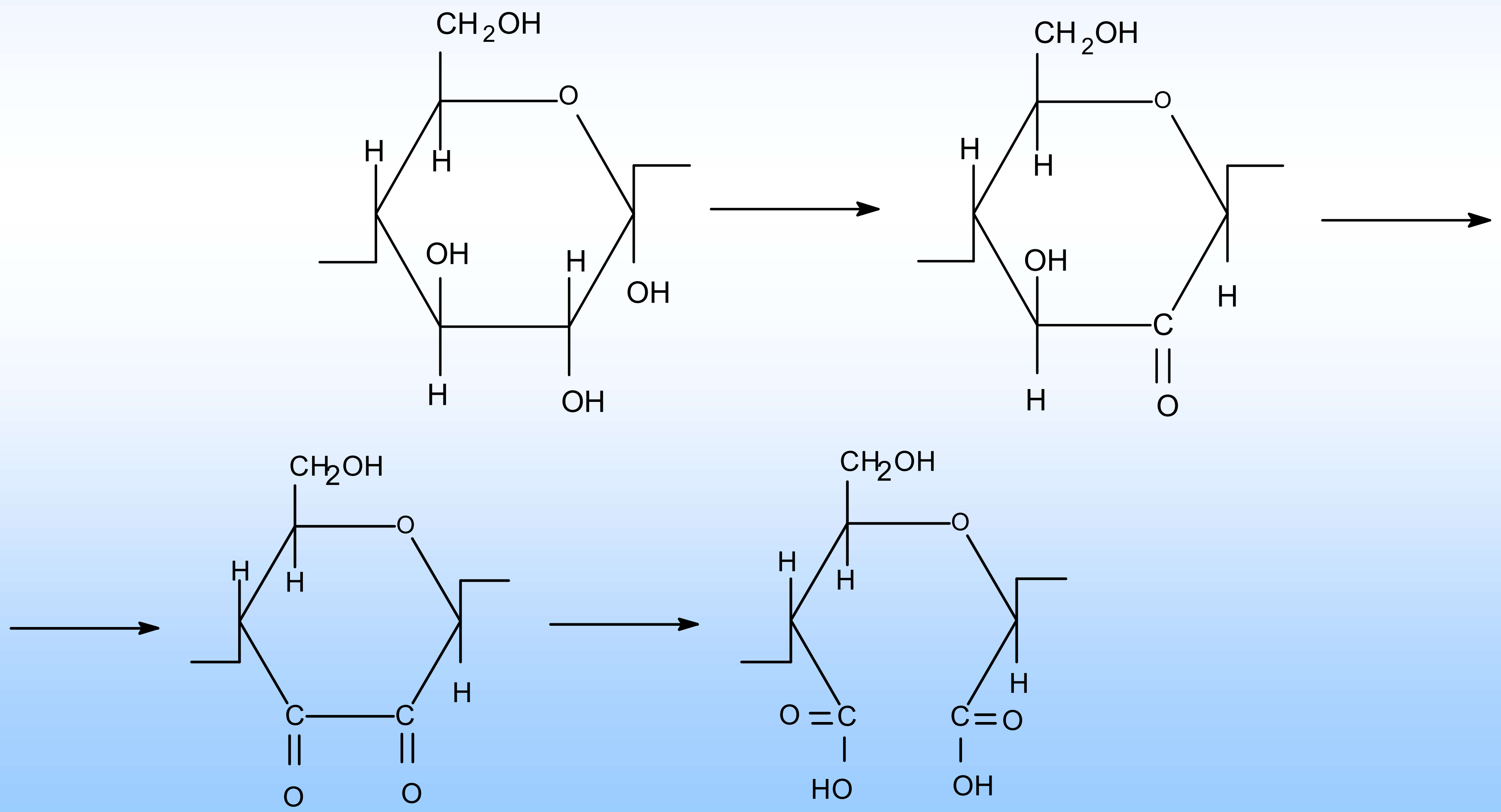
First step of oxidative damage – aldehydic group in the carbon 6, in the next step: carboxylic group

Reductive properties without decrees of polymerization degree



Oxidative damage of cellulose

Deeper oxidation of secondary hydroxyl groups (lower reactivity) on C_2 a C_3 . – keton groups and opening of cycles.



Alkali treatment

Physical and mechanical changes – structure of cellulose is more open then in the water in pH = 7

- Swelling

- Solubility of low polymerized parts of cotton (hemicellulose, viscose fibers n= 500 !!!)

- Chemical changes in cellulose – alkali cellulose ids create (background of higher reactivity and sensibility of cellulose in alkali)

$$\text{Cel - OH} + \text{NaOH} \rightarrow \text{Cel – ONa} + H_2O$$

akalicellulose

Mercerization: (Irreversible changes of fiber morphology)

$$\text{Cel – ONa} + H_2O \rightarrow \text{Cel – OH} + \text{NaOH}$$

$$|$$

$$(H_2O)n$$

hydrated cellulose

Heat and Light damage

damaged by high temperature (Pyrocellulose)

damaged by light (Photocellulose) – viscose is more sensitive (TiO_2 delustrant)

- Textiles are yellowish,
- Lose strength

<u>similar chemical changes as by acid or alkali treatment</u>

Differences:

Photocelulose – typically only from one side of fabric (direction of irradiation)

x Chemical damage – from both sides !!

Cyclic damages

Bases: damaged fibers are mode sensitive to other damages

Wetability is better, intensively swelling (in shorter time)
Is more reactive – the chemicals can find more different groups in fibers, deepness of attack is higher

Cyclic exposition „washing –drying - ironing – using„
Up to 100x !!!

Long life – minimal damage of fibers in pretreatment, low damage in life cycles (no NaClO, alkali solutions with O2...)

Damage

Before testing: removing of impurities (we would like to know the properties of fibers!!!) – the weight of fibers is important !

Damaged cotton:
-Polymarization degree
-More chamical groups (aldehyde and carboxilic)
-Mechanical properties

Damage - overview

Damage by	**Name of product**	**Content of aldehydic groups**	**Content of carboxylic groups**	**Polymerization degree**
acid	hydrocelulose	high	normal	low
oxidation	oxycellulose	low / high	normal / high	normal / low

Result: identification of damage reason is complicated !!!

Damage of cellulose

TEXTILE CHEMISTRY

Mechanical and chemical damage

<u>Chemical damage</u> = change of polymer chemical properties

- Change of chemical groups, change of polymerization degree

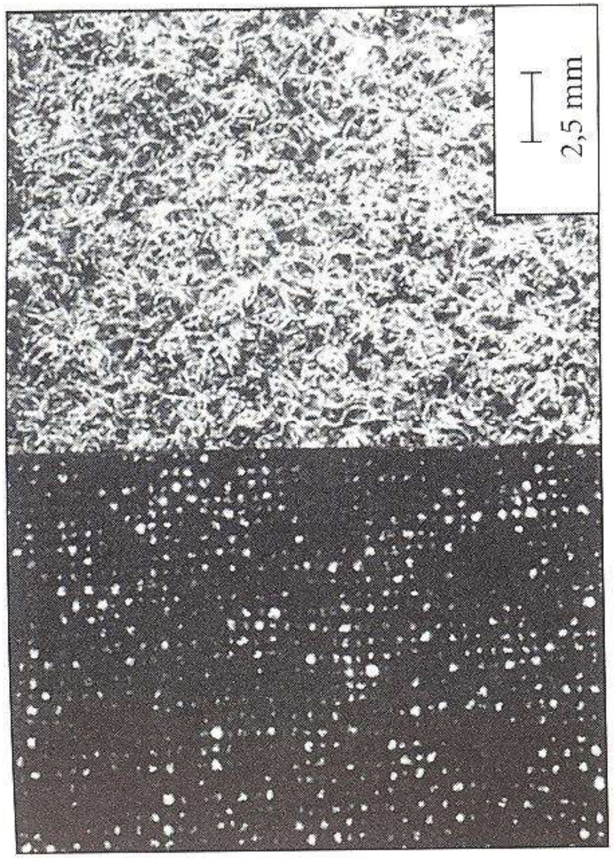
Oxycellulose … aldehyde and carboxyl groups

