NATURAL POLYMERS

FIBROUS PROTEINS II

KERATIN & FIBROIN

Dr. Ladislav Pospíšil

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 – celullose**
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

1. **Keratin**
2. **Fibroin**

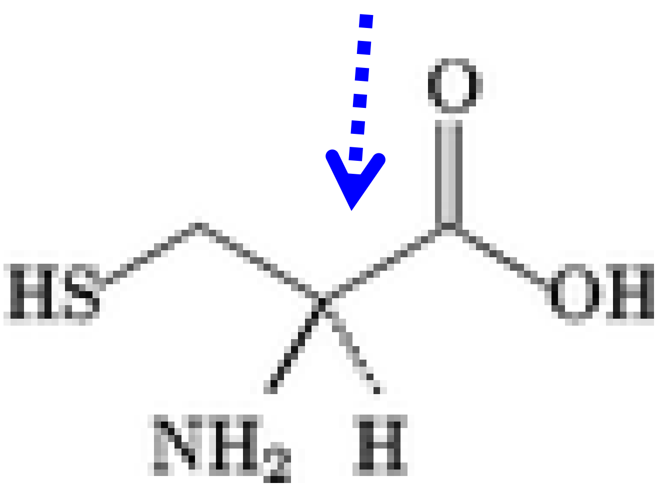
2. Keratin

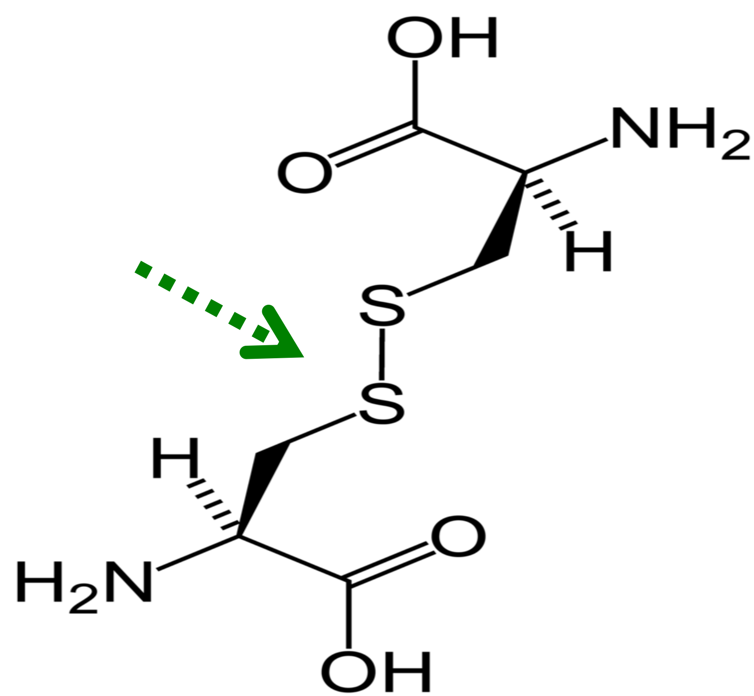
Where is found KERATIN?

- **The Skin Structures** – Hair, Feathers, Animal Hair, Bristle
- **ENDS of the Fingers and Limb** – Nails, Claw, Hooves
- **OBJECT from the Horny Tissue** – Horns
- **Outer Skin (Humans)** - Horny Tissue like Layer (old Skin)

What is KERATIN characterized by 1

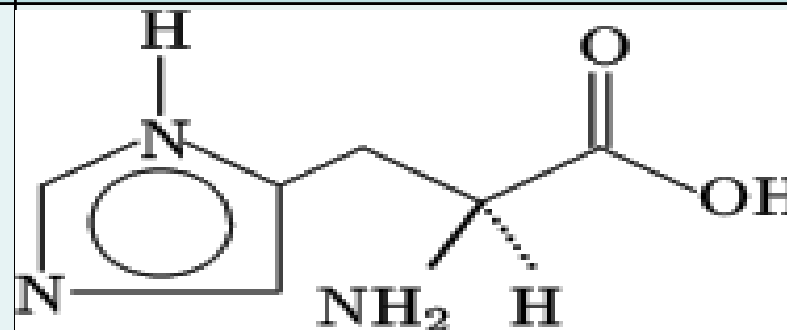
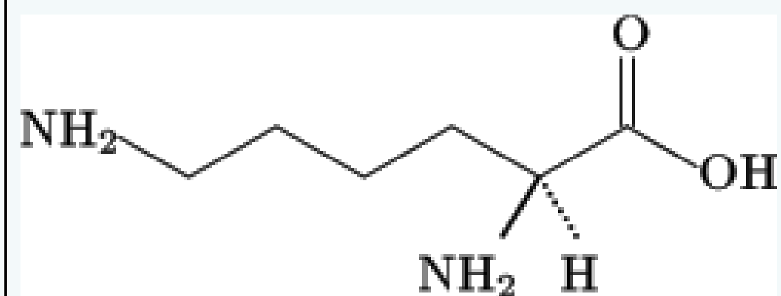
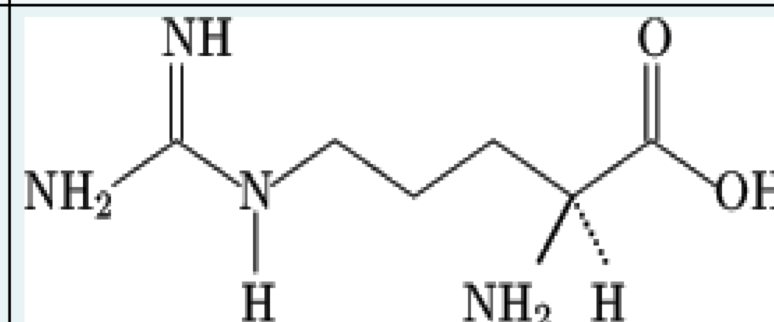
The PROTEIN'S Chains are **CROSSLINKED** via SULFIDIC BRIDGES (-S–S-) formed via – SH Groups of **CYSTEINE** and the **CYSTINE** is the **Result**





What is KERATIN characterized by 2

RATIO (approx.) of the three Main AMINO ACIDS in the KERATIN

AMINOKYSELINA	PODÍL	VZOREC
HISTIDINE	1	
LYZINE	4	
ARGININE	12	

What is KERATIN characterized by 3

- WATER INSOLUBLE
- **RESISTANT TO DILUTED ACIDS**
- NONRESISTANT TO BASIS (e.g. NaOH, KOH etc.) > to clean the Keratin made Brush in the NaOH must be done very carefully, because the natural Bristles can be dissolved entirely!
- **The most important KERATIN Fiber is the Sheep's Wool**

What is KERATIN characterized by 4/1

Composition of the AMINO ACIDS in the KERATINS of various Origin					
AMINO ACID	Human's Skin	Human's Hair	Horny Tissue	Hen's Feathers	Pig's Bristle
Glycine	10,4	4,1 – 4,2	9,6	7,2	NA
Alanine	4,3	2,8	2,5	5,4	NA
Valine	3,3	5,9	5,5	5,8	5,9
Leucine	8,3	6,4 – 8,3	8,3	7,4 – 8,0	8,3
Isoleucine	3,3	4,7 – 4,8	4,8	5,3 – 6,0	4,7
Phenyalanine	4,0	2,4 – 3,6	4,0	4,7 – 5,3	2,7
Tyrosine	4,7	2,2 – 3,0	5,6	2,0 – 2,2	3,5
Serine	11,5	7,6 – 10,6	6,1	4,4 – 4,8	NA
Methionine	1,6	0,7 – 1,0	2,2	0,4 – 0,5	0,5
Proline	2,7	4,3 – 9,6	8,2	8,8 – 10,0	9,6
Arginine	5,7	8,9 – 10,8	10,7	6,5 – 7,5	10,9
Histidine	1,6	0,6 – 1,2	1,1	0,7	1,1
CYSTINE	1,5	16,6 – 18,0	15,7	6,8 – 8,2	14,4

SOFT KERATIN - Hen's & Chicken Feathers is easily cleaved by Inorganic acids and Bases to Amino acids > ANIMALS'FEEDING

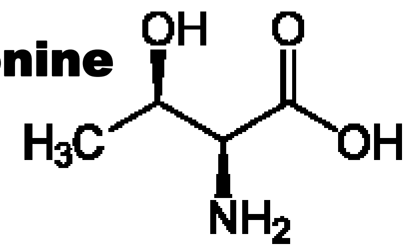
What is KERATIN characterized by 4/2

Composition of the AMINO ACIDS in the KERATINS of various Origin					
AMINO ACID	Human's Skin	Human's Hair	Horny Tissue	Hen's Feathers	Pig's Bristle
Asparagic acid	9,35	3,9 – 7,7	7,9	5,8 – 7,5	8,9
Triptophane	1,0	0,4 – 1,3	0,7	0,7	NA
Lysine	5,2	1,9 – 3,1	3,6	1,7	3,8
Threonine	4,3	7,0 – 8,5	6,1	4,4 – 4,8	NA
Glutamic acid	15,3	13,6 – 14,2	13,8	9,7	17,9
AMIDIC NITROGEN	0,9	1,2	1,1	1,1	NA
TOTAL NITROGEN	19,6	15,5 – 16,9	16,9	16,2	NA
TOTAL SULPHUR	0,8	3,0 – 4,0	5,2	3,9	NA

NA – Not Available

CYSTINE > contains –S-S- Bond

Threonine



SOFT KERATIN - Hen's & Chicken's Feathers is easily cleaved by Inorganic acids and Bases to Amino acids > ANIMALS' FEEDING

What is KERATIN characterised by 4/3

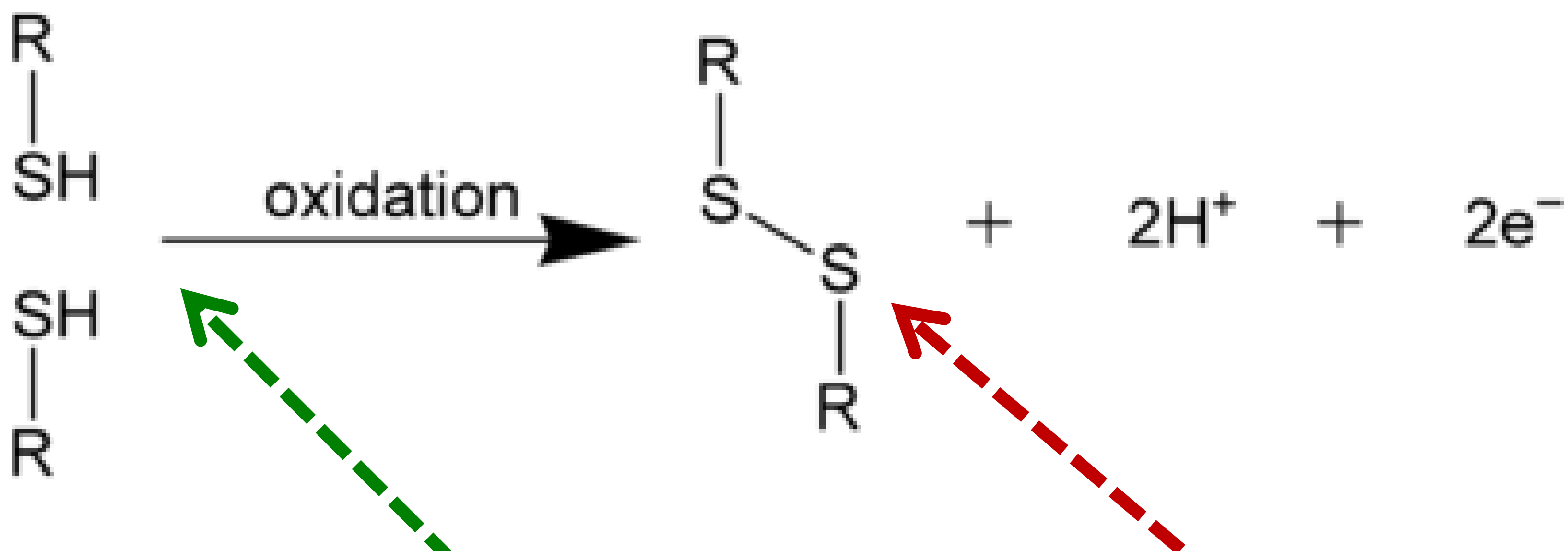
KERATIN Composition it so different for the different Parts of the Human or Animal Bodies and also for different Animals (It is not given in the previous Table)

KERATIN is sometimes sorted to SOFT (approx. 2 % w/w of Cystine) and HARD (up to 20 % w/w of Cystine)

SOFT KERATIN - Hen's & Chicken's Feathers is easily cleaved by Inorganic acids and Bases to Amino acids > ANIMALS'FEEDING

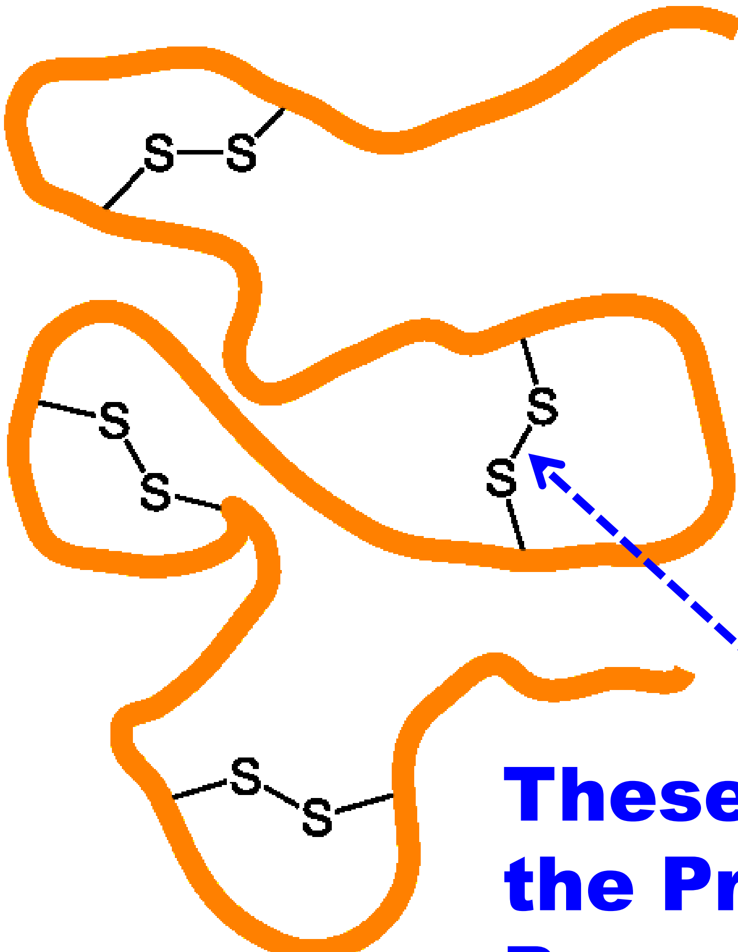
What is KERATIN characterized by 5

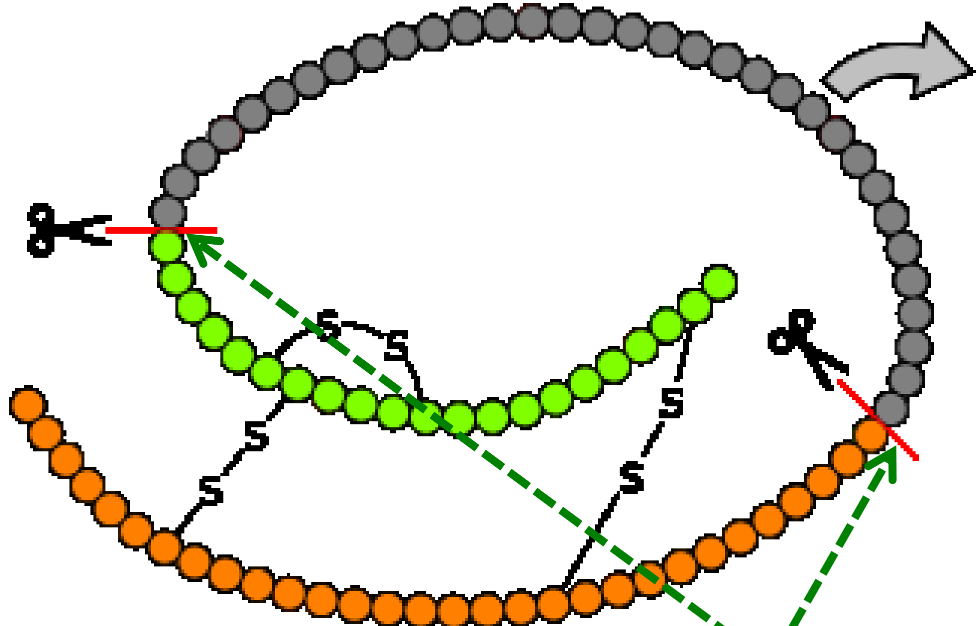
- **Ability to form Connection between Fibres by Chemical Bond > it is Analogue to Rubber Crosslinking or to the Hide Tanning**



Two Cysteines > one CYSTINE

What is KERATIN characterized by 6





These Bonds are the Principle of the Permanent wave of Hair

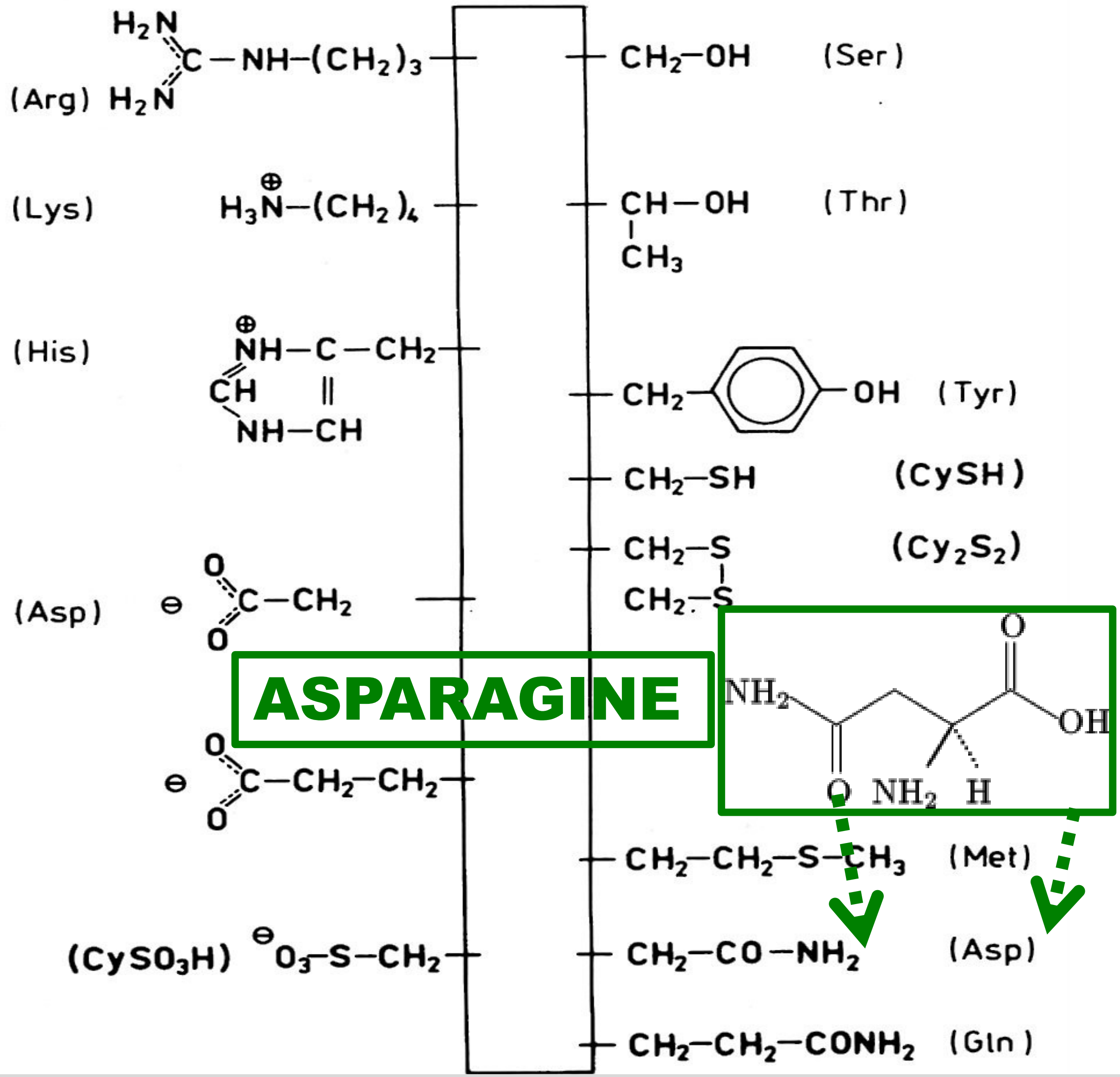
Enzymatic Cleavage of the Backbone

What is

KERATIN

characterized by 7

KERATIN is so very chemicaly reactive Fibre



The reactive Sites of the KERATIN'S Amino acids

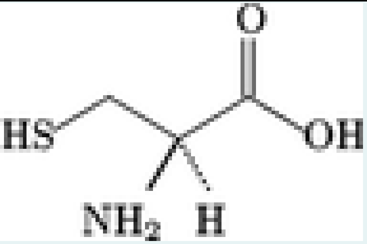
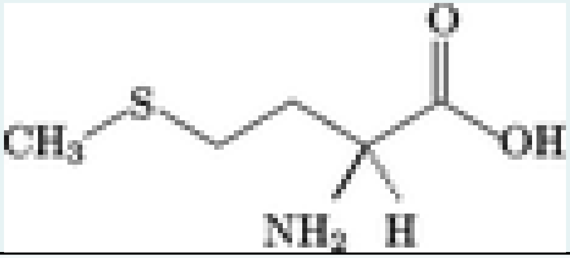
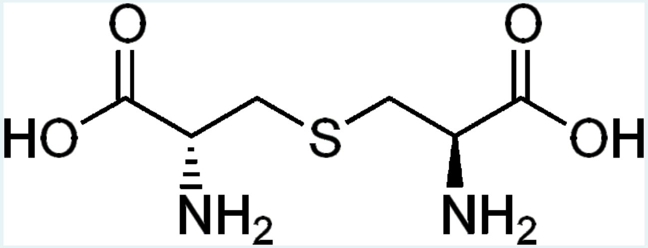
What is KERATIN characterized by 8/1

AMINO ACIDS in the KERATINS- Dividing into various Groups (the Sheep's Wool)		
AMINO ACID Group	AMINO ACID	AMINO ACID Content (mg/g Wool)
Kationic	Arginine	570
	Lysine	228
	Histidine	66
Anionic	Asparagic acid	-----------------
	Glutamic acid	772
Alcoholic -OH	Serine	888
	Treonine	528
Phenolic –OH	Tyrosine	300
Sulphur	Cystein	24
	Cystin	500
	Methionine	29
	Cysteinsulfonic acid	15

What is KERATIN characterized by 8/2

AMINO ACIDS in the KERATINS- Dividing into various Groups (the Sheep's Wool)		
AMINO ACID Group	**AMINO ACID**	**AMINO ACID Content (μg/g Wool)**
Polar covalent Bond	**Asparagine**	------------------
	Glutamine	**822**
Nonpolar covalent Bond	**Alanine**	438
	Valine	487
	Leucine	643
	Isoleucine	275
	Proline	570
	Phenylalanine	239
	Tryptophane	32
	Glycine	749

What is KERATIN characterized by 9

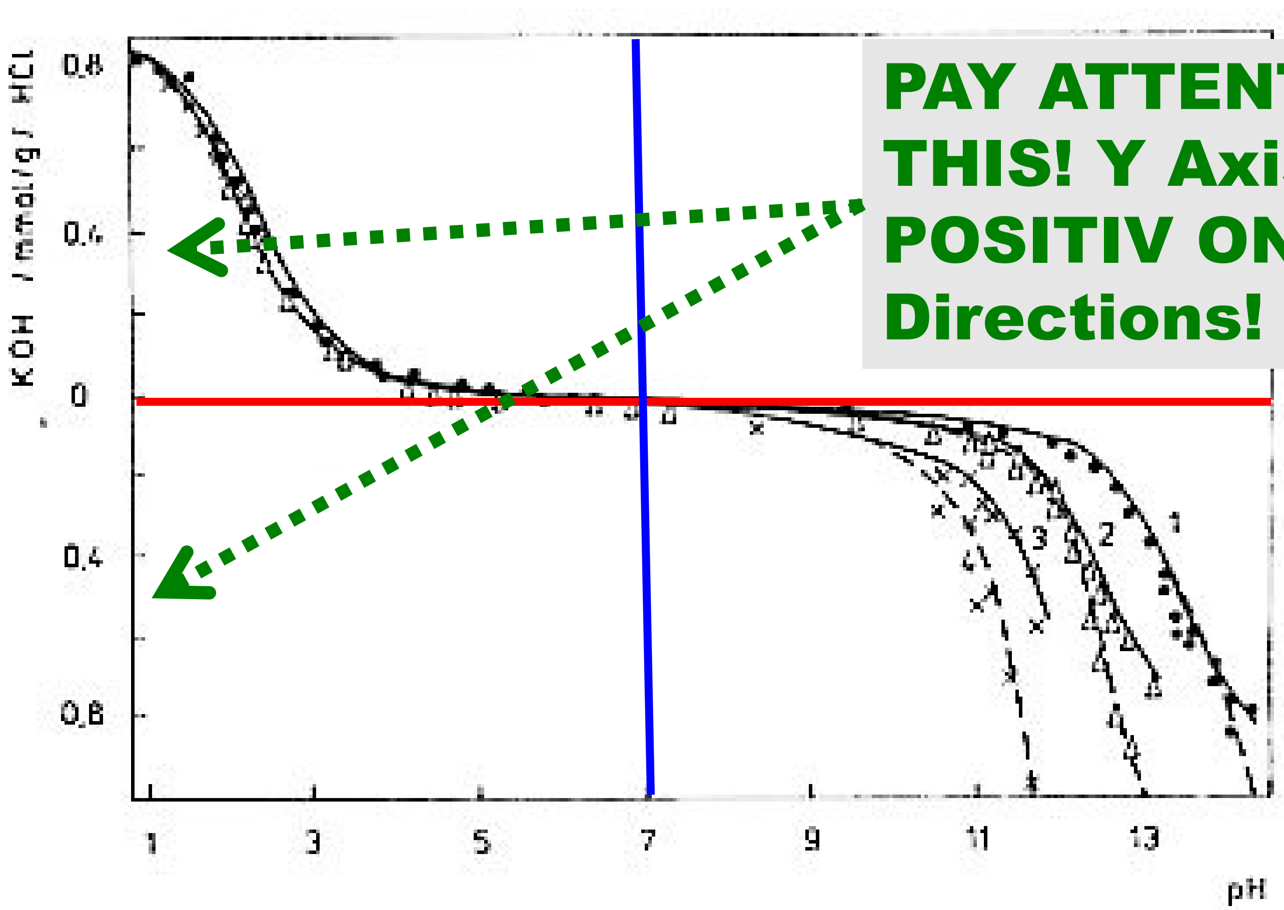
AMINO Acid	Formula
Cisteine	
Cistine	It is formed only by the Reaction of two Cisteine Molecules by intermolecular or intramolecular Way
Methionine	
Cysteinsulfonic acid	It is formed only by the Reaction (OXIDATION) –S-S- Bringe (Bond) in Cistine
Lanthionine (two ALANINES bonded via –S-)	

Value of Heat of Hydration for Wool with Water and Alcohols at 20 °C		
Hydration Agent	**Moly Volume at 20 °C (cm^3/mol)**	**Heat of Hydration (J/g)**
Water	30	100
Methanol	67	91
Ethanol	97	54
Acetic acid	95	119

Why the wet Wool provides Heat?

The **molar volume**, symbol V_m, is the volume occupied by one mole of a substance (chemical element or chemical compound) at a given temperature and pressure. It is equal to the molar mass (*M*) divided by the mass density (ρ). It has the SI unit cubic metres per mole (m^3/mol), although it is more practical to use the units cubic decimetres per mole (dm^3/mol) for gases and cubic centimetres per mole (cm^3/mol) for liquids and solids.

The Sorption Properties of the KERATIN



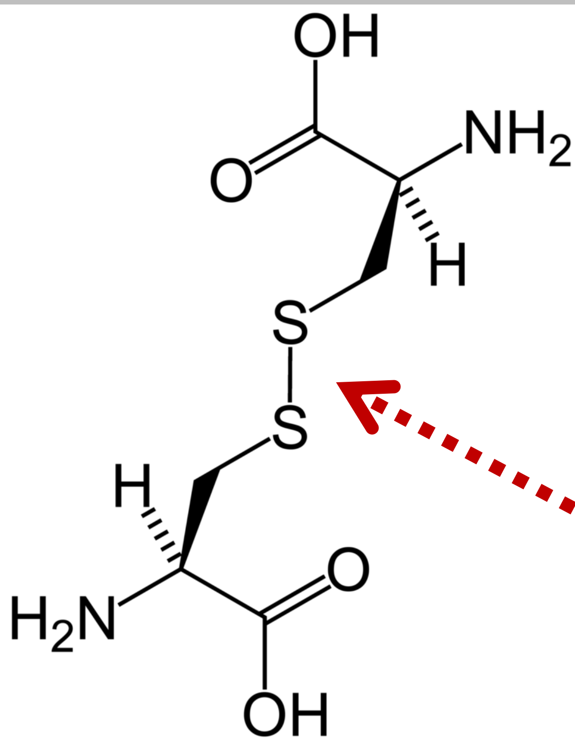
PAY ATTENTION TO THIS! Y Axis is the POSITIV ONE in both Directions!