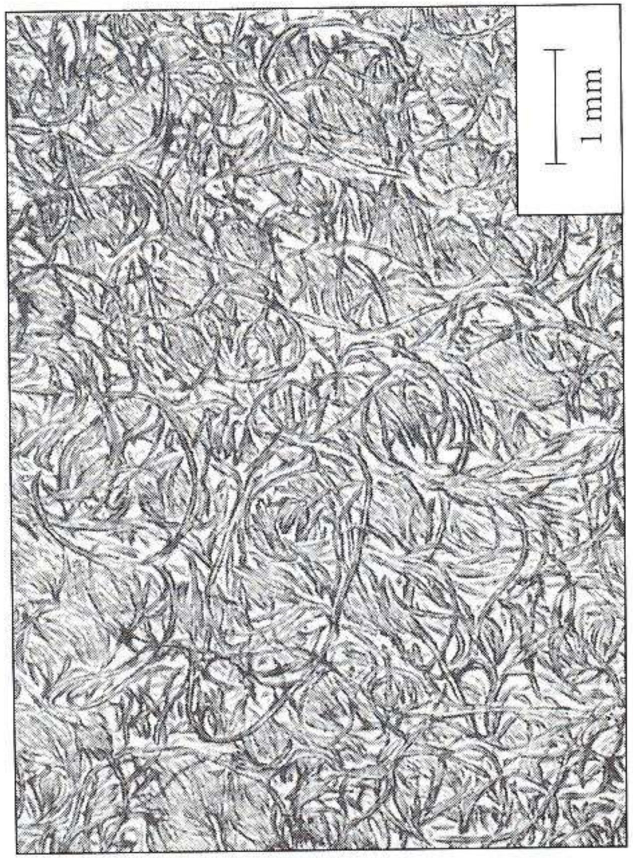
Hydrocellulose … aldehyde groups

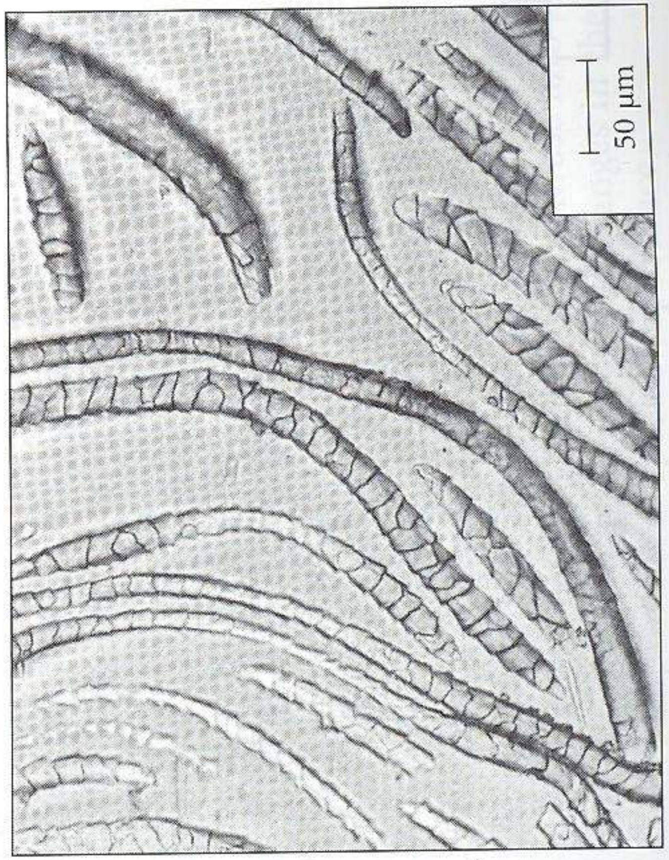
<u>Mechanical damage</u> = change of fiber geometry

- Change of ends of fibers, appearance of fibers

Fabric visualization



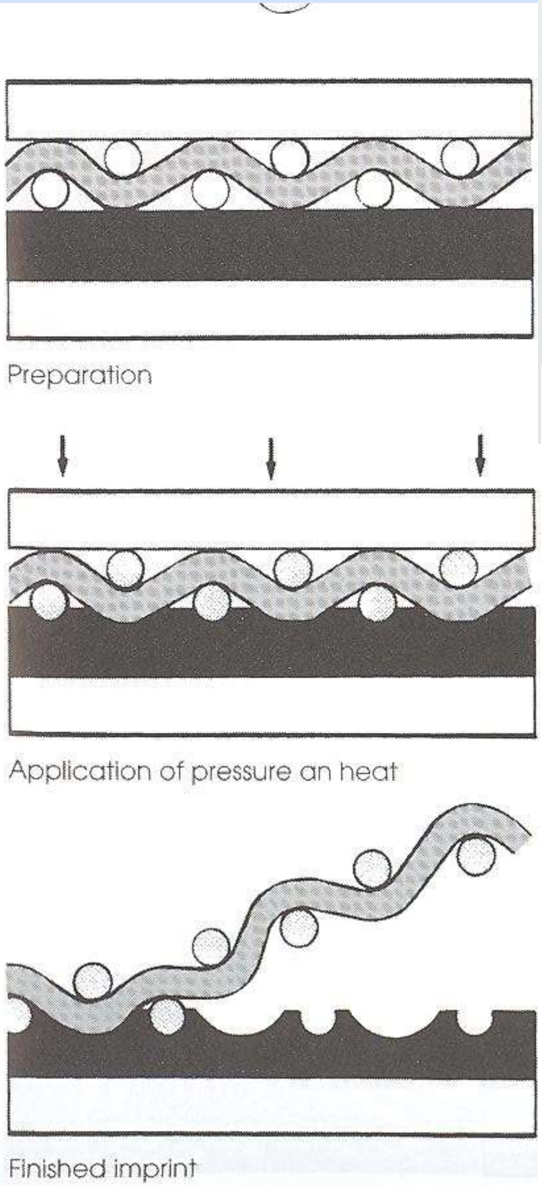


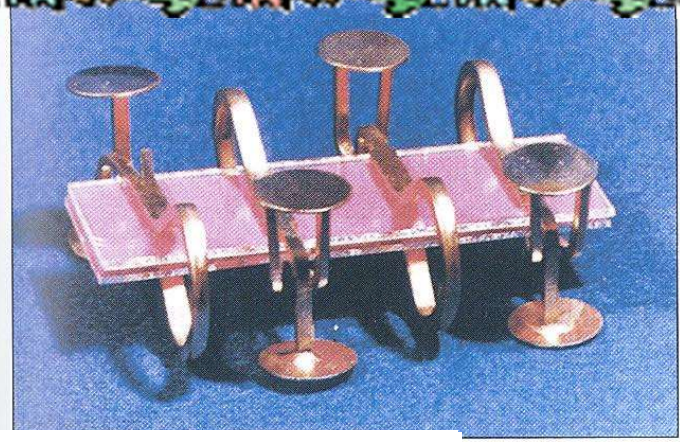


Woolen cloth, in transmitted light (down) and in

Film imprint of the cloth

Imprint





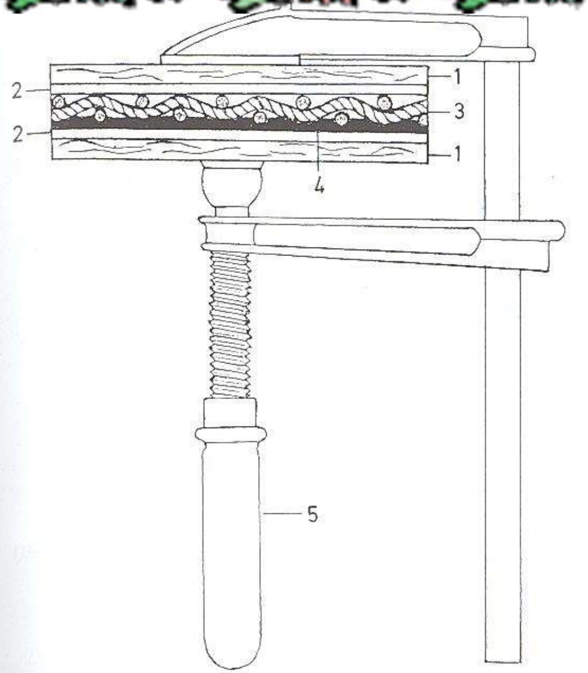
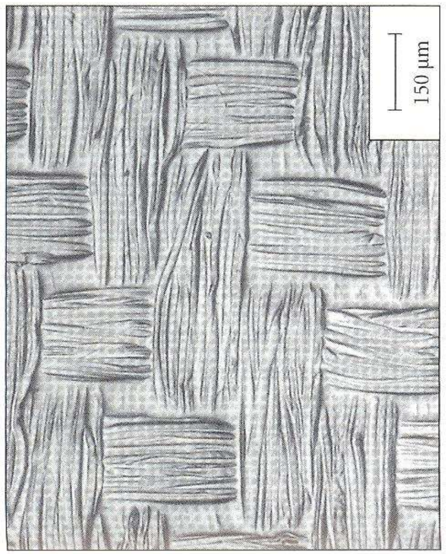
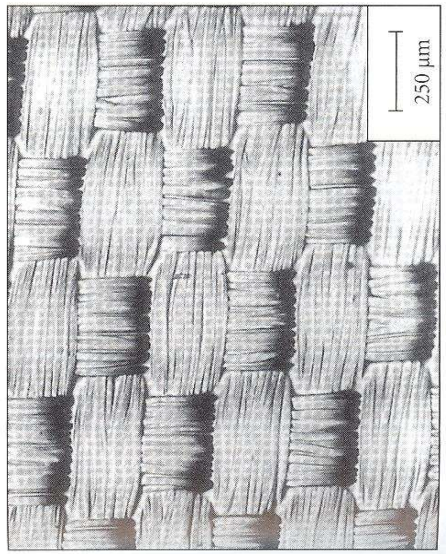


Fig. 4. Imprint of textiles on thermoplastic films compressed between polished metal plates with the size of microscope slides.
1 Wooden plate
2 Polished metal plate
3 Fabric
4 Film
5 Screw clamp

Fig. 5. Preparation of a surface imprint on a thermoplastic film (schematical). Samples produced in such a way are referred to as film imprints.





Preliminary testing

Mechanical testing

(Only for large samples)

- Strength
- Elongation

Microscopic testing

(for small samples)

- Dyeing tests
- Fiber damage morphology (mechanical damage…)

Short time testing

Only for basic orientation

Fiber swelling

In solution of NaOH

Microscopic observation

- Undamaged or mechanical damaged cotton– swelling on the ends of fibers, „mushrooms swelling“
- Low chemical damaged cotton – swelling along the fiber (all mass), „cylinder swelling“
- High chemical damaged cotton – fiber decomposition

Copper number

- Testing with Fehling solution
- Testing of hydrocellulose
- Proportion to aldehyde groups contain
- “quantity of reducted Cu from Fehling solution by 100 g of absolute dry fibers‟

- Sensitive to other reductive chemicals in fibers – it is necessary to wash (extract) fibers before testing

Undamaged cotton: 0,2 - 0,3

Damaged cotton: up to 10

Testing by AgNO3

Preparation of test: $AgNO_3 + NH_3$ (complex)

Temperature: 80°C
Time: few minutes
Washing off in the NH3 solution = more visible results

Results: damaged places are colored on yellow or brawn color according the degree of damage

Reductive groups testing (aldehyds)

Nessler method

$KI + HgCl_2 = HgI_2 + KCl$ add KOH
…. **K_2HgI_4 Nessler's reagent**

Oxidative damaged places: orange or yellow color
(Hg containing compounds)

Methylene blue test

Basic (cationic) dyes will be sorbed by carboxylic groups in oxycellulose

Test is standardized with Methylene blue (old cationic dye)

Principle: short dyeing in Methylene blue solution (at low or high temperature – different times), after dyeing follows the intensive washing.

Oxycellulose hold the cationic dye more intensively. Damaged places are colored darker.

Fiber after mercerization or created from regenerated cellulose are blue in this test – are damaged.

Haller´s reaction on oxycellulose

Heavy metals ions (Pb or Sn) are sorb by oxycellulose from the solutions

Sorbed metals can be detected by fabric color changes

A/ Lead ... Pb(II)

Only oxycellulose (*not hydrocellulose*) sorbs from the solution Pb. Testing is based on application of cochenila (natural dye) – on the places with Pb are the places colored to violet color (or after application of Na_2S we obtain the gray color)

B/ Tin ... Sn(II)

Only oxycellulose (*not hydrocelulose*) 1 hour in the solution 1% - SnCl2 with acetic acid. The tested samples absorb the SnCl2. Textile sample will be putted to $AuCl_3$ solution – on the damaged places will be reducted the „Gold purple" (nanoparticles of Gold). It is a very sensitive reaction – red color is typical result...

Iodine I_2 sorption

Iodine I_2 sorption

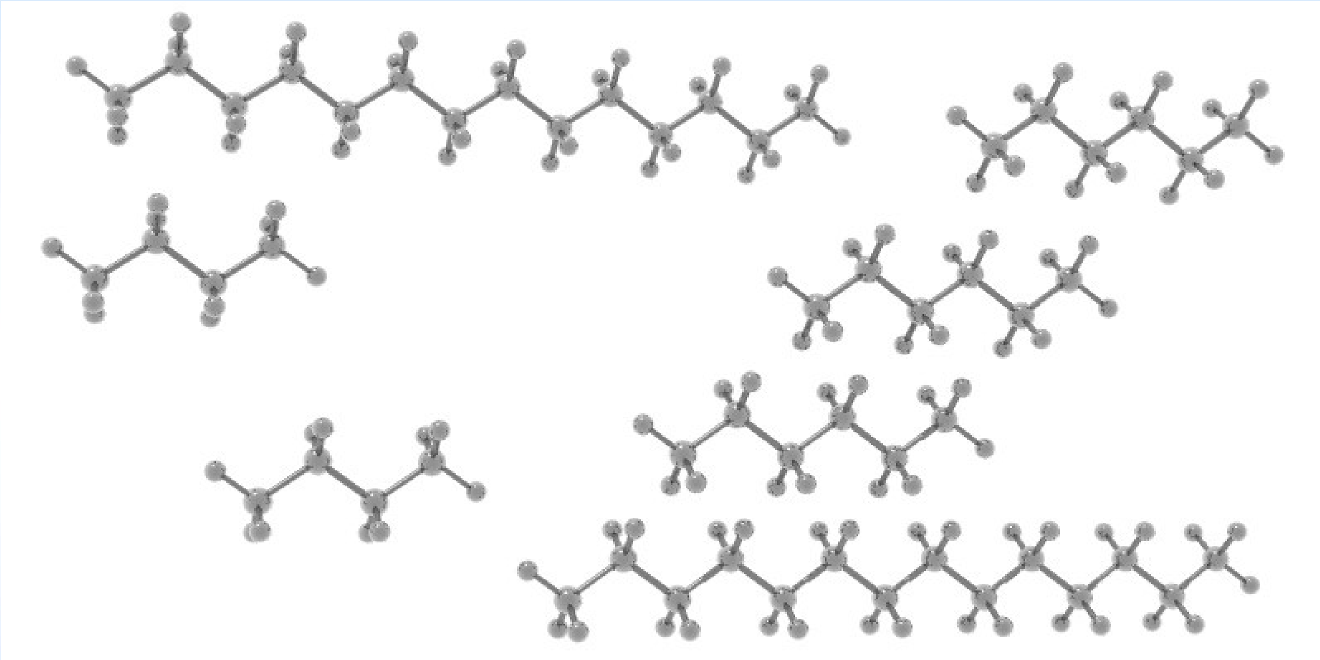
I_2 sorption is equal to contain of amorphous part of cellulose

Comparison of damaged and undamaged fibers

Without change = without chemical damage

- **Raw cotton= 45-50**
- **Alkali boiled= lower then 40**

Average polymerization degree



Molecular weight calculations are provided for a system where there are: 4 molecules with degree of polymerization 2

3 molecules with degree of polymerization 3

2 molecules with degree of polymerization 7

Average polymerization degree

Molecular weight calculations are provided for a system where there are: 4 molecules with degree of polymerization 2
3 molecules with degree of polymerization 3
2 molecules with degree of polymerization 7

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i \frac{w_i}{M_i}}$$

Number Average Molecular Weight

Example numbers: 2,2,2,2,3,3,3,7,7

4.(2) + 3(3) + 2(7) / (8 + 9 + 14) = 31/9= 3.444 4

From this it should be obvious that the numbers 2,3, and 7 correspond to "molecular weights" which are represented by the variable M(i), and the numbers 4,3 and 2 correspond to "number average counts", which are represented by the variable N(i).

The symbol i is just an index. For the above data we would have

Average polymerization degree

Molecular weight calculations are provided for a system where there are: 4 molecules with degree of polymerization 2
3 molecules with degree of polymerization 3
2 molecules with degree of polymerization 7

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i}$$

Weight Average Molecular Weight

Example numbers: 2,2,2,2,3,3,3,7,7
(4(2)2 + 3(3)2 + 2(7)2) /(4(2) + 3(3) + 2(7))=(16 + 27 + 98)/31= 4.548
It should be clear that M(i) and N(i) are the same as for the Number Average Molecular Weight example.

Average polymerization degree

Complicated (especially in cellulose)

Principle: viscosity of solution depends on polymerization degree

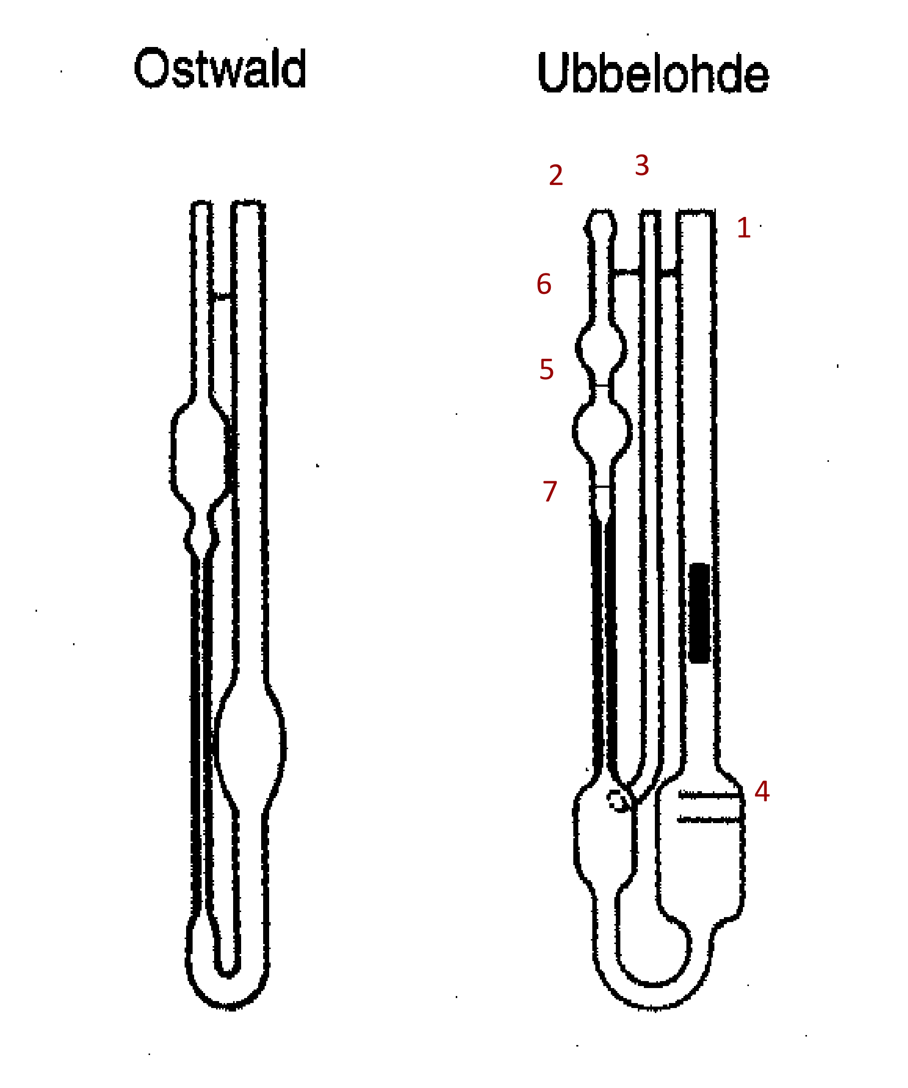
Low polymerization = low viscosity

Practical sample:
CMC (carboxymethylcellulose) x sugar
Polysaccharide x disaccharide
Low viscose x high viscous

The viscosimetric method is more often used method for determination of polymerization degree. Determination is based on relation between limiting viscosity number of polymeric solution and degree of polymerization (average molecular weight)

…. Weight Average Molecular Weight

Average polymerization degree



Use the Ubelohde viscometer for measuring viscosity (see fig.). Put the viscometer vertically into holder.