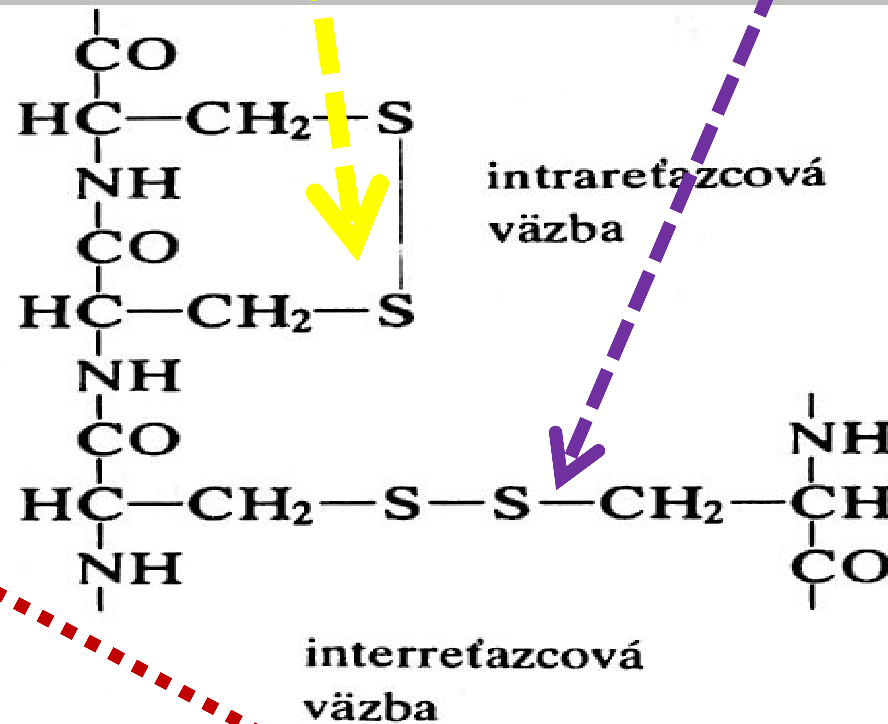
The Interaction of the WOLL with HCl and KOH Solutions (mmol/g) in Dependance on pH Value: 1 – at 0°C, 2 - at 25°C, 3 - at 40°C, 4 - at 50°C

KERATIN Reactivity 1

It is based on the Reactions of the CYSTEIN

CYSTINE can create both INTERMOLECULAR and ITRAMOLECULAR Bonds





Two Cysteines > one CYSTINE

KERATIN Reactivity 2

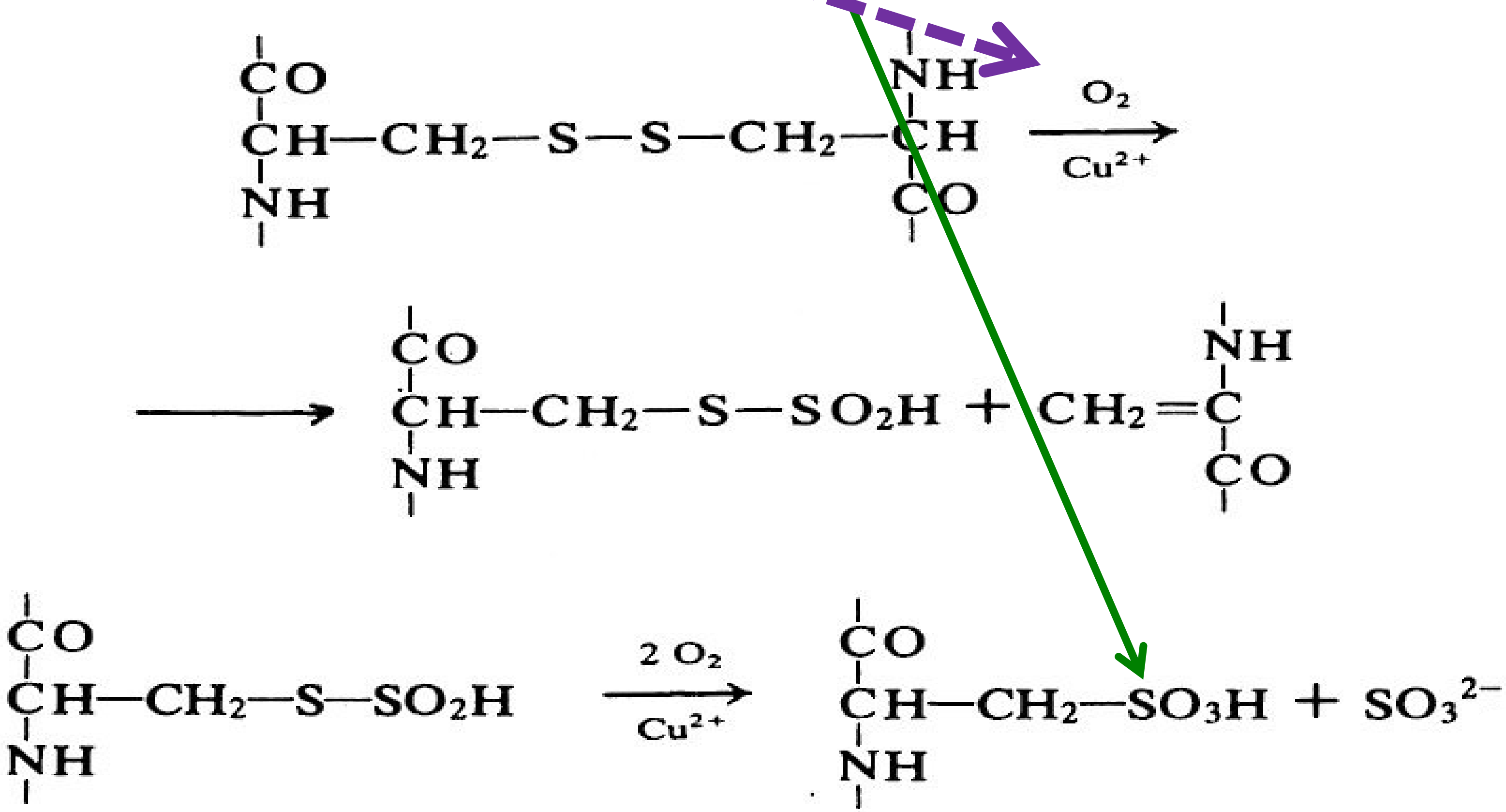
It goes on preferably the

DISULFIDIC BRIDGE (Bond)

- **Hydrolysis of the DISULFIDIC BRIDGE (Bond)**
- **Oxidation**
- **Reduction**

KERATIN Reactivity 3

CYSTEINSULFONIC ACID arises only by Reakction (OXIDATION) –S-S- BRIDGE (Bond) of the CYSTINE



The four Fractions of the KERATIN 1

The Observation of the Reaction of the Wool with Bases (Alkali), Hyhrogensulfite, Formaldehyde and Thioglycolic acid was revealed, that Cystine in the Wool is possible to divide into two primary Parts (A+B) and (C+D) and four secondary Parts(A, B, C, D). The various Behaviour of the particular Parts of the Cystine is explained so, that Cystine is in the Wool bonded with various Amino acids, which have various Sidegroups. The most reactive Part (A+B) je either near to or surrounded by polar Sidegroups, whereas less reactive Part is connected with nonpolar Sidegroups.

The four Fractions of the KERATIN 2

Creation of the new BRIDGES (Bonds)

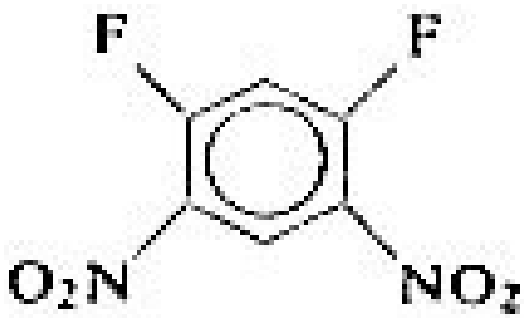
Except for minor Exceptions is the Wool different from another textile Fibres by that, containing Covalent Cross Bonds which connect the main Peptide Bonds of the Backbone. As a Consequence (Result) of this, the Wool is insoluble in the Polar Solvents and is swollen by in such Solvents, having relatively high wet Strength. These Properties can be changed by cleavage of the disulphide Bonds. The wet Strength is decreased in direct proportion to the Number of the ruptured Cross Bonds. The Endeavour is focused for long time already to establish (constitute) a new Cross Bonds, more resistant than disulphide Bonds.

The Constitution of the new Cross Bonds in the Wool has not only scientific Importance, but also a practical one also. So e.g. by the Constitution of the new Cross Bonds is lowered a Tendency to Wool felting power as the Results of the lower elasticity of the Wool Fibres. The Resistance to Alkali and the common clothes Moth is also increased.

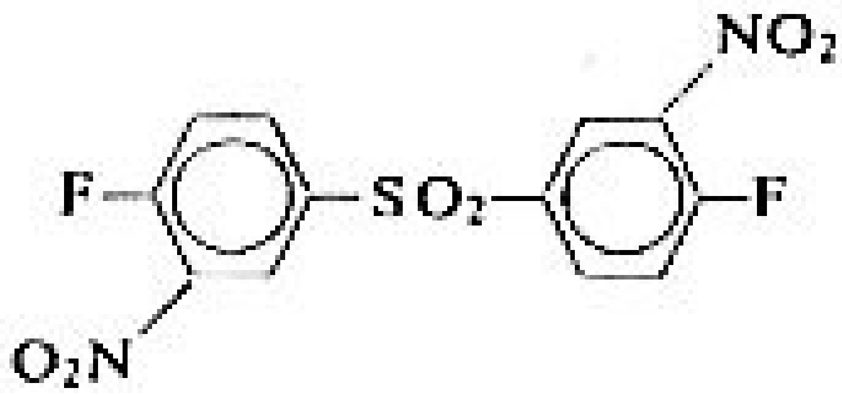
The Cross Bonds can be constituted in the Wool by scission of the disulphide Bonds and their replacing by other, more resistant Bonds. The Way is the Reaction with polyfunctional Compounds, which can react other reactive amino Groups, amide Groups, carboxylic Groups, Phenolic Groups.

KERATIN Crosslinking 1

Crosslinking Reagents

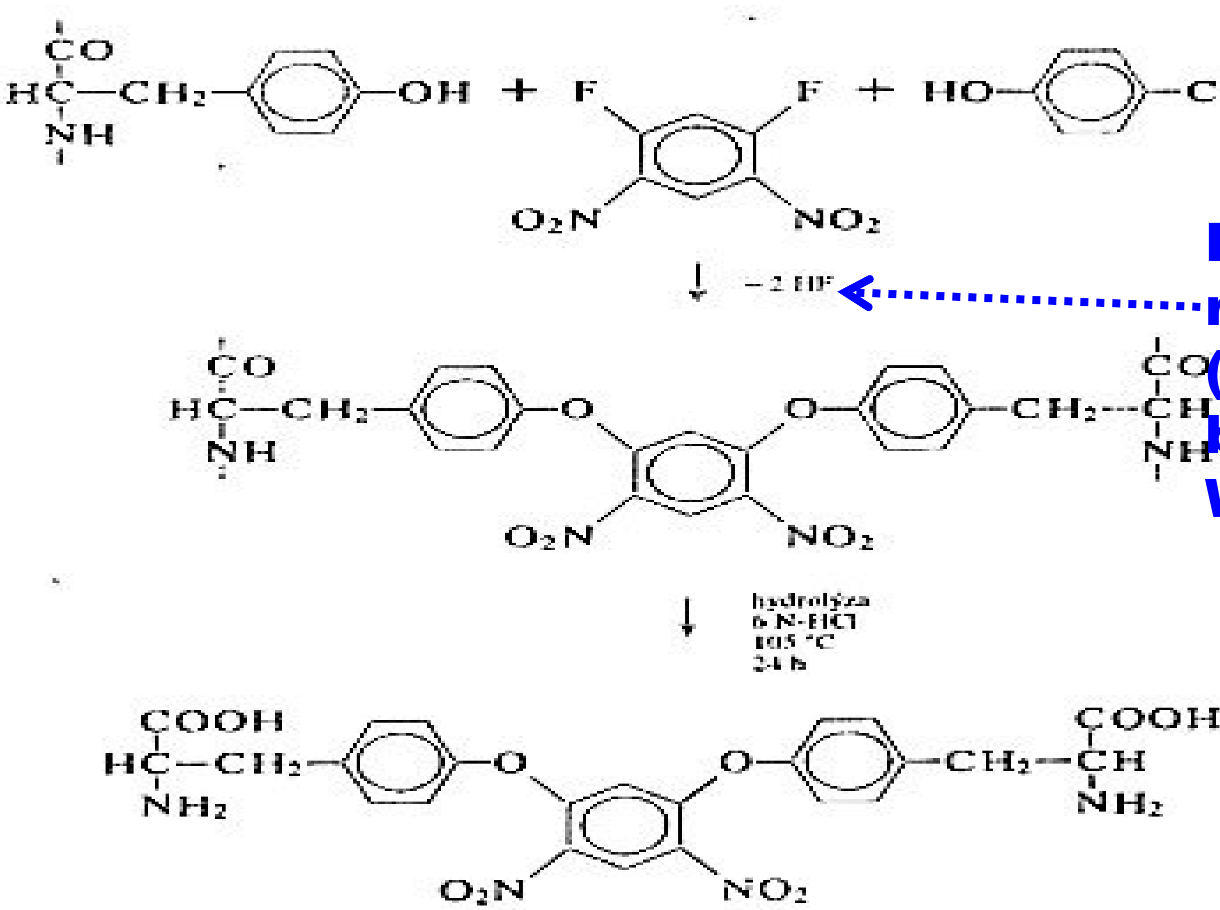


FFDNB



FF-sulfón

KERATIN Crosslinking 2

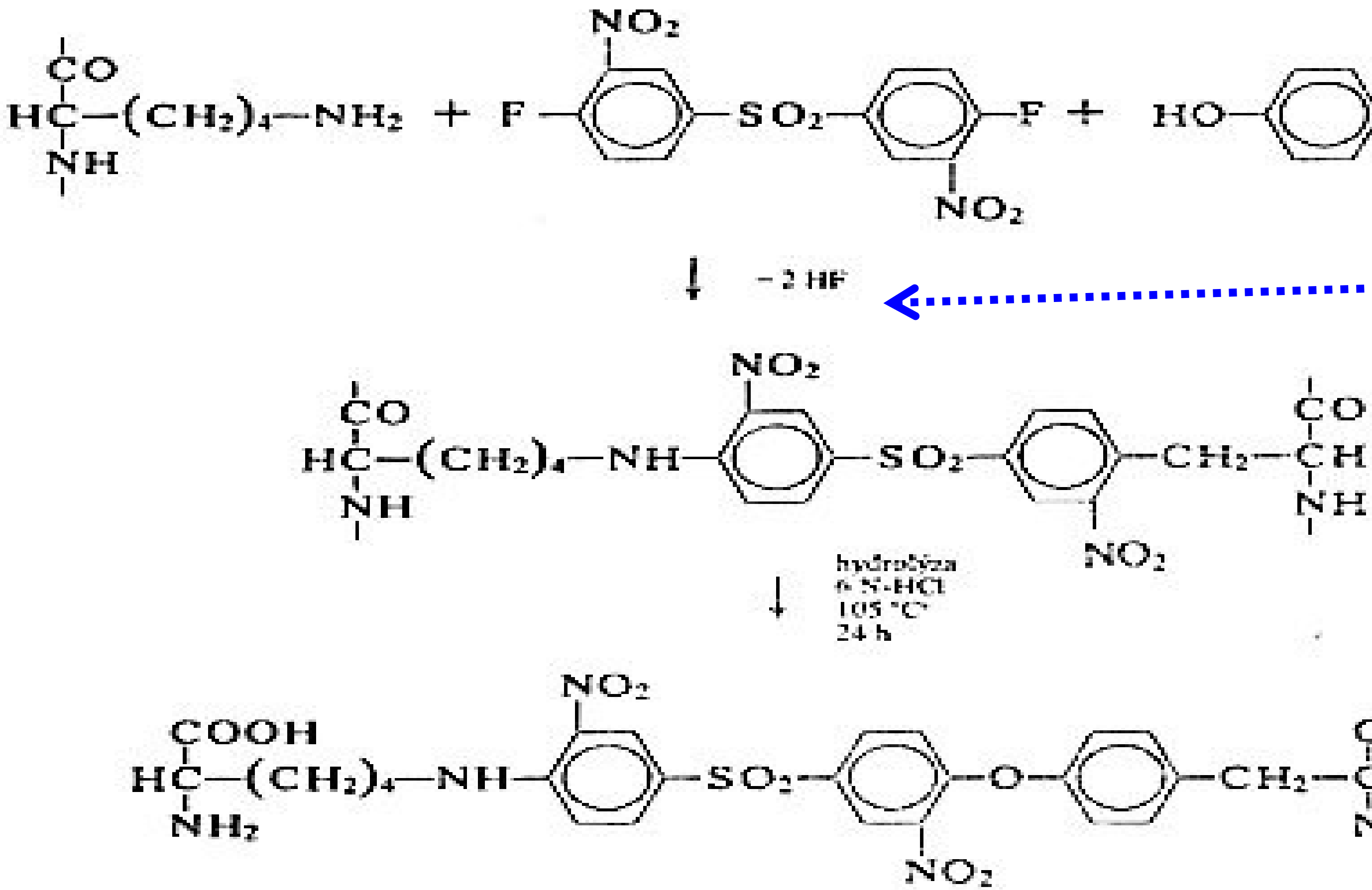


HF must removed (neutralised) by some Way!

O,O'-dinitrofenylén-bis-tyrozín

Obr. 12.15. Vznik symetrickej väzby *O,O'*-dinitrofenylén-*bis*-tyrozínu v keratíne účinkom FFDNB.

KERATIN Crosslinking 3



HF must removed (neutralised) by some Way!
ovat

N,*O*-dinitrodifenylsulfón-lyzin-tyrozin

Obr. 12.16. Vznik zmiešanej väzby *N*,*O*-dinitrofenylsulfón-lyzinotyrozínu účinkom FF-sulfónu na keratín.

KERATIN Crosslinking 4 - FORMALDEHYDE

$$R\text{-}NH_2 + HCHO \longrightarrow R.NHCH_2OH$$

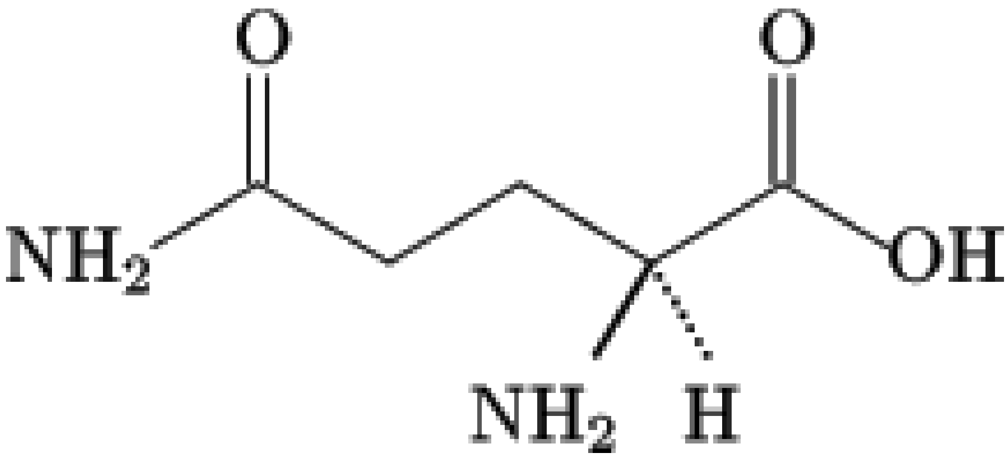
$$R\text{-}NH.CH_2.OH + H_2N\text{-}CO\text{-}R' \longrightarrow R\text{-}NH.CH_2\text{-}NH\text{-}COR'$$

The Optimal reaction Course at Proteins is with 4 % w/w Formaldehyde at 70 °C and pH 3 – 7.

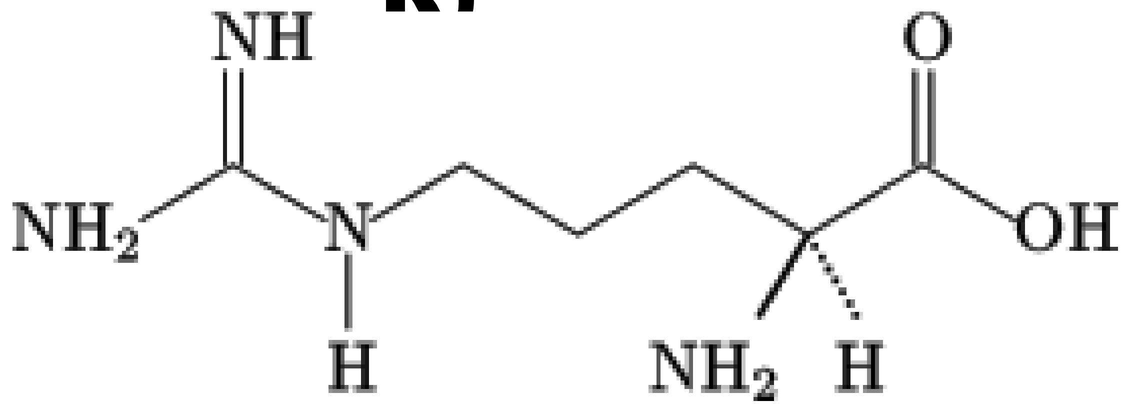
The Cross Bonds in the Wool in the Acid Environment are created by Reaction of the Glutamic acid with the Guanidyl Residue from Arginine. The Cross Bonds created by this way are Resistant to Alkali, but are broken by Acids. The Wool Solubility in Alkalis so treated Wool deceases from approx. 13 % w/w.

AMINO ACIDS presented In the Equations are written as the Functional Groups only! The Formulae are not corresponding to the AMINO ACIDS presented bellow.

Glutamic acid (Glu, E)



Arginine (Arg, R)



KERATIN Reakctions – Grafting of other Monomers

Creation of the POLYMERS in the Fibre

The POLYMERISATION from the Solution or form the Gas Phase creates the Increase of the Wool Weight, Strength and Decrease of the felting Power. The most well known is the Ethylenesulphide, especially in the Presence of various Catalysts (Peroxides, Per sulphate).

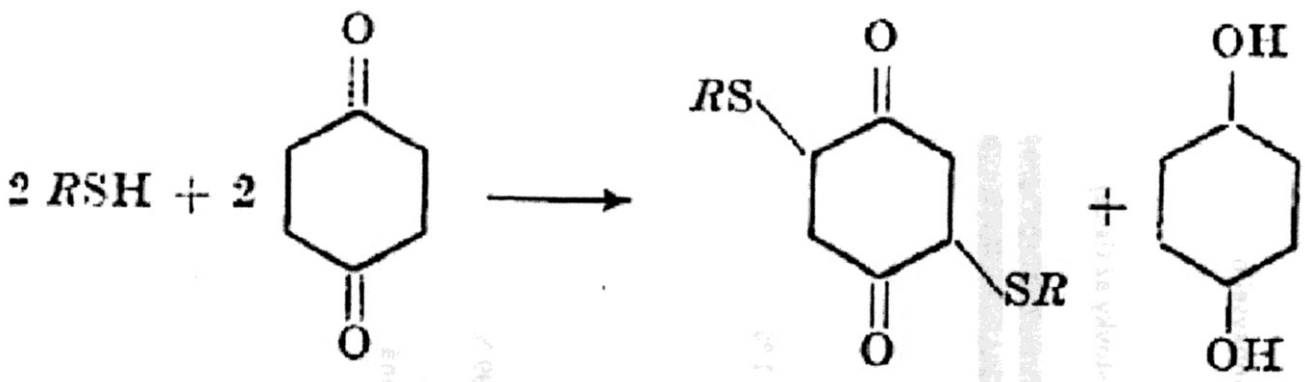
The Ethylenesulphide reduces the Disulphidic Bonds at first and then the POLYMERISATION in the Fibre start and goes on.

The Methylmethacrylate and the Metacrylic acid are also suitable for this POLYMERISATION in the Fibre.

$$R\text{-}CH_2\text{-}SH + n\ (CH_2)S \longrightarrow RCH_2S(CH_2.CH_2.S)_{n-1}.CH_2CH_2SH$$

KERATIN Crosslinking - Quinone

Benzoquinone reacts with the Amino group or with the –SH Group as follows:



The Optimal reaction Course is at pH 3 – 7. Reaction with **Quinone** is employed for the Wool increase of Strength since a long time ago. The **Quinone** treated Wool is more resistant to chemicals and has lower tendency to the felting Power. The Tensile Strength Increase is higher than using other Reagents able to create the Cross Bonds. It is explained by the easy ability of the **Benzoquinone** polymerise in the Wool.

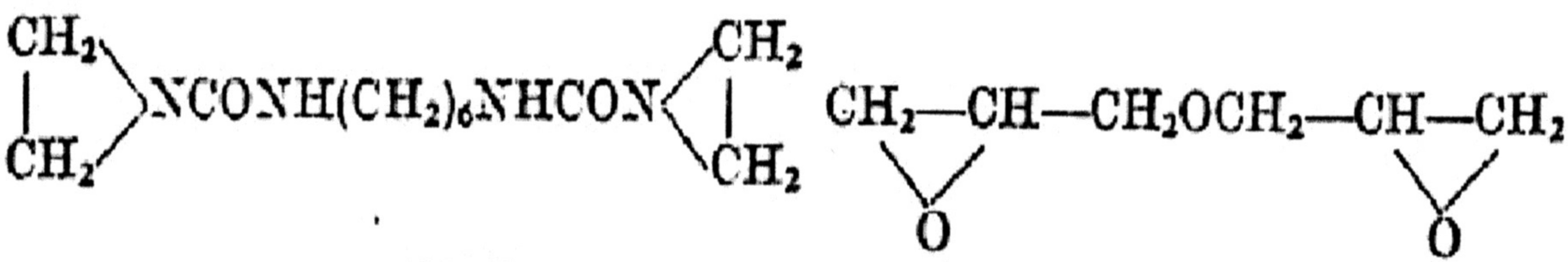
KERATIN Crosslinking – Polyfunctional Alkylation Reagents 1

Chlormethylethers react with the Wool in the organic Solvents Medium and creates the Cross Bonds.

The Reaction goes PROBABLY as follows:

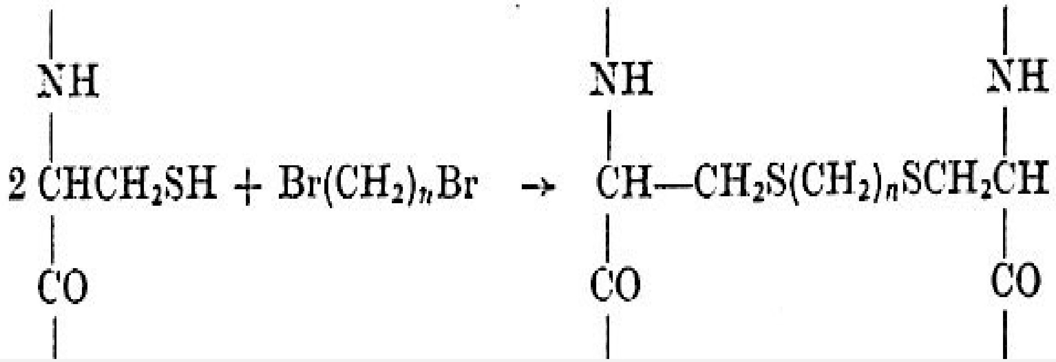
$RNH_2 + ClCH_2OCH_2Cl > RNHCH_2OCH_2Cl + R_1COOH > RNHCH_2OCH_2OOCR_1$

The other bifunctional Reagents, e.g. Ethyleneimis, 1,3-difluoro-4,6-dinitrobenzen, bisepoxides, were tested also:



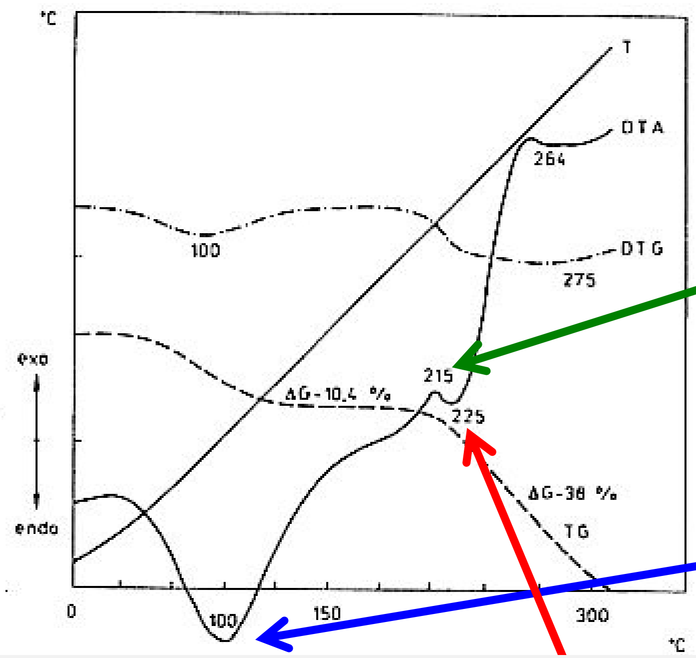
It was revealed by this that in the acetylated Wool cannot be created the Cross Bonds, whereas in the esterified Wool it was possible.

KERATIN Crosslinking – Polyfunctional Alkylation Reagents 2



So modified Wool is much more resistant to Bases, Acids, Oxidising Agents a Reduction agents

Phase Transitions of KERATIN 1



α Keratin (**Coil**) > β Keratin (Folded (**Pleated**) Sheet)

Evaporation of the Water

DTA and TG Curves 100 % w/w of Wool heating up to 300 °C in Air

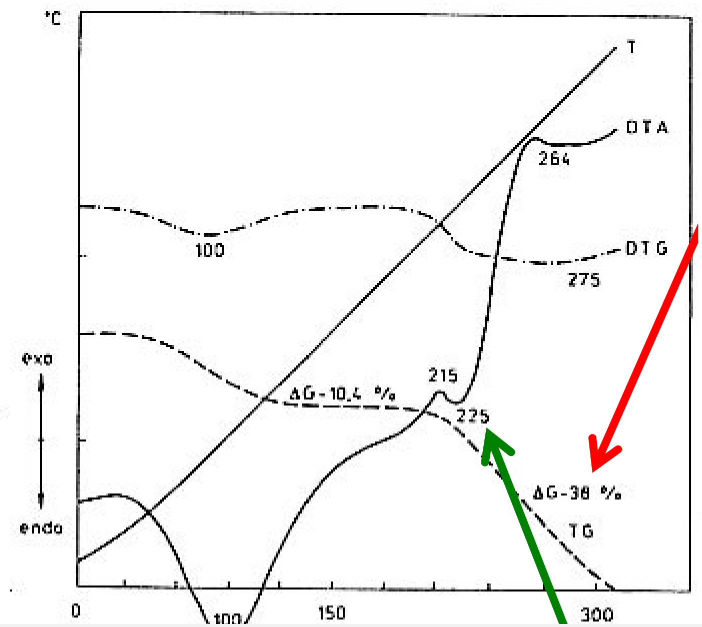
The greatest Decrease of the Phase Transition Temperature of KERATIN goes with Increase of the Water Content in the interval 12 – 17 % w/w.

The Phase Transition Temperature of the α KERATIN goes in Temperature Region 210 – 213 °C. The Phase Transition Temperature of the enlarged (strained) β KERATIN Wool Fibre (β **Keratin (Folded (Pleated) Sheet)** into Amorphous KERATIN is in the Temperature Region 220 – 225 °C.

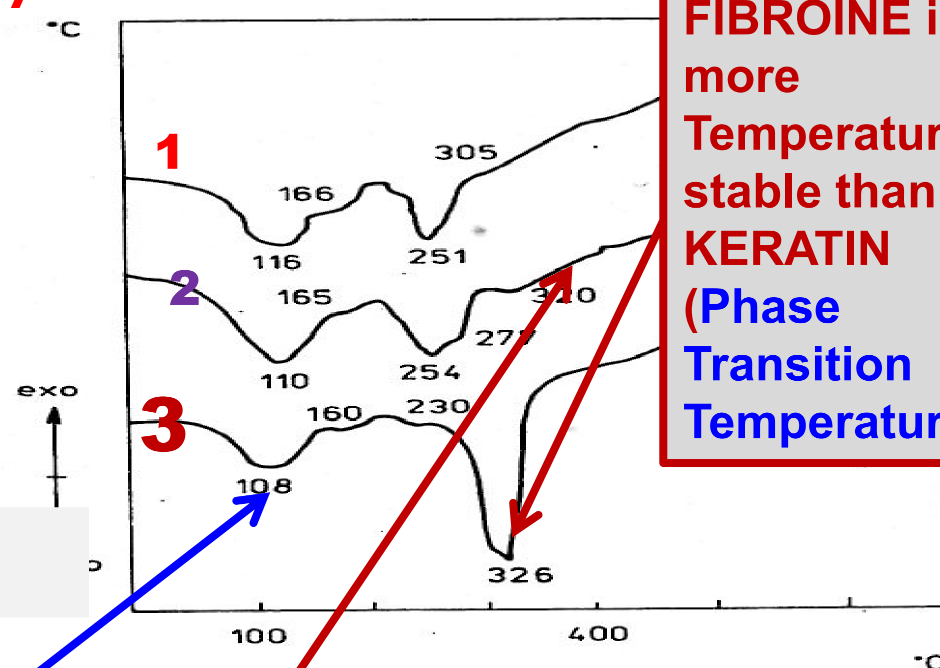
It is clear from this, that the β Keratin (Folded (Pleated) Sheet is more resistant to the Influence of the Temperature.