The sample is poured to tube **1** till the surface in the bowl **4** lies between lines.

Put the hose of the end of tube **2**.

Plug the tube **3** by finger and suck the liquid over to line **5** (not more than half of bowl **6**). Then release ends of tubes **2** and **3**.

Measure the time of flow of liquid between lines **5** and **7** – observe the liquid surface.

Average polymerization degree

The measuring of dynamic viscosity η_0 for suitable dissolving agent is necessary to finding LIMITING VISCOSITY NUMBER $[\eta]$.

The defined amount polymer is dissolved and viscosity η is measured. The relative viscosity is defined by relation:

η is dynamic viscosity of polymer solution

η_0 is dynamic viscosity of pure solvent

ρ is density of polymer solution

ρ_0 is density of dissolving agent

t is time of flow of polymer solution

t_0 is time of flow of dissolving agent

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho . t}{\rho_0 . t_0}$$

Because the solutions of polymer are very much diluted can be written:

specific viscosity $\eta_{sp} = \eta_{rel} - 1$

The concentration of polymer in solution is known, then:

C is concentration of polymer in solution [g/100 ml]

$$[\eta] = \lim c \rightarrow 0(\frac{\eta_{sp}}{c})$$

Average polymerization degree

Viscosity depends on temperature at the measurement – the viscometer should by thermostated at **20** ± **0,1 °C.**

$$[\eta] = K \, . \, M^a$$

[η] viscosity number

K, a constants

M molecular weight

Both constants (K, a) are specify for each kind of polymers. These constants can be found in literature.

Results:

Undamage cotton = 3000

Undamage viscose = 500

Damage … decrease of values sensitive test !!!

Typical analyses : compare the results before and after

Solvents for cellulose

Cellulose is not soluble in any organic solvent – is necessary use the inorganic solvents containing water and some inorganic chemicals, which create intensive forces to cellulose macromolecules.

Reason of this solution is measurement of polymerization degree – we should dissolved the cellulose without any depolymerization processes.

Possible problems: crosslinking by finishing agent, insoluble finishing (silicon) agent

Solvents:

1/ CUOXAM copper /ammonia (Schweizer solution).

easy solubilization, but unstable to oxygen from the air

2/ CADOXEN Cadmium / etylendiamine complex

3/ IRON COMPLEX alkali complex of iron tartrate , Ideal properties

Other methods of dissolving:

/ Nitrocellulose

After nitration are the cellulose fibers soluble in acetone

/ NaOH

Viscose fibers are soluble in 10% NaOH at low temperature

Catalytic damage

Identification = identification of catalysators

Similar to oxidative damage

Typical problems: damaged places are destroyed, the dyeability of low damage places is more intensive (substantive, reactive dyes…)

Analyses of catalysator: (Fe, Cu !!)

- Identification by the standard tests (Rhodanide or Prusian blue)

Without catalysators: standard oxidative damage

- testing by Götz solution (Boiling in 1%-solution of silver acetate ($Ag^+(CH_3COO)^-$) after 5 -10 minutes is the positive results brawn color of Ag)

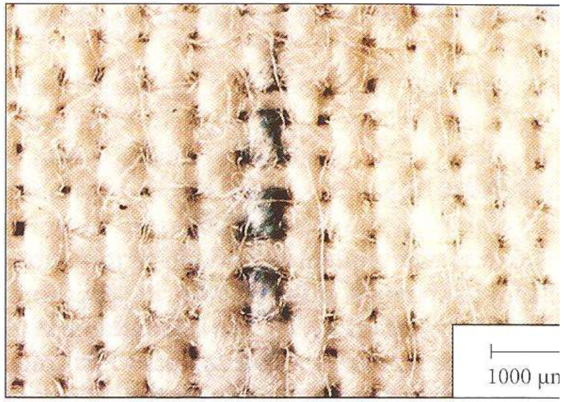


Fig. 81. Stains that contain abraded metal in a cotton warp, leading to catalytic bleaching damage. Iron detection with the Prussian Blue reaction.

Fig. 82. Cotton fabrics with small holes after bleaching, typical of catalytic bleaching damage. Areas of damage with positive Oxycarmin test.

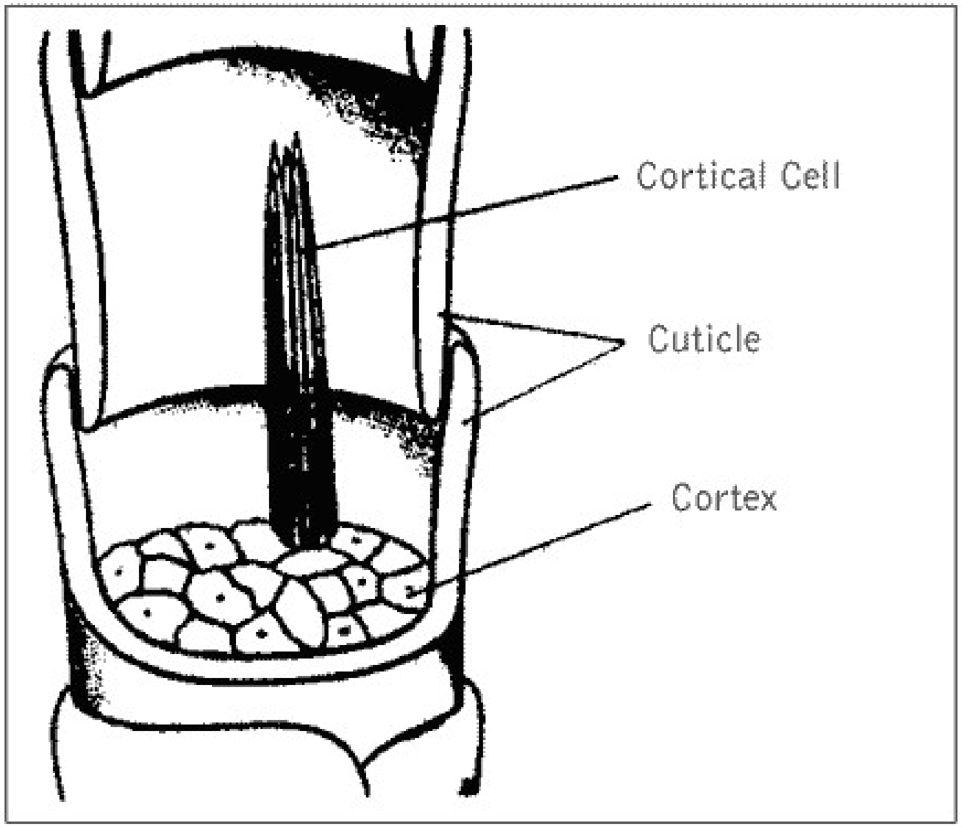
Wool fiber damage

Wool - morphology

Wool fiber are typical with its complicated morphological structure
This structure is connected with many basic properties of wool fibers.

From the morphological point of view:
- **Cuticle**
- **Cortex**
- **Medula**

<u>**1 fiber = large quantity of cells !!!**</u>



The cortex of a wool fibre

Cuticle

Fiber protection
Hydrophobic layers
Organized to scales
1 mm2=900-3500 scales
Only 1/3 of scale is visible (2/3 are in the fiber)
Different scales geometry …
Identification of fibers by microscopy

Scales can be removed of damaged by enzymes or chemicals
Cuticle scales (cells) are created from many layers

Cuticle - scales

Cuticle

Epicuticle

Only 5-10 nm, 0,1% of weight, many fats and waxes, lipoproteins – extremely hydrophobic (in undamaged state)

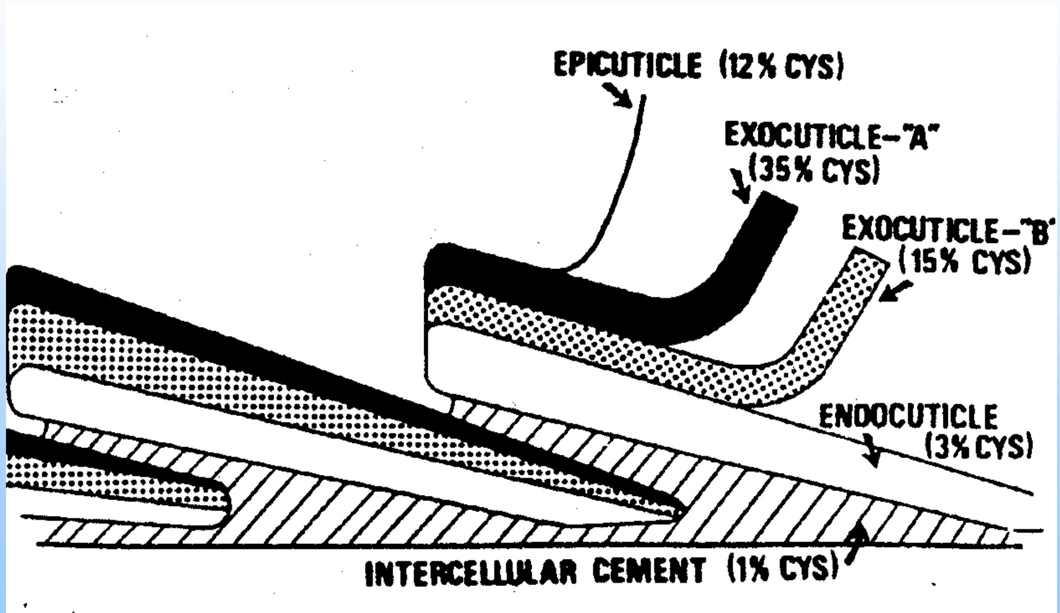
Can be damaged by chemicals and mechanic treatment

Exocuticle

Main part of cuticle, 150 nm, morphologically A and B

Endocuticle

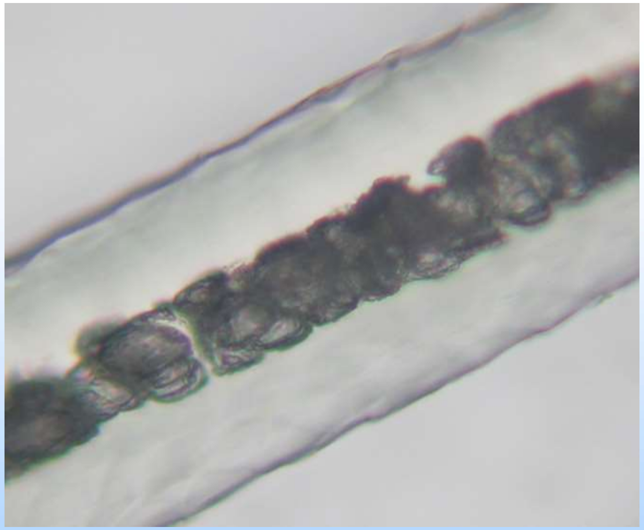
Small cells, mechanically and chemical stable, 8% from the cuticle



Cortex and Medula

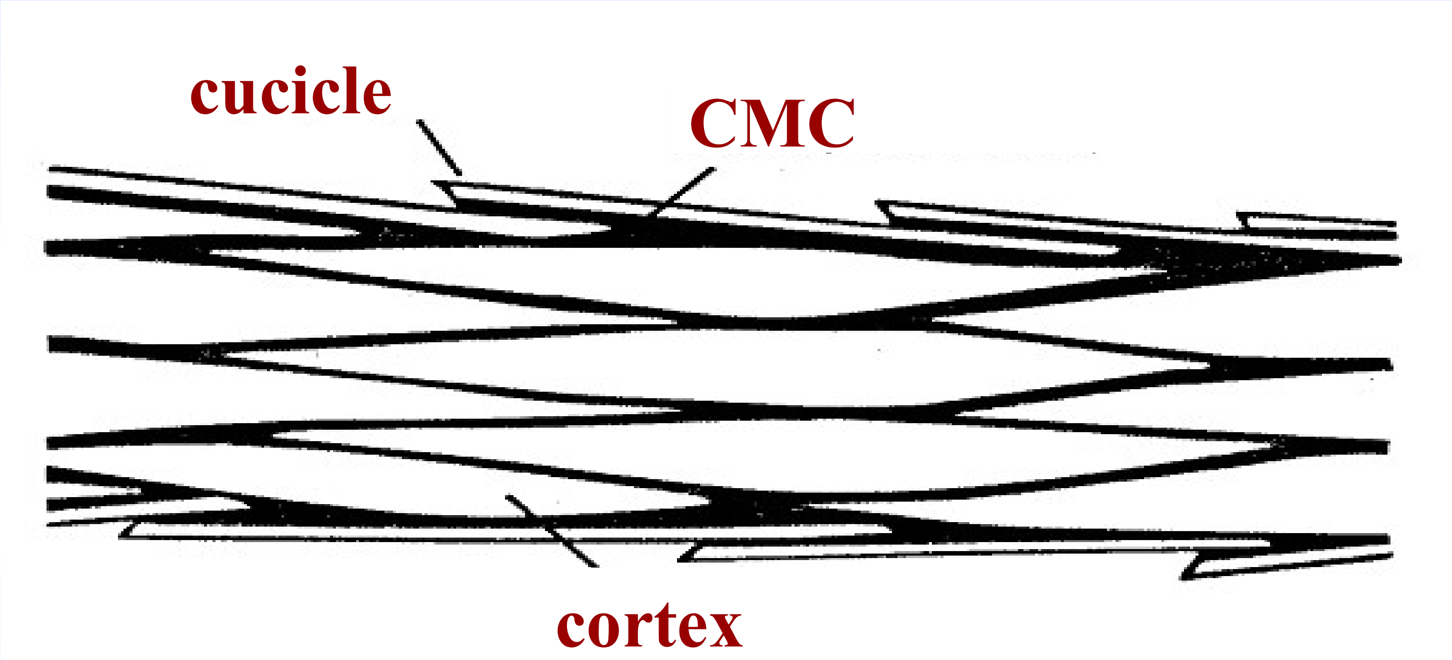
Cortex (fiber mass)
Approximately 80% of fibers
From long cells (diameter 4um, length 100um)
Ortocortex and paracortex

Medula is a central hole in wool fibers
- High quantity of pigments, only in the case of fibers with diameter above 35 µm



Medula in course wool fibers (diameter 37 um)

Cell-membrane complex



cell-membrane komplex (CMC)

„glue“ among cortex cells

Chemical basis of wool

Wool fibers are based on proteins

-Organic polymer from α-aminoacids (bonded by peptide bonds – reaction products between carboxilic acids and amino groups)

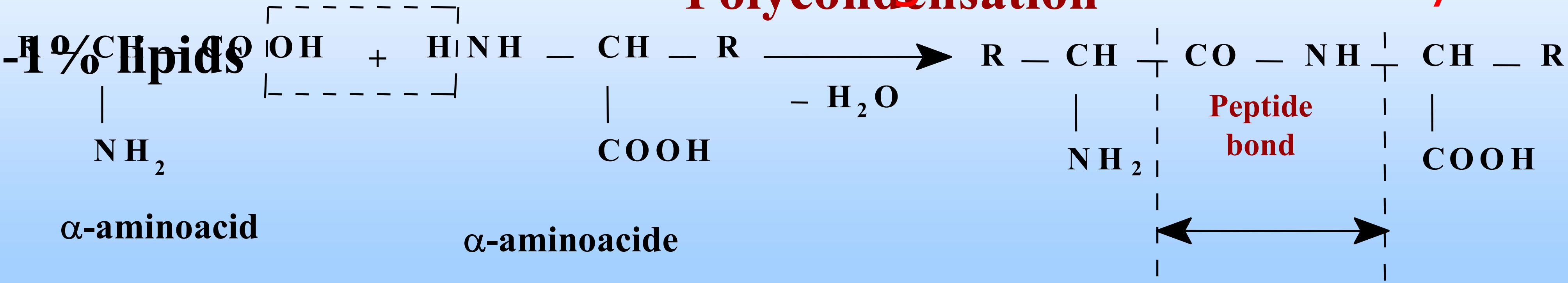
Chemical composition of wool:

Molecular weight of keratin is about 90
– 60000
50% main chain, 50% secondary chain
Keratin – high chemical stability

-80% keratin

-19 % other peptides

-1 % lipids



α-aminoacids

α-aminoacids

18 different in keratine (from 20 in the nature)
Concentrastion depends on the growing conditions of wool
Different amiacides = differentchemical properties

Aminoacids in wool

Aminoacid	[%]	„R“ rest of aminoacid
GLYCIN	8,2	*hydrophobic*
ALANIN	5,4	
FENYLALANIN	2,8	
VALIN	5,7	
LEUCIN	7,7	
ISOLEUCIN	3,1	
SERIN	10,5	*Polar (-OH)*
THREONIN	6,3	
TYROSIN	3,7	
KYSELINA ASPARAGOVÁ	6,6	*acid (-COOH)*
KYSELINA GLUTAMOVÁ	11,9	
HISTIDIN	0,8	*alkali (-NH_2)*
ARGININ	6,9	
LYSIN	2,8	
METHYONIN	0,4	*Sulphur containing*
CYSTIN	10,0	
TRYPTOFAN	6,4	*heterocyclic*
PROLIN	7,2	