Phase Transitions of KERATIN & FIBROIN 2

On Air > OXIDATION > Burning already at approx. 230 °C



DTA and TG Curves 100 % w/w of Wool heating up to 300 °C in Air



FIBROINE is more Temperature stable than KERATIN (Phase Transition Temperature)

α Keratin (**Coil**) > β Keratin (Folded (**Pleated**) Sheet)

DTA Curves in the NITROGEN: 1) Human Hair, 2) Mohair Wool, 3) Natural/Genuine silk

Evaporation of the Water

Decomposition in NITROGEN is only at higher Temperature and is more slowly

Keratin Colouring

The so called REACTIV COLOURS creates covalent Bonds with the functional Groups of Keratin.

The REACTIV COLOURS can either ACIDIC or BASIC.

The Decrease of the Reactivity to the ACIDIC REACTIV COLOURS is achieved by Decrease of the –NH_2 Groups in the Side Chains of the Amino acids. The chemical Reactions are as follows:

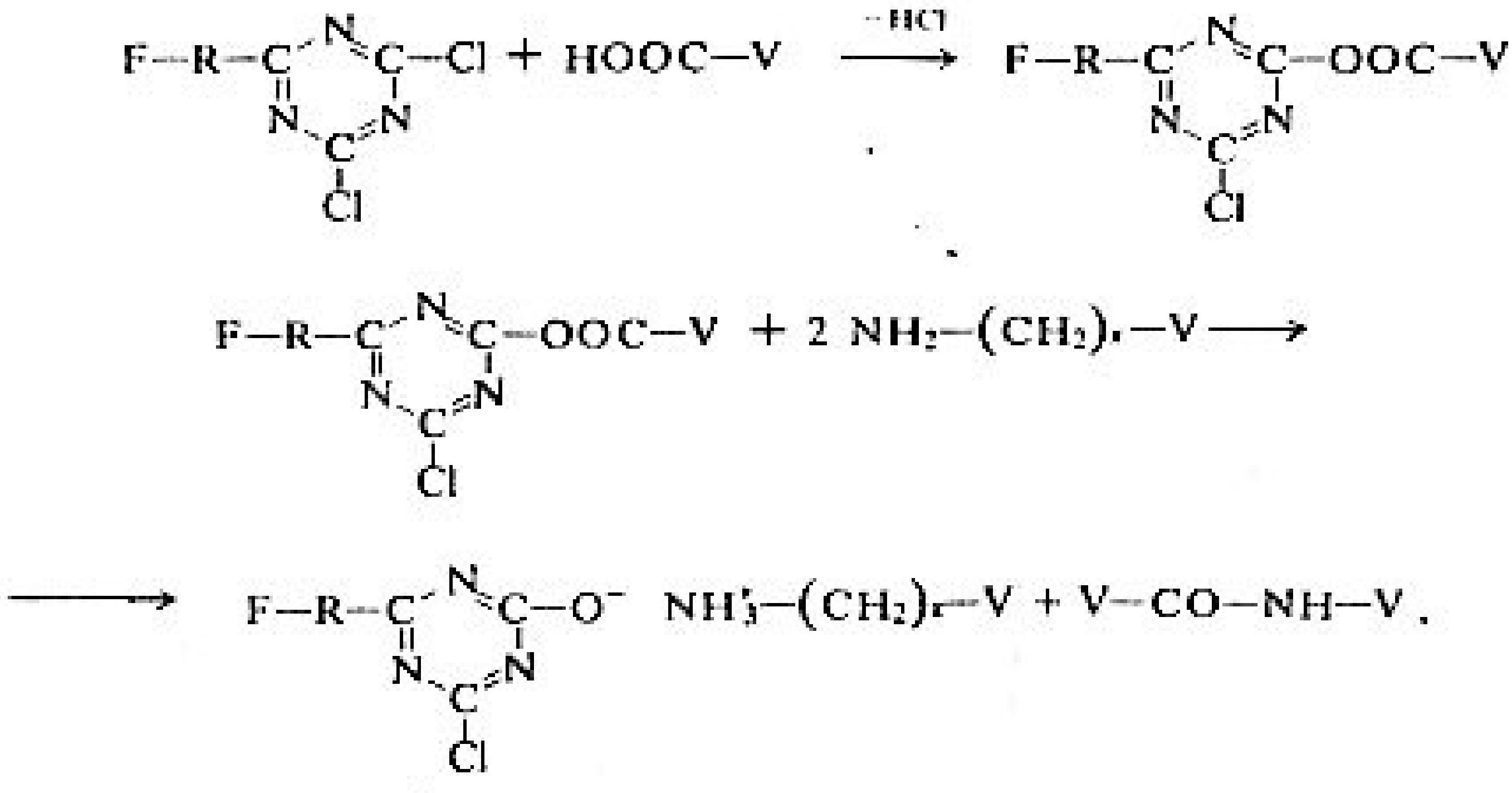
$$-V-NH_2 + HNO_2 > -V-OH + N_2 + H_2O$$

$$-V-NH_2 + (CH_3CO)_2O > -V-NH-CO-CH_3 + CH_3COOH$$

The Decrease of the Reactivity to the BASIC REACTIV COLOURS and so to INCREASE the Affinity to the ACIDIC REACTIV COLOURS is achieved by-ESTERIFICATION of the –COOH Groups (Asparagic acid, Glutamic acid) by Alcohols, Epoxides, Alkylhalogenides, Diazomethane, Alkylsulphone acid.

The Quantity of the esterificated –COOH Groups decreased accordingly with the MW of the Alcohol. So the MeOH gives 67 %, but propanol gives 54 % only.

REACTIV COLOURS for KERATIN



Preservation of Keratinu against to clothes Moth

Pest Hindrance of Wool and Furs against to clothes Moth are employed either Substances without bond to the Keratin Molecules or the Substances directly bonded to the Keratin Molecules.

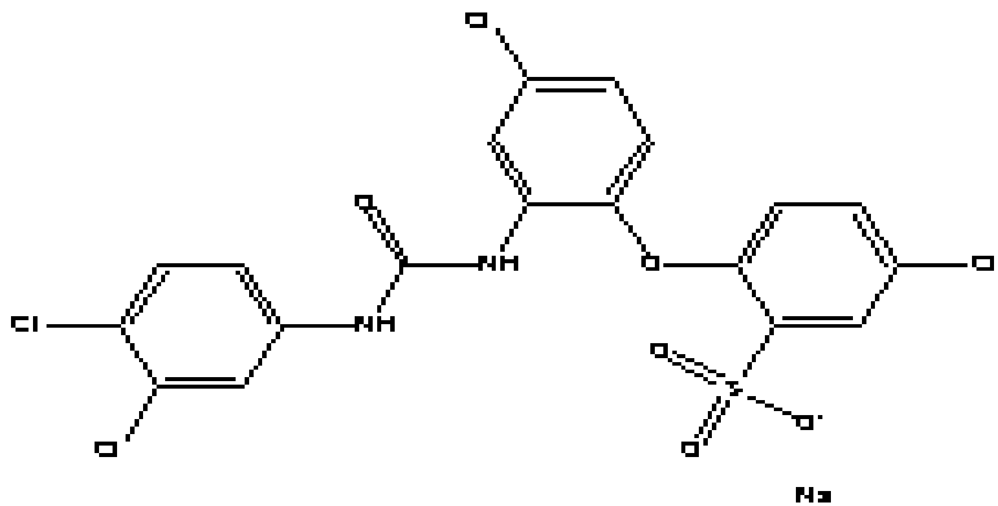
These bonded Substances are usually Chlorine containing Compounds, e.g. dichlorodiphenyltrichlormethan. This Compound is bonded to Keratin irreversibly and is impossible to extract it. This Bond is also hydrolytic stable.

There are also other Possibilities to get permanent Resistance to clothes Moth. The Situation is changed from time to time, because new Data regarded to the Danger to Humans.

An well known Example is so called DDT (Substance without bond to the Keratin Molecules), which was banned years ago already.

Preservation of Keratinu against to clothes Moth – an EXAMPLE of the Reactiv (PERMANENT)

Substance directly bonded to the Keratin Molecules



MITIN FF

Sheep's Wool - Structure of the KERATIN Part

- It can be in two Chains' Secondary Structures:
  - α **Left-handed Helix**
  - β **Folded (Pleated) Sheet**

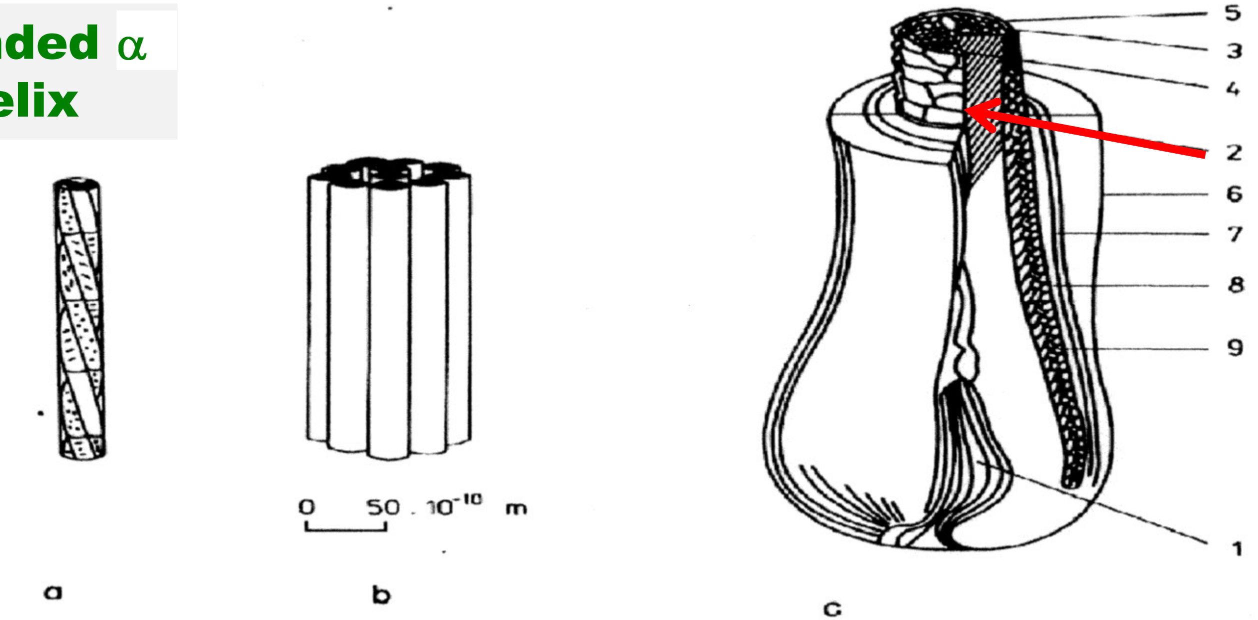
❖ α **Helix** is changing during elongation at higher Temperature (approx. 85 °C) to β **Folded (Pleated) Sheet**

❖ β **Folded (Pleated) Sheet** forms the INTERFIBRES' PART between α **Left-handed Helixes** and their Aggregate (Complex) creates the **MACROSCOPIC Sheep's Wool Fibre**

- **Sheep's Wool Fibre** is so **Composite Structure, where are some Components and cross Design (Bonds between particular Macromolecules)**

Sheep's Wool - Structure Hierarchy 1

Left-handed α triple Helix

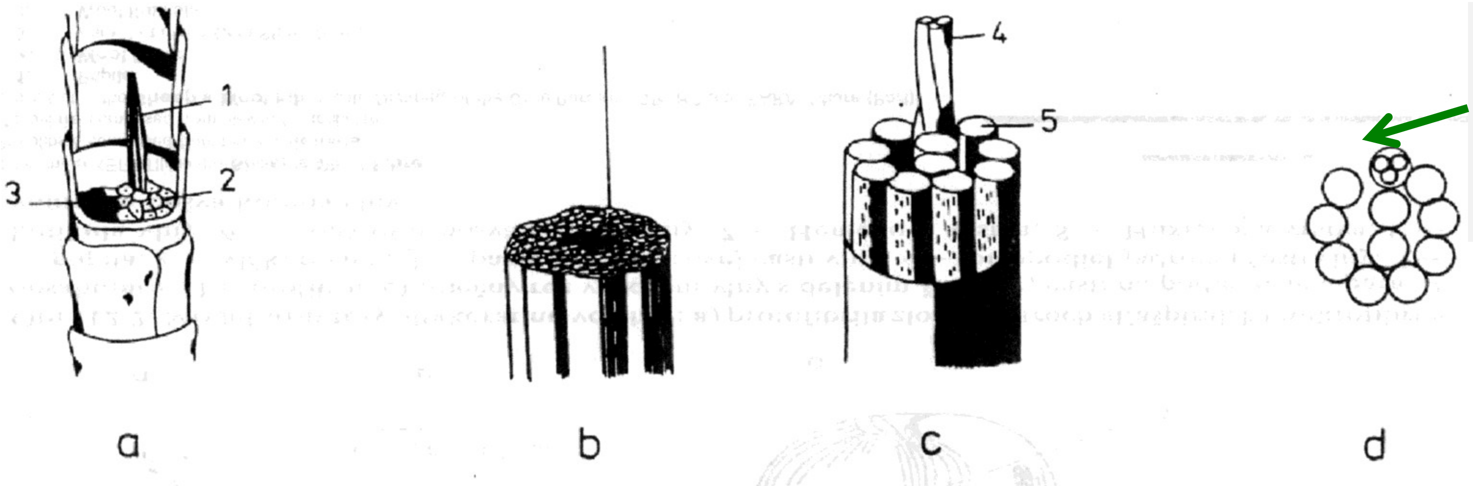


The Model of the a KERATIN in the Sheep's Wool Fibre:

a) Protofibril composed from **three α Helixes**
b) Microfibril composed from eleven Protofibrillas
c) Cross Cut of the **Sheep's Wool Fibre** with Dividing of the Core Part into ORTHO and PARA Share (Part):

1. Papilla
2. **Wool Fibre**
3. Para Part of the Core Share (Part)
4. Wool Cuticle
5. Outer Sheath of the Wool's Root
6. Henley's Layer
7. Huxley's Layer
8. Inner Sheath of the Wool's Root