Aminoacids in wool

Aminoacids are changed by chemical damage of wool – possible test of wool damage is based on wool aminoacids analyses

Aminoacids are in wool fibers in polymeric form (peptides)

-For the analyses of aminoacids is necesery to separate aminoacids

By H2SO4 (10 hours, 105°C, 3M H2SO4)

3M = ? g/liter 1M=1mol/liter 1mol of H2SO4=98g (2x1+1x32+4x16)

3m=3x98=294 g/litre

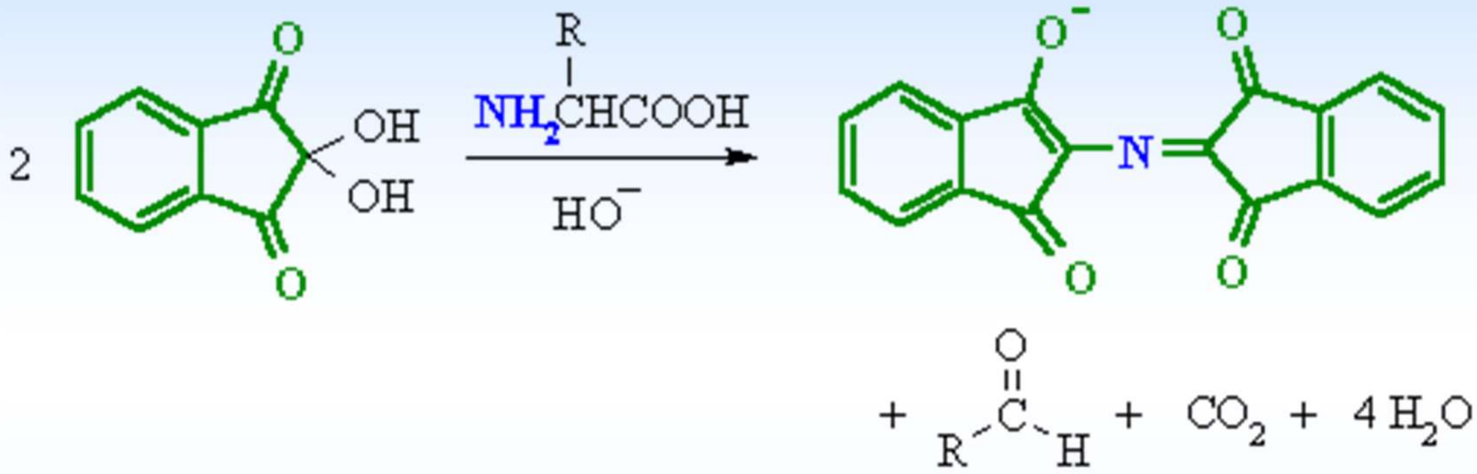
This procedure didnt change the concentration of aminoacids !!!

Analyses of aminoacids:

- separation from the solution by chromatography or electrophoreses

- „colorration“ of aminoacids by ninhydrin

Aminoacids in wool



Amines (including α-amino acids) react with ninhydrin to give a coloured product.

It can be used qualitatively (*e.g.* for chromatographic visualisation) or quantitatively (*e.g.* for peptide sequencing).

The α-amino acids typically give a blue-purple product.

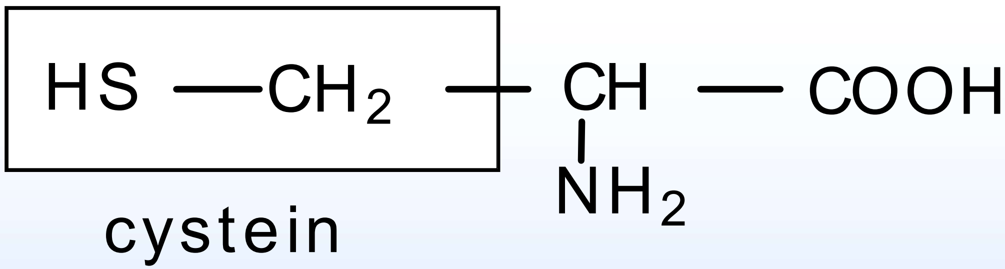
Proline, a secondary amine, gives a yellow-orange product.

The test is sensitive enough that ninhydrin can be used for the visualisation of fingerprints.

Aminoacids in wool

From the analytical point of view are importent following aminoacids:
cystin, cystein, cystein acid, lanthionin, tyrosin

Cystein



Cystein contain increses by the treatment in reductive baths (reductive bleaching, antichloration, decolorization…), washing, heating, dyeing, bleaching by H2O2…

Aminoacids in wool

Cystine

$$HOOC - \underset{NH_2}{\underset{|}{CH}} - \boxed{CH_2 - S - S - CH_2} - \underset{NH_2}{\underset{|}{CH}} - COOH$$

cystin

Undamaged wool: 11,5 – 12% of cystine

Cystin is decomposed by: UV light, alkali traetment, bleaching, chlorine treatment, steaming,…

Light damage = 10%

Hard damage = up to 7%

<u>Principle of testing</u>: by adding of $Na_2S_2O_5$ to hydrolysed wool wil be ceisten changed (reducted) to cystein

Cystein can be detected by phosfowolfram acid (Folinovo reagent): blue, measurable color

Aminoacids in wool

Products of cystin decomposition:

<u>Cystein acid</u>
Created by oxidative chemicals
R- SO_3^-
Undamaged wool: 0%

<u>Lanthionin</u>
Created by alkali solutions, steaming, dyeing above the ph=5
-S-S-
Undamaged wool: 0,2 %

Aminoacids in wool

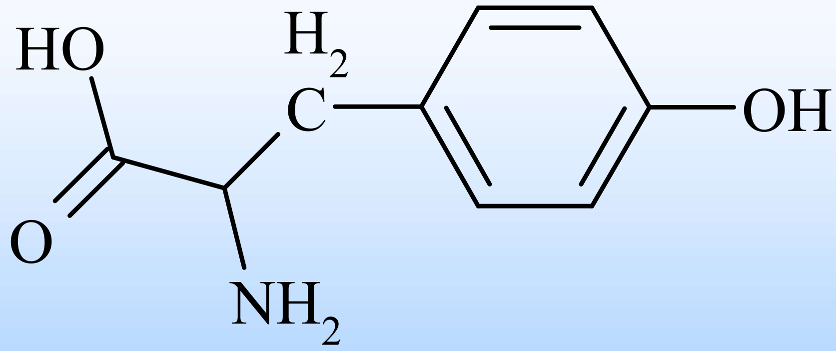
Tyrosin

-Sensitive to chlorine damage of wool

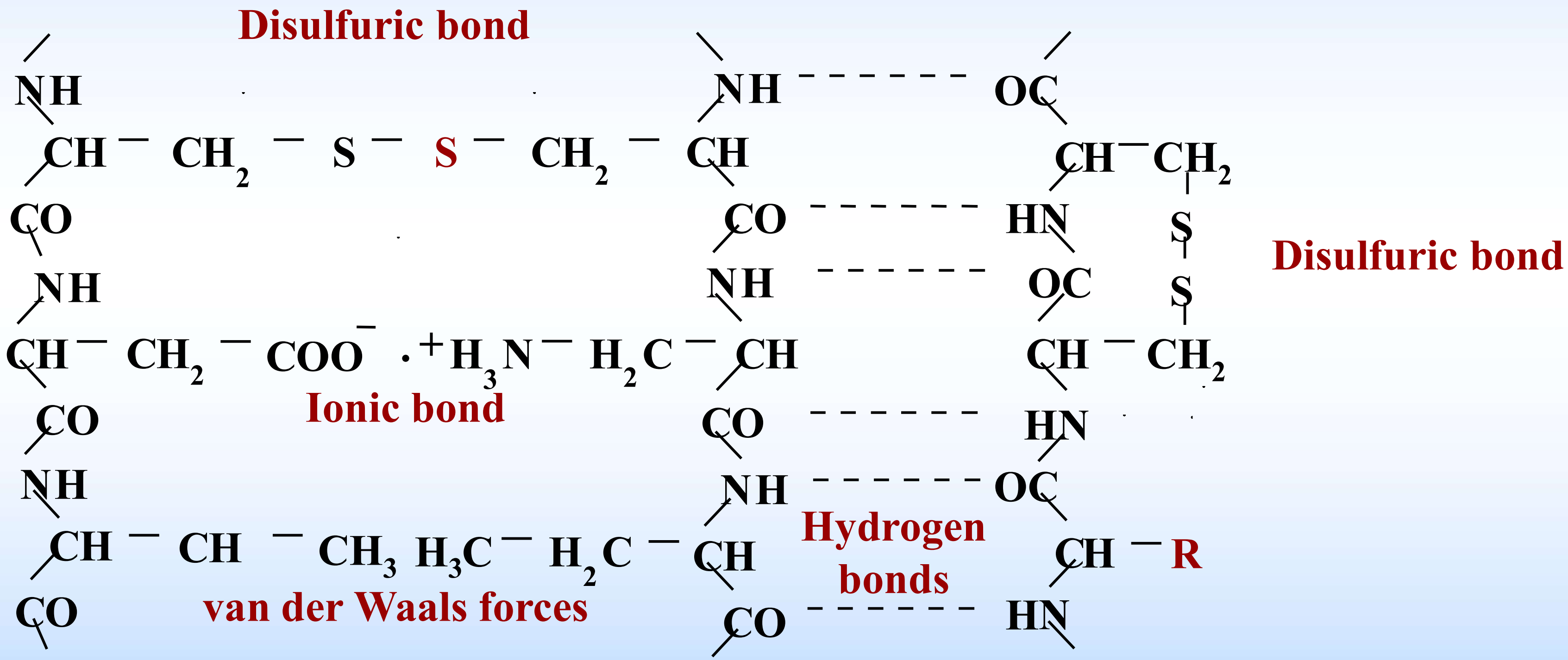
-Undamaged wool: 5,8 %

-Low damaged wool: 5,3 %

-Higher damaged wool: 4 %



Bonds in wool (between molecules)