Sheep's Wool - Structure Hierarchy 2



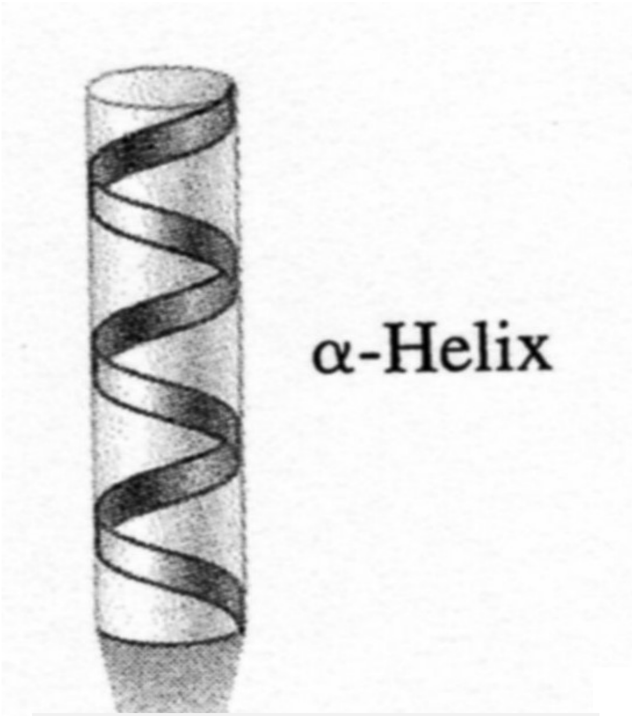
Left-handed α triple Helix

The Model of the Sheep's Wool Fibre:

a) Wool Fibre
b) Fibrilla (Fibril)
c) Microfibril
d) Microfibril Cross Cut

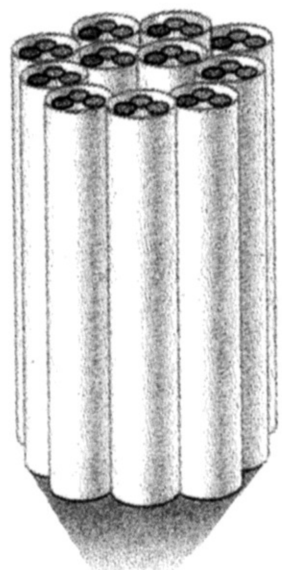
1. Cortex Cell
2. ORTHO Cortex
3. PARA Cortex
4. Left-handed α triple Helix
5. Protofibril

Sheep's Wool - Structure Hierarchy 3



Left-handed α Helix

Protofibril



Microfibril

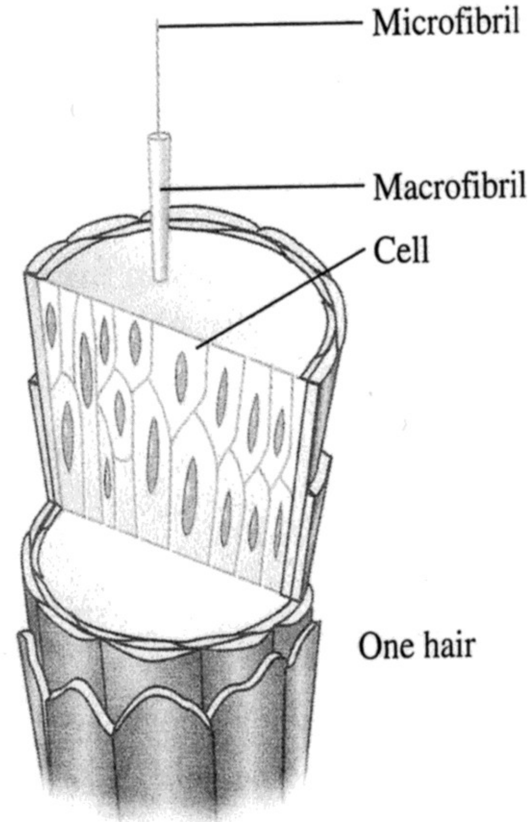


Figure 18.6 Structure of the α-keratins. These proteins are assemblies of triple-helical protofibrils that are assembled in an array known as a *microfibril*. These in turn are assembled into macrofibrils. Hair is a collection of macrofibrils and hair cells.

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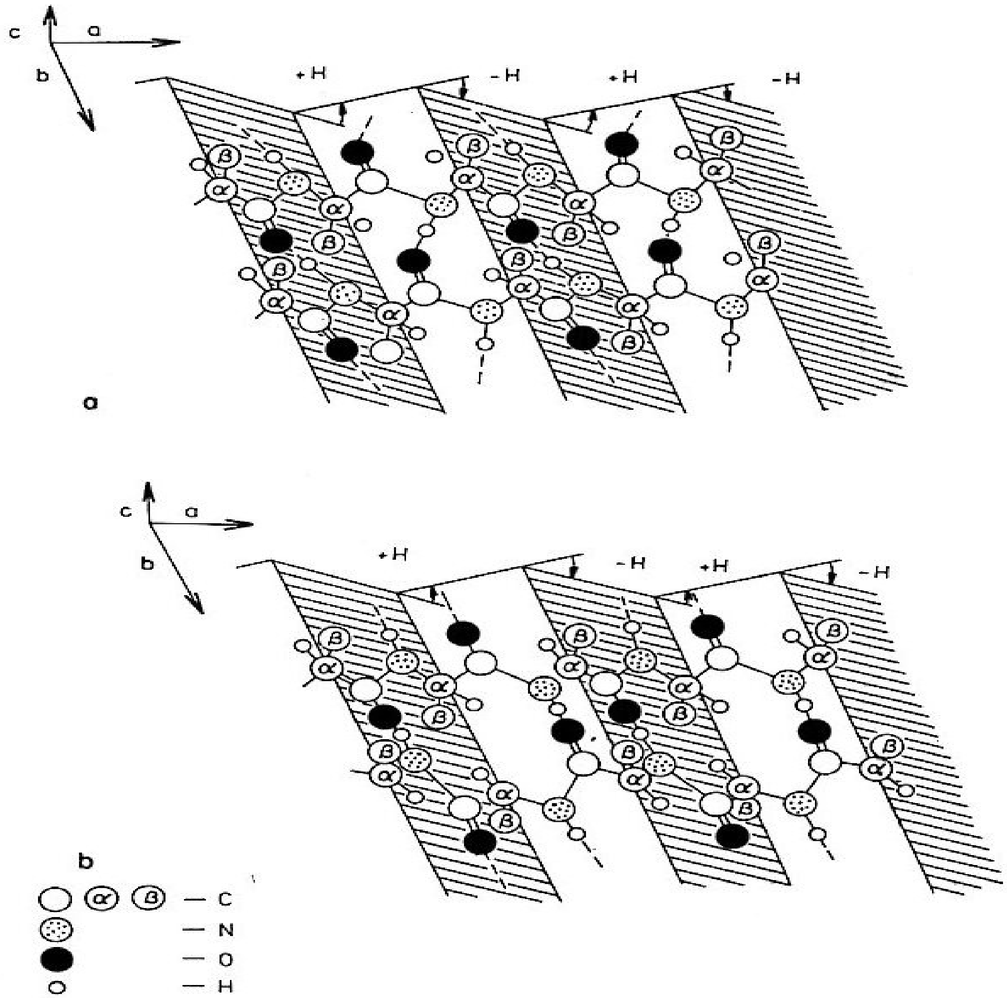
Sheep's Wool – Fibre's Morphology

- **Outer Sheath = CUTICLE** = cell Wall which creates Scale Surface of the Fibre oriented Points (Darts)
- **Inner Sheath = CORTEX** = cortical Part formed by Fibres oriented in the Fibres Direction
- **Pith = Medulla** = it cerates inner Part of the Fibre and is divided into closed Air Bubbles **> it is the Reason of the Thermal isolation properties Part of the Wool**

Sheep's Wool - β Keratin (Folded (Pleated) Sheet)



Schema showing the Protein's β Keratin (Folded (Pleated) Sheet) Structure

a) PARALEL arrangement

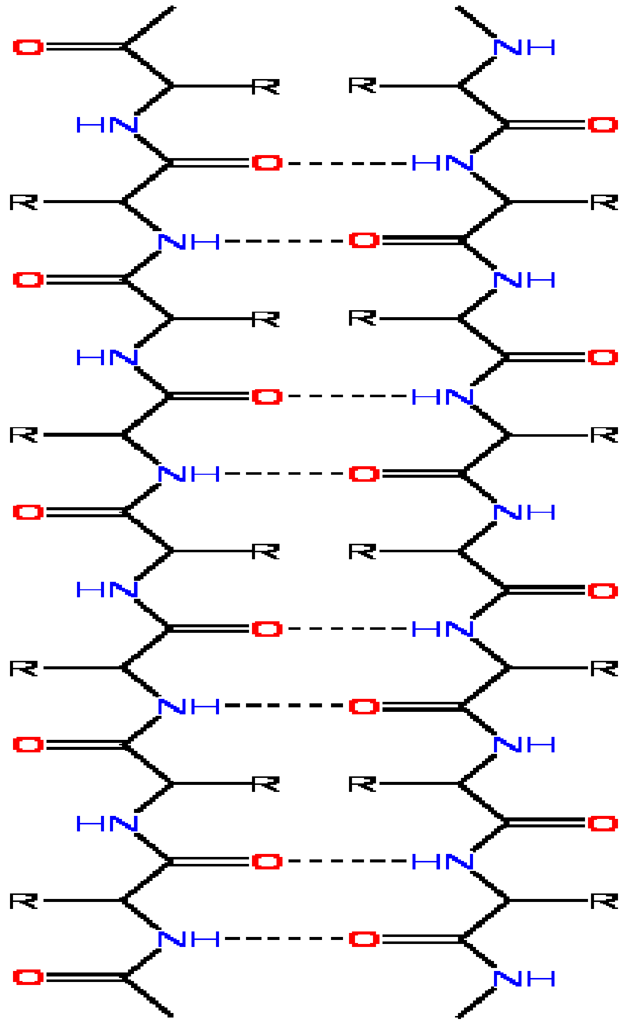
b) ANTIPARALEL arrangement

The Backbone is bonded by the Covalent Bonds in the a Axis Direction.

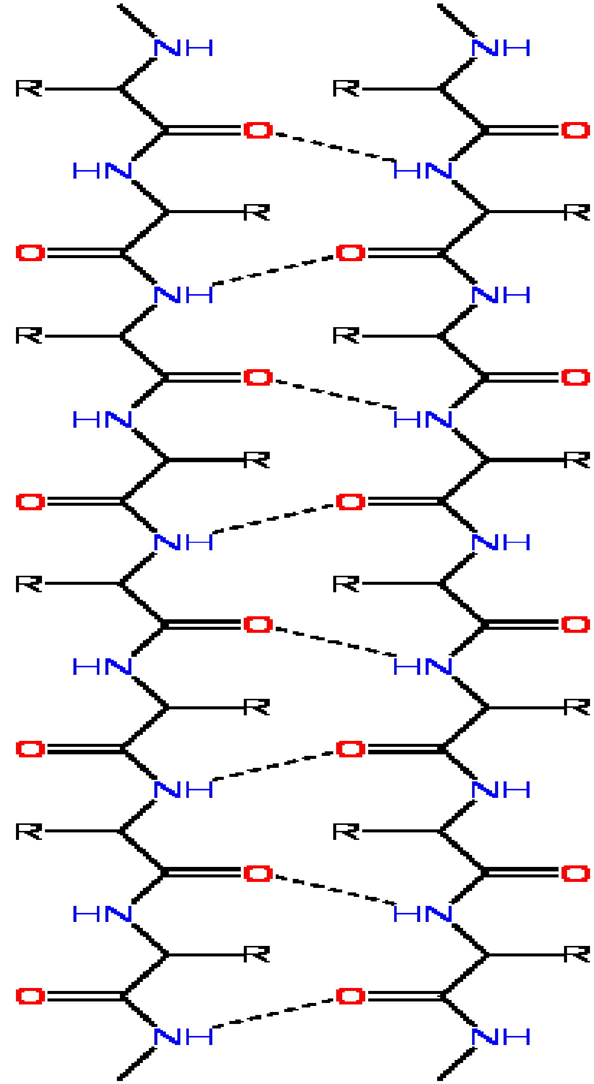
The Backbone is bonded by the Hydrogen Bonds in the b Axis Direction.

The Backbone is bonded by the Wan der Waals Forces in the c Axis Direction.

Sheep's Wool - β Keratin (Folded (Pleated) Sheet)



ANTIPARALEL arrangement

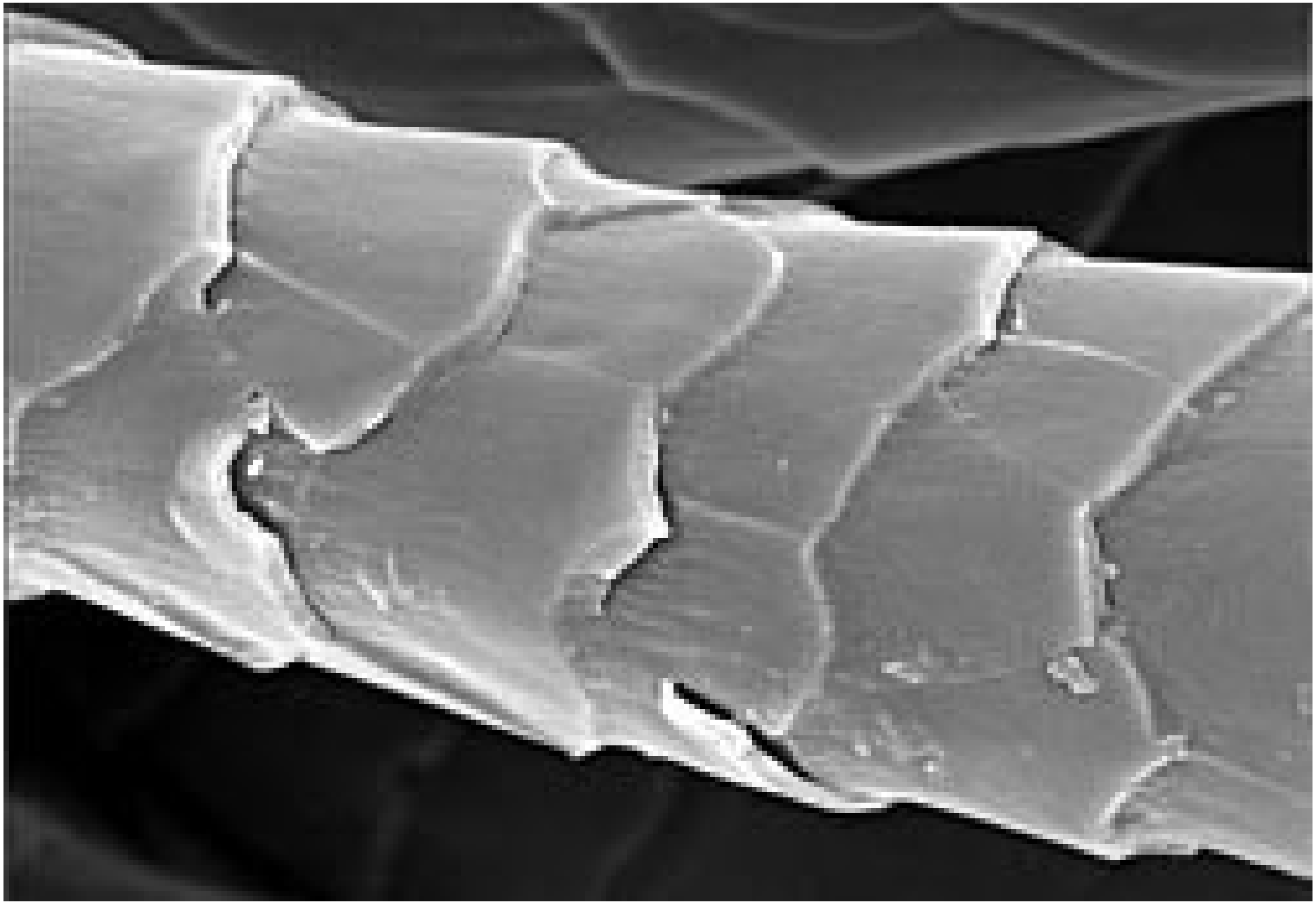


PARALEL arrangement

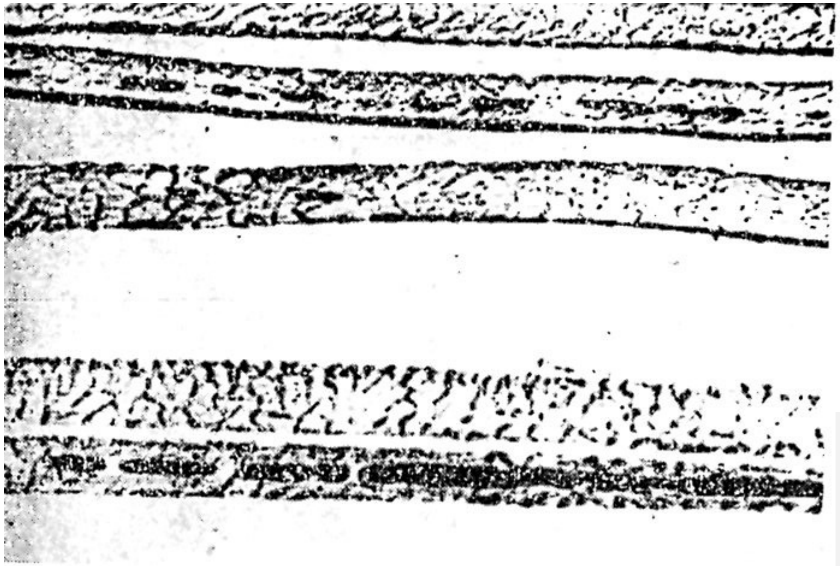
Sheep's Wool - Composition

Component	% w/w	Remark
MAIN FIBRE (KERATIN)	Rest up to 100 % w/w	
SHEEP'S FAT (LANOLIN)	5 – 15	Acid Esters Mixture (it is stated up to 36) with Alcohols (it is stated up to 23 aliphatic), Sterols (mainly Cholesterol)
Impurities	5 – 20	
Plant Rest	1 – 5	
Moisture	8 - 12	

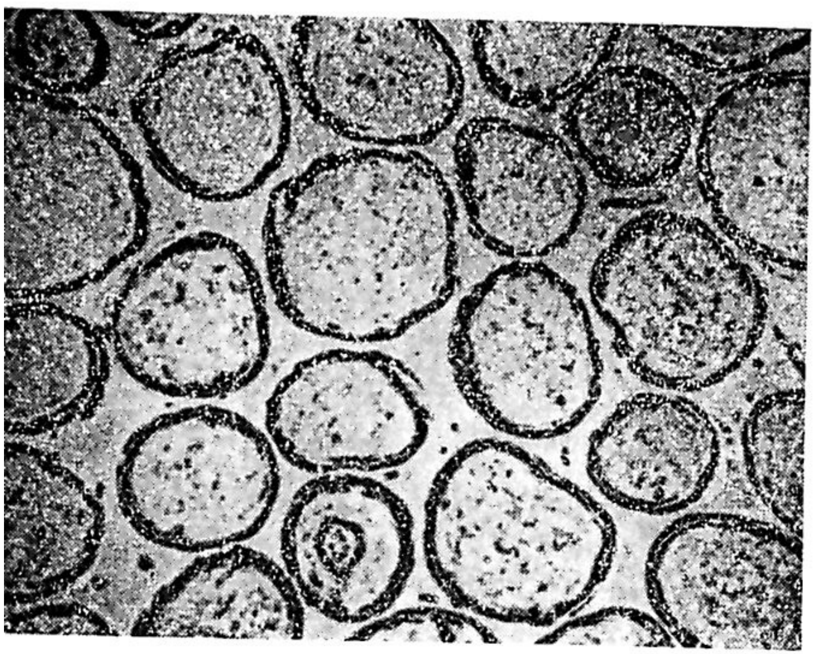
Scale like Structure of the Sheep's Wool



Optical Microscop, it is not given, which Animal is the Source

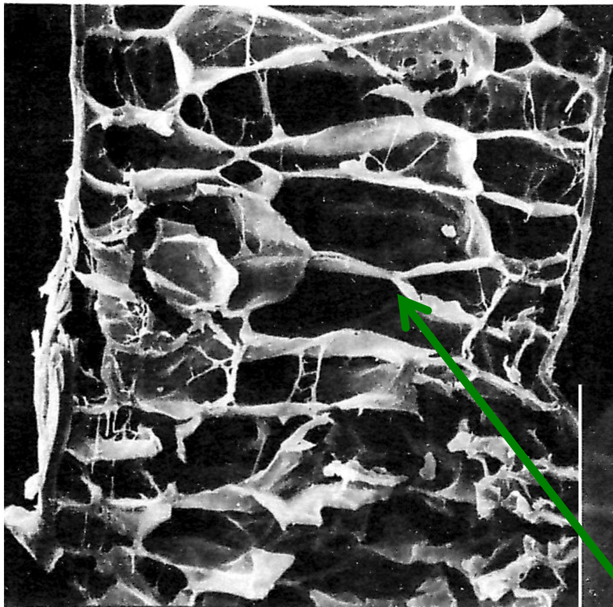


Wool Magnificatin 180 x

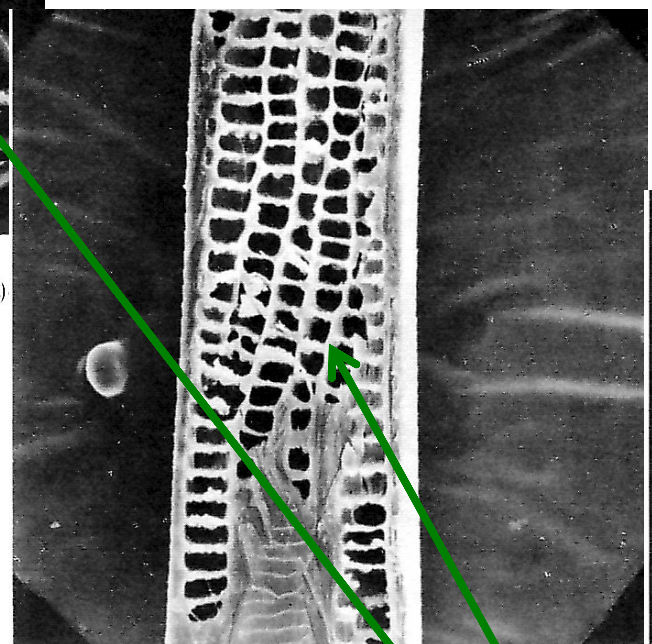


Wool Cross Cut Magnificatin 500 x

Inner Structure Sheep's Wool and other Animals' Hairs



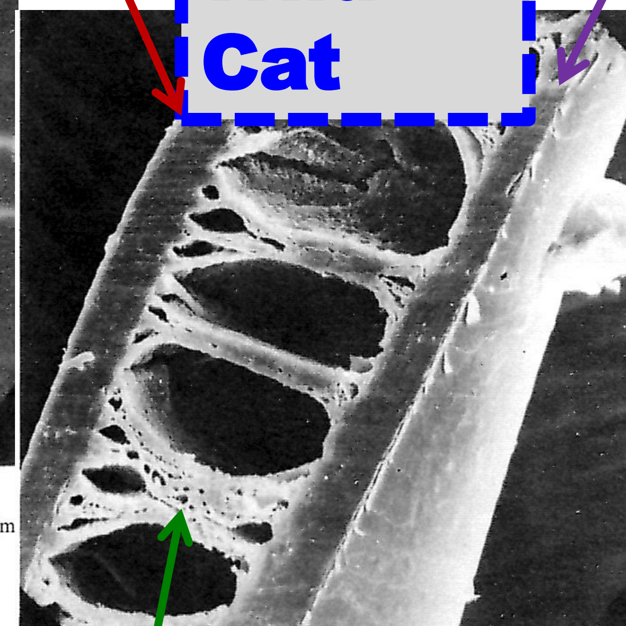
Sheep



g

Obr. 1/14. Podélný řez některých chlupů s výrazou dření (medullou) (m
g – králík domácí (400krát); h – hříbě (1 000krát);

Rabbit



e

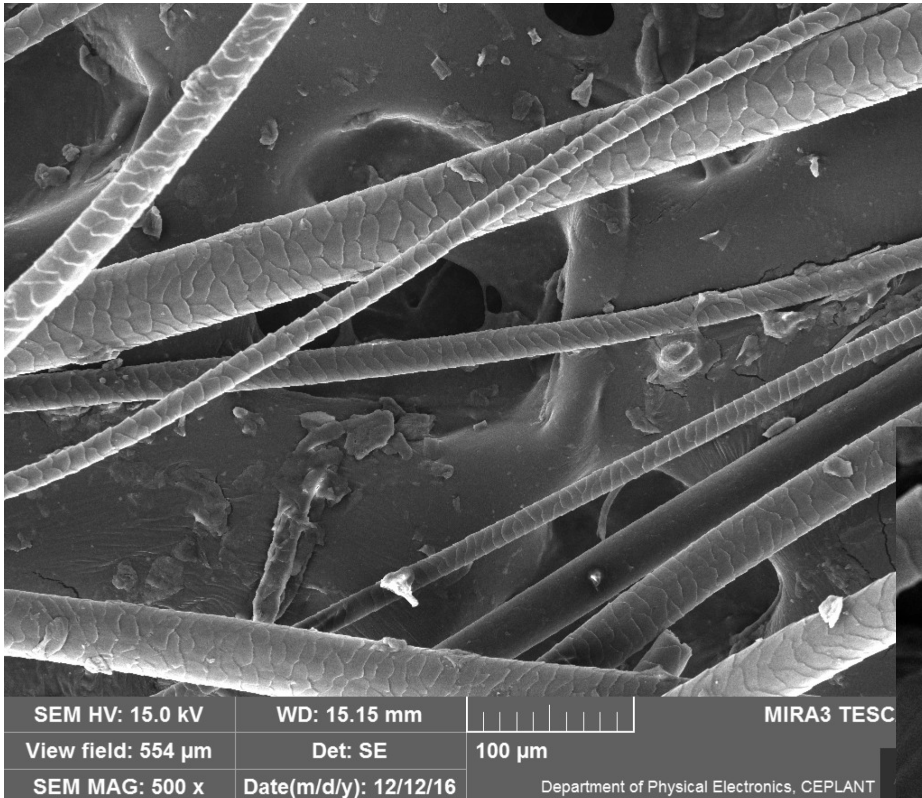
Obr. 1/14. Pod lný řez některých chlupů s výraznou dření (medullou) (m
e – kočka di oká (600krát); f – ocelot (1 000krát);

UNDERHAIR is the fine, thick, usually unmarked coloured and functions as the ISOLATION LAYER. It is constituted from the fine, dense grown short Fibres. It forms the typical structure, called WOLL of some domestic or wild Animals (Sheep, Camel, Rabbit, Lama etc.). The UNDERHAIR function is the thermal Insulation during both Summer (Heat) and Winter (Cold).

GUARD HAIR is the long, rough, straight Hair, which overhangs UNDERHAIR and functions as the Guard. GUARD HAIR is of various Length and thick and is carries out the typical Colour of the particular Animal's Colour.