Wool damage

Sulfur bonds (cystein bonds)

- S-S-
- Chemical bond
- extreme stability of keratin !!! – high chemical and mechanical properties
- sensitive to: alkaline decomposition (produced is cystein) – especially at high temperature

Ionic bonds

- between cationts NH_3^+ and anionts COO^- in keratin

-Highest quantity in isoionic point

-Sensitive to pH

α-aminoacids with amino groups (basic) *can be bonded with anionic dyes, surfactants*…

α-aminoacids with carboxyl groups (acid) *can be bonded with cationic dyes, surfactants*…

Hydrogen bonds

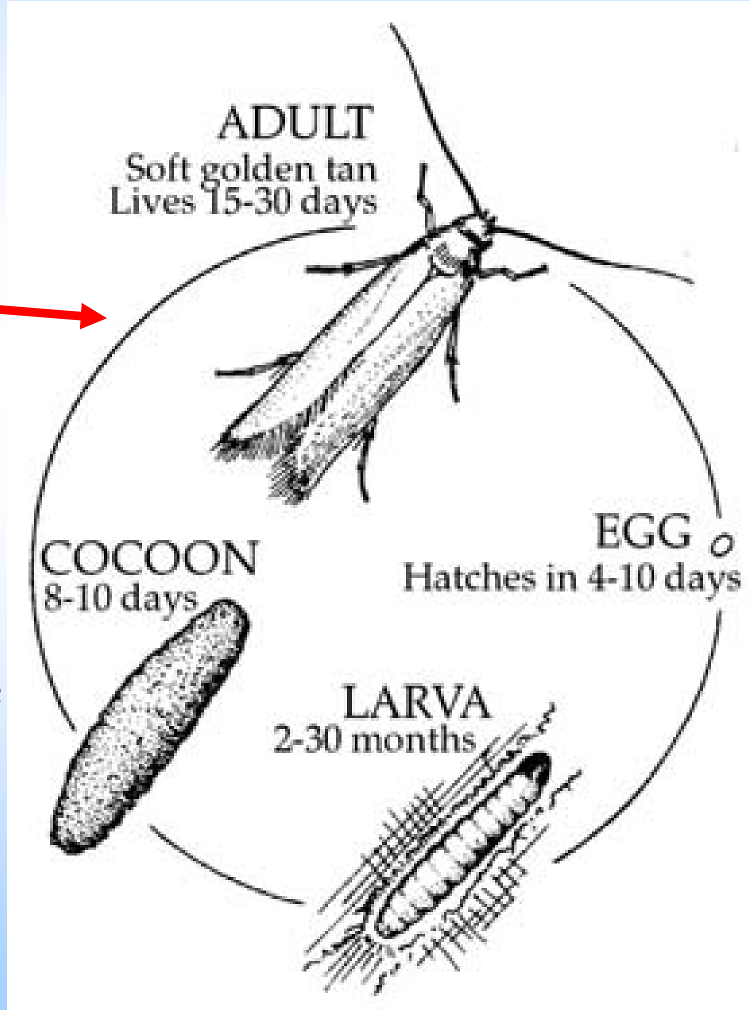
-Between structures containing high polar groups (OH, NH2…)

-Hydrofility of wool (high water absorption)

Wool damage

Wool: complicated structure = more methods of damage

Mechanical: friction, damage of scales
Identification: imprint, microscopy…



Insectical (clothes moth worm)
Identification: microscopy…

Bacterial (only in the case of wrong starage high humidity,, high quentity of wool…)
Identification: microscopy…

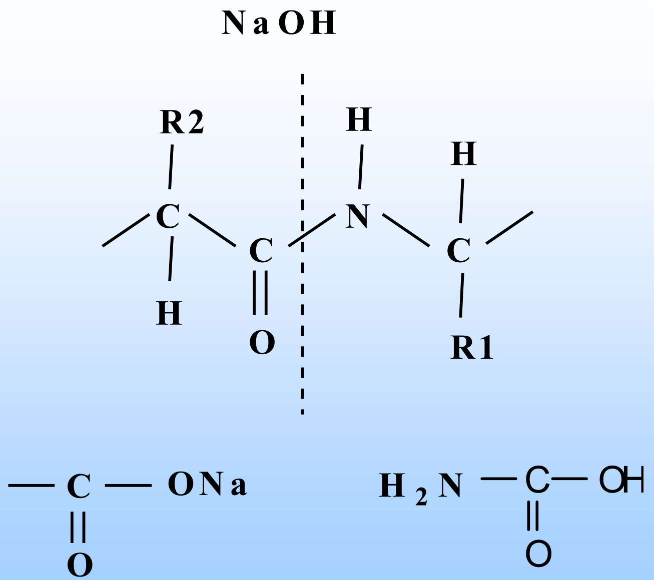
Thermal (over 110°C)
-Changes of handle, mechanical strength

Wool damage

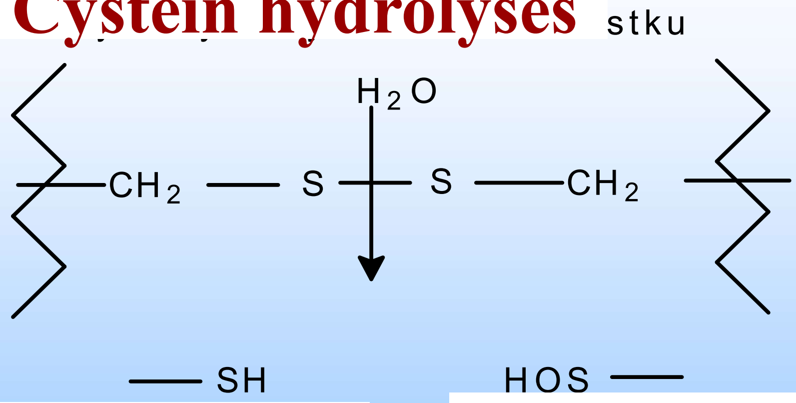
Influence of alkali solutions:

-Cystein x Cystin changes (up to single aminoacids, but changed – not useful for aminoacides identification !!!)

-Opening of peptidic bond



Cystein hydrolyses

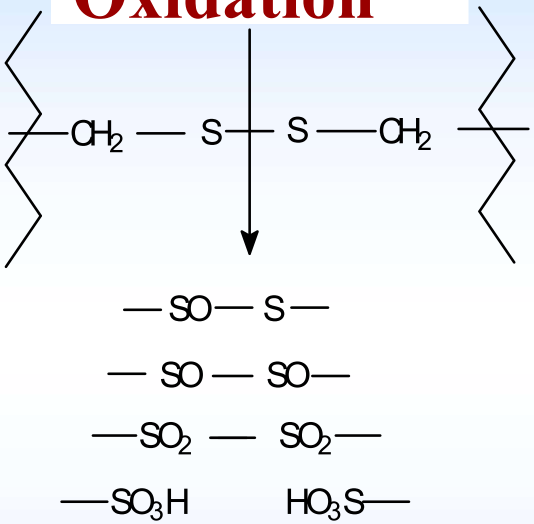


Cystin

Sulfen acid

Oxidative damage

Oxidation



Damaged wool is more soluble in alkali solutions and is more dyable

Reduction

$$- CH_2 - S - S - CH_2 - \longrightarrow - CH_2 - SH \longrightarrow S^{2-}$$

Pauly´s reaction

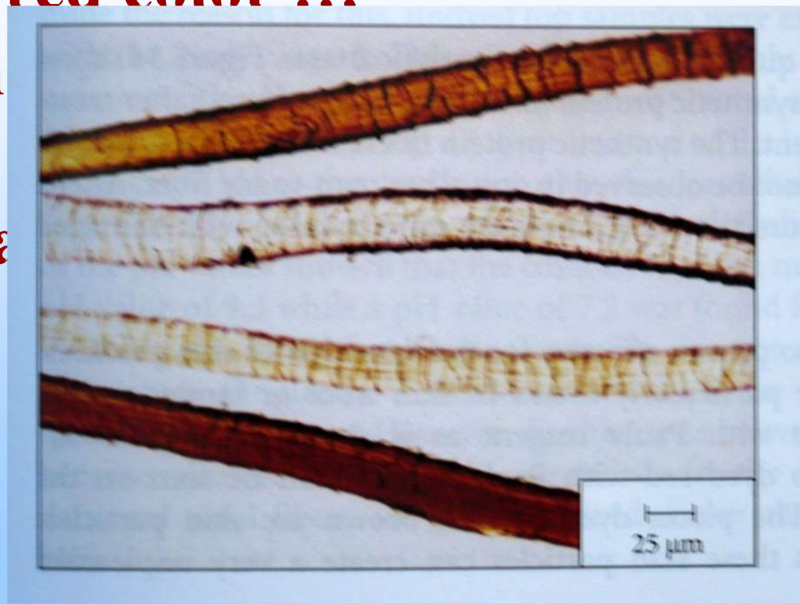
Based on reaction of Tyrosin (aminoaced from cortex) with diazocompounds

If are the wool fibers undamaged: the fiber surface is stable and hydrophobic – diazocompounds can not react with Tyrosin

Test result: white color, slightly colored ends of fibers

In the case of damaged wool is the fiber structure open – the diazocompounds can react with Tyrosin - red color !!!

Test result: color depth according the dam



Test reagent:

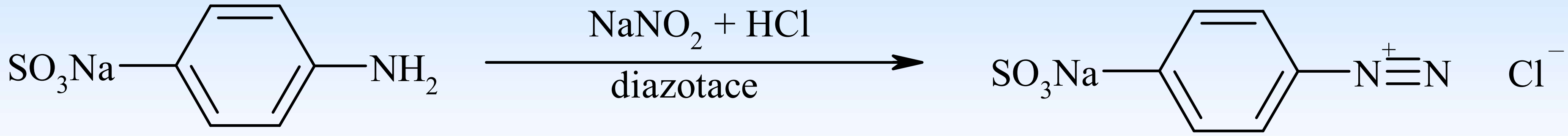
Diazocompound (by the dazotation of sulfa

acid by $NaNO_2$ + HCl).

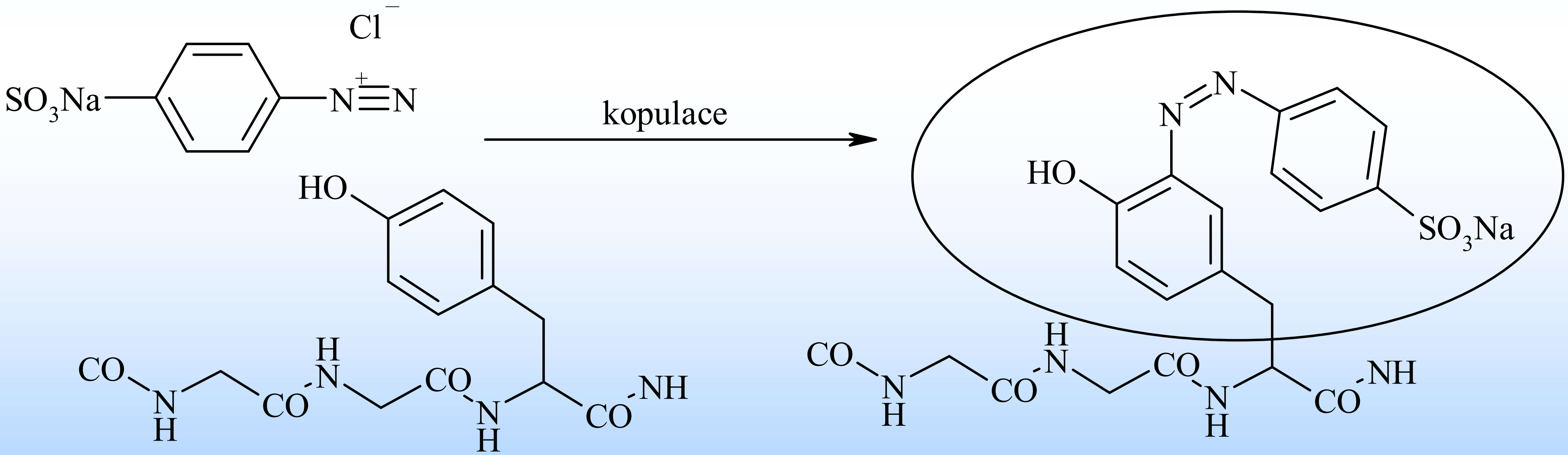
Test conditions:

15 minutes, rinsing, microscopy analyses

Pauly´s reaction



Sulfanil acid **diazocompound**



Tyrosin in polypeptide **Color product**

Metylen blue test

Cationic dye

- Sorption to COOH groups

- Quantity of COOH increase by the oxidation damage (Cl2)

Heavy metals ions

Alkali treatment – decomposition of disulfur bonds (cystin)... Cystein and sulfur ions are produced

These products we can detect by Heavy metals ions (Sn, Pb, Ag...):

SnCl2 + S2- ⟶ SnS + 2 Cl-

or

Pb (CH3COO)2 + S2- ⟶ PbS + 2 CH3COO-

Insoluble products are brown or black ... Easy detection

Reaction conditions: soluble heavy metal salt is boiled together with wool fibers approximately 30 minutes

Darker shade = more damaged fibers

Wool tippines (Tippy wool)

Wool fibers are protected by a natural hydrophobbic layer – epicuticle

Damaged wool is more open – the epicuticle is broken (destroyed)

By the using of hydrophilic dyes we can see differences: damaged places are dyed to deep shades, undamageg places are colorles

By this method we can test the natural damage of wool – the ends of wool fibers are damared by the the wether

Fiber swelling

Solubility and swelling of fibers depends on the chemical properties of fibers – especialy the quantity and quality of intermolecular bonds

Damaged wool – different behavior in aggressive solvents

<u>Allwörden´s reaction</u>

$Cl_2 + H_2O$ reacts with cystin and tyrosin by production of gas

In the undamaged wool fibers can not the gas leave the fiber and creates bubbles below the epicuticle

Damaged wool – damaged epicuticle – gas leaves the fiber without problem and any bubbles...

Limited damage: wool treatment in 10% solution of Na_2CO_3 at 35°C or 0,1% NaOH at 40-50°C.

Biuret reaction

Test:

Water extract of wool fibers (1 hour, 1% Na2CO3, 60 - 65°C)

Quantity of dissoluted keratin depends on wool damage

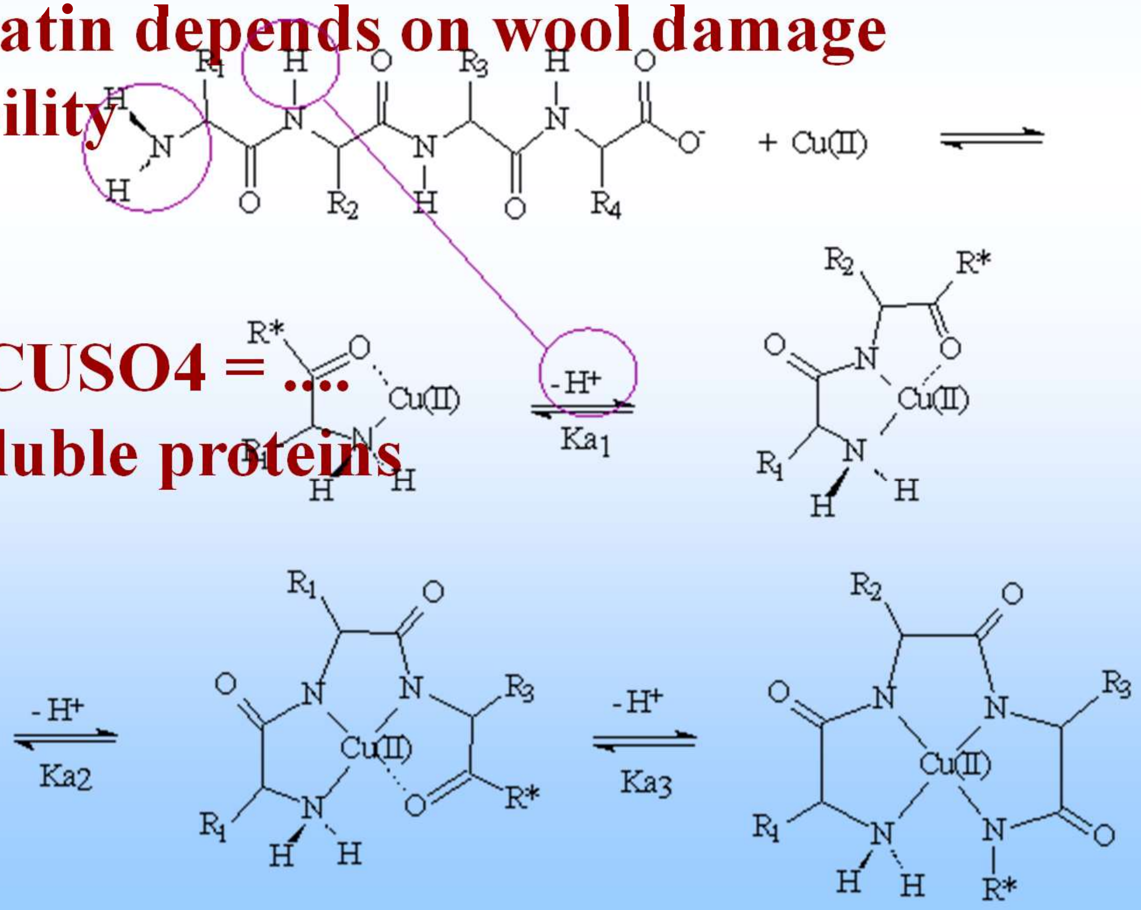
High damage = high solubility

Biuret reaction

Water extract + NaOH + CUSO4 = ...

Damaged wool ... More soluble proteins

... Deep Violet/blue color



Classification of polymers

Thank you for your attention!