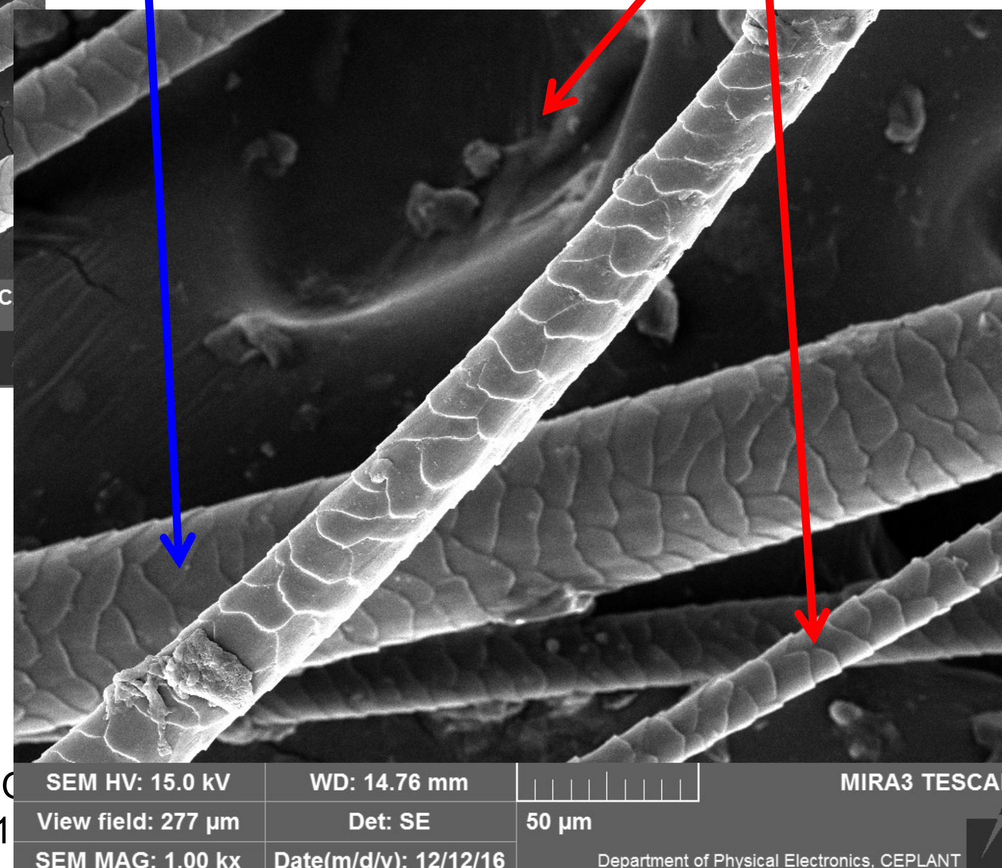

Cat Male Hugo is the HOME CAT, but
well hairy for the outdoor Life

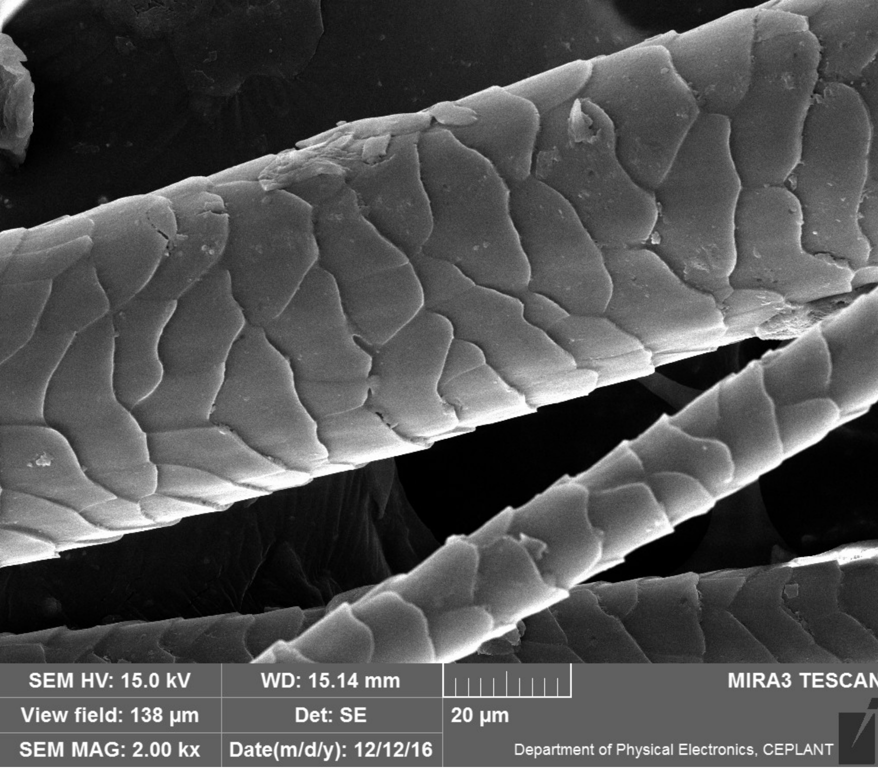
Hugo’s Hair



GUARD HAIR

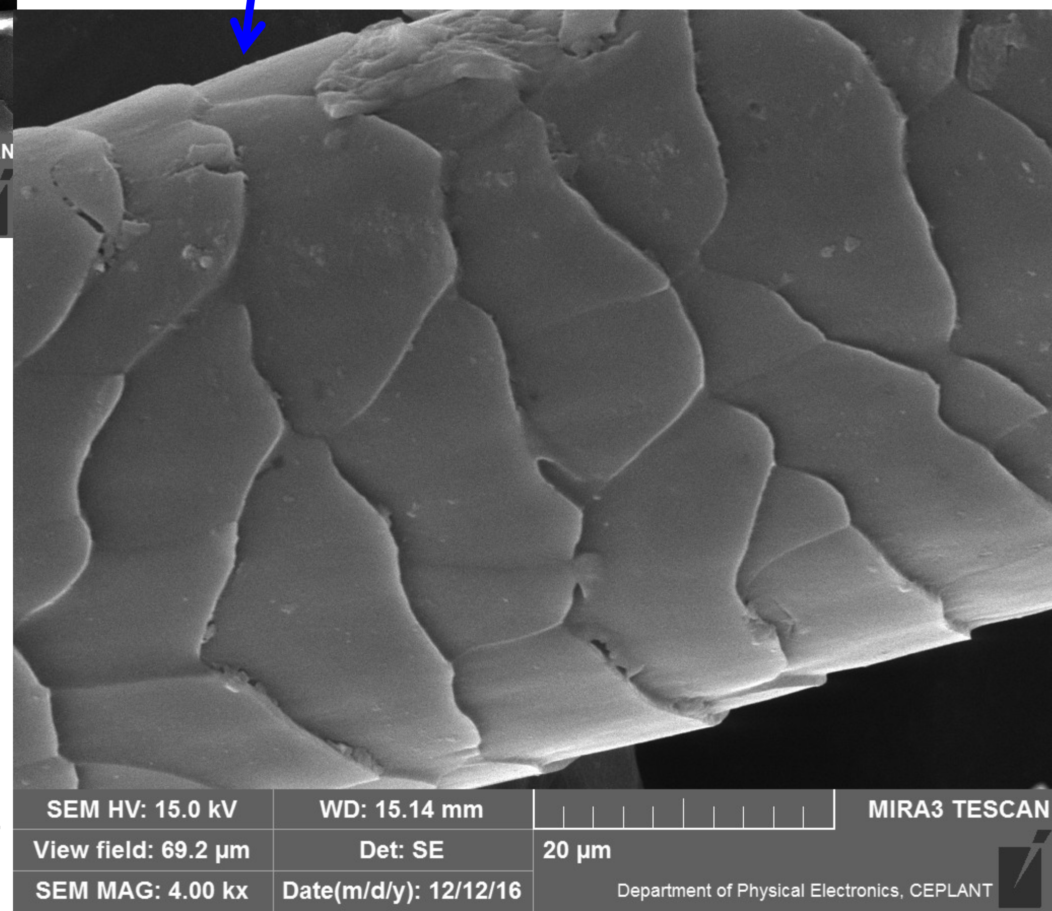
UNDERHAIR





GUARD HAIR

Hugo’s Hair



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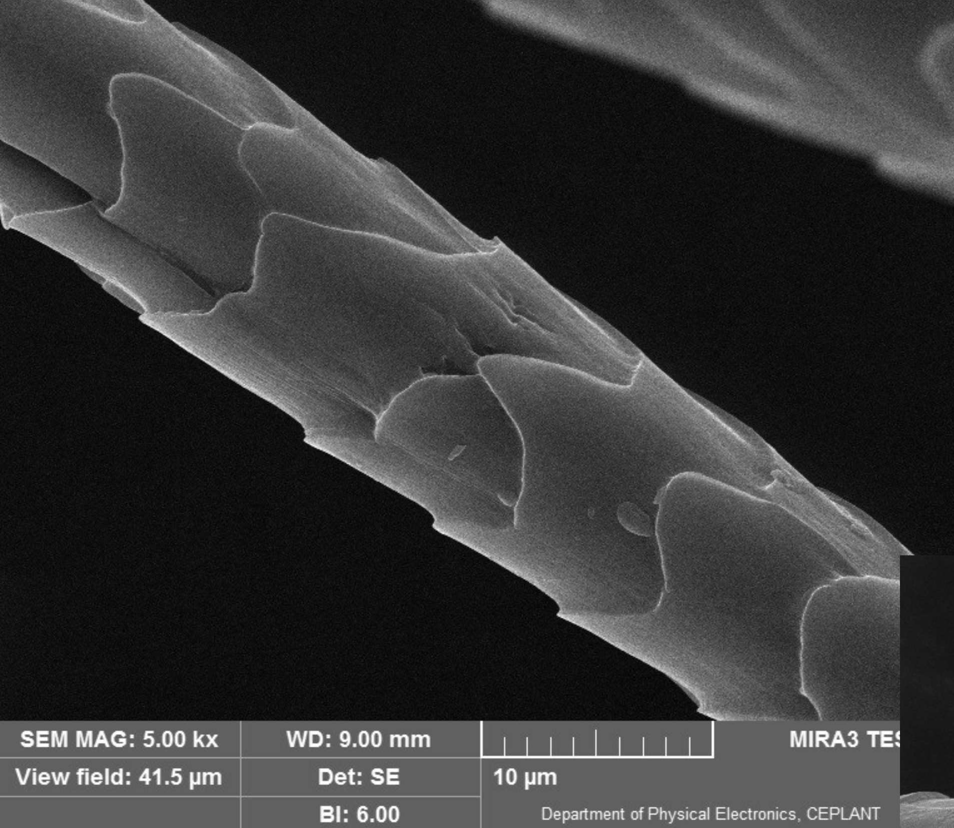
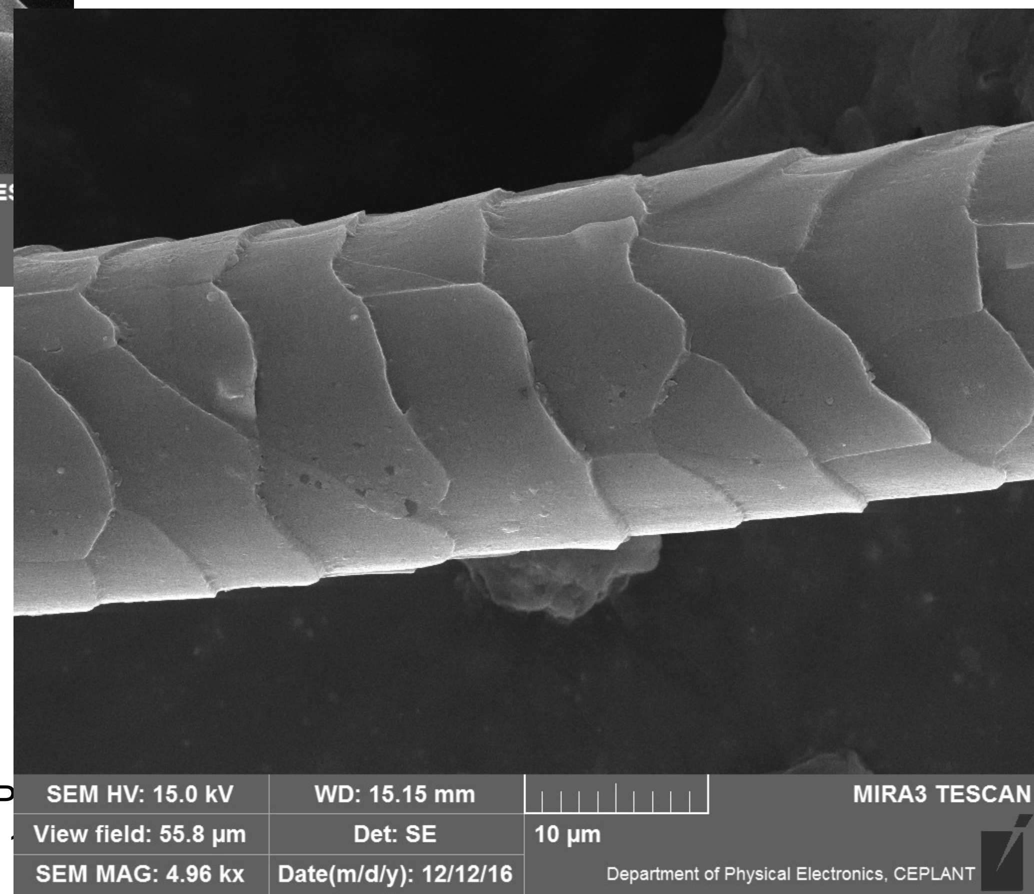
NATURAL



Hugo's Hair UNDERHAIR

Rabbit – unknown Origin



Main Sources of the KERATIN Fibres

- **Sheep**
- **VICUNA**, that is ***Lama vicugna*** (***Vicugna vicugna***) it is the wild Species of Llama
- **Lama pacos**, that is **Alpaka** – domesticated Llama **with silky Fleece**
- **Mohair** from angora **Goat**
- **Angora Rabbit**
- **…………………**

From the Sheep's Wool to the Felt

1. **NONWOVEN TEXTILE**
2. **Wet Felting**
3. **Needle Felting**

- **Sheep's Wool is very suitable for the Felting, because having small scale KUTIKULA**

Fibre's „Thickness" dtex

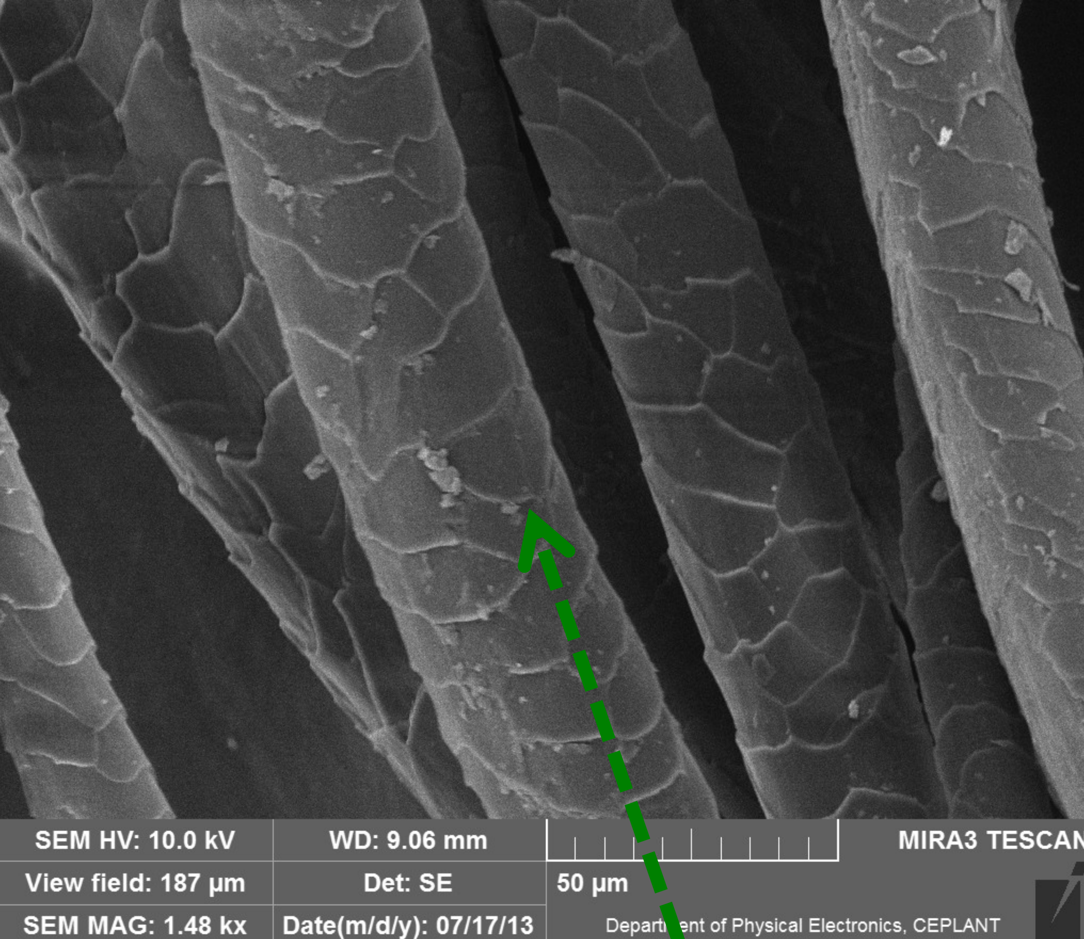
- **dtex – it is not any REAL THICKNESS!**
- **dtex** - it is the Mass of the 10 km of Fibre expressed in Grams
- The English Unit is ***denier***, what is the Mass of the 10 000 yards (approx. 9000 m) of Fibre expressed in Grams
- **The Units dtex** and **denier** are used for Expression of the Textile Fibres Strength. Its Strength is measured as the Force (N), not as the Mechanical Stress (N/m^2)
- So called „**Textile Strength**" is then expressed as (in) **cN/dtex** (***cN/denier***)

Sheep's Wool Strength

Fibre	Tensile Strenght (cN/dtex)	Elongation at Break (%)	E-Modulus (N/tex)	Moisture uptake (%)
Woll	0,90 – 2,18	25 – 35	0,34	16 –18
Polyester	4,00 – 6,50	15 – 40	9 –11,5	0,5 – 0,8
Viscose	1,80 – 3,50	15 – 30	5,4	26 – 28

The Source don't get Information, if these Values are for Measurement „At dry" or „At wet".

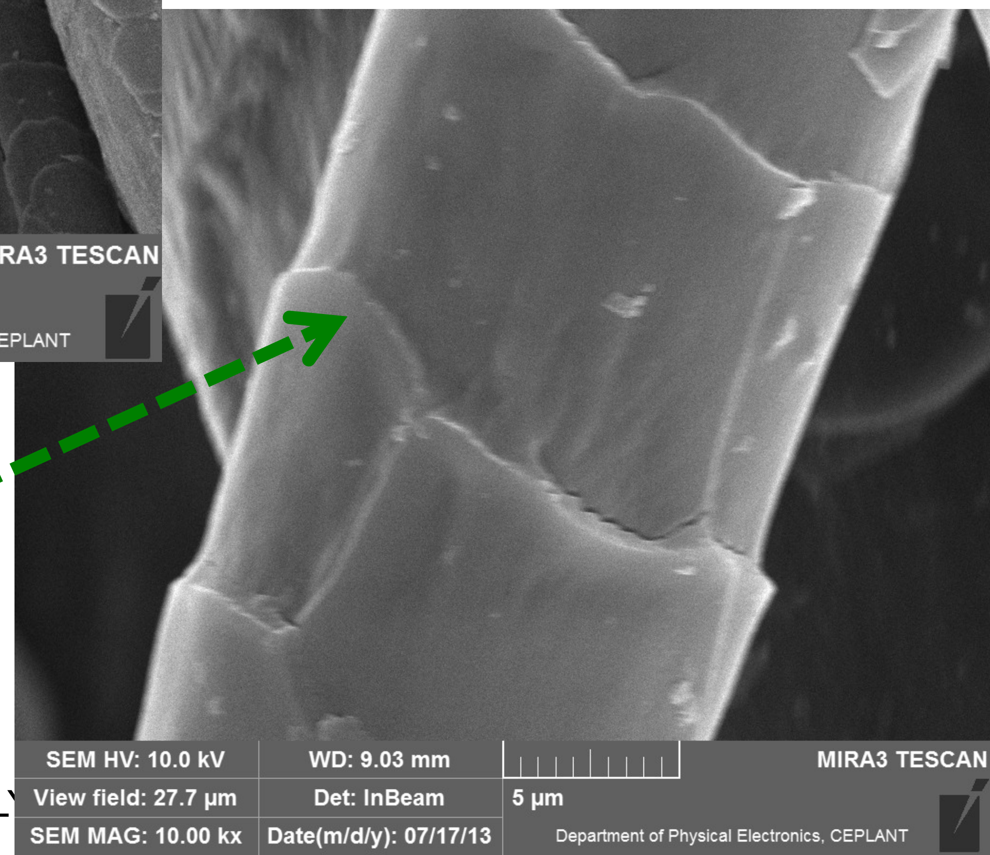
PROBABLY IT COULD BE „At dry", because Values „At wet" are usually lower then state here.



Sheep's Wool, coloured, treated, TEXTIL FIBER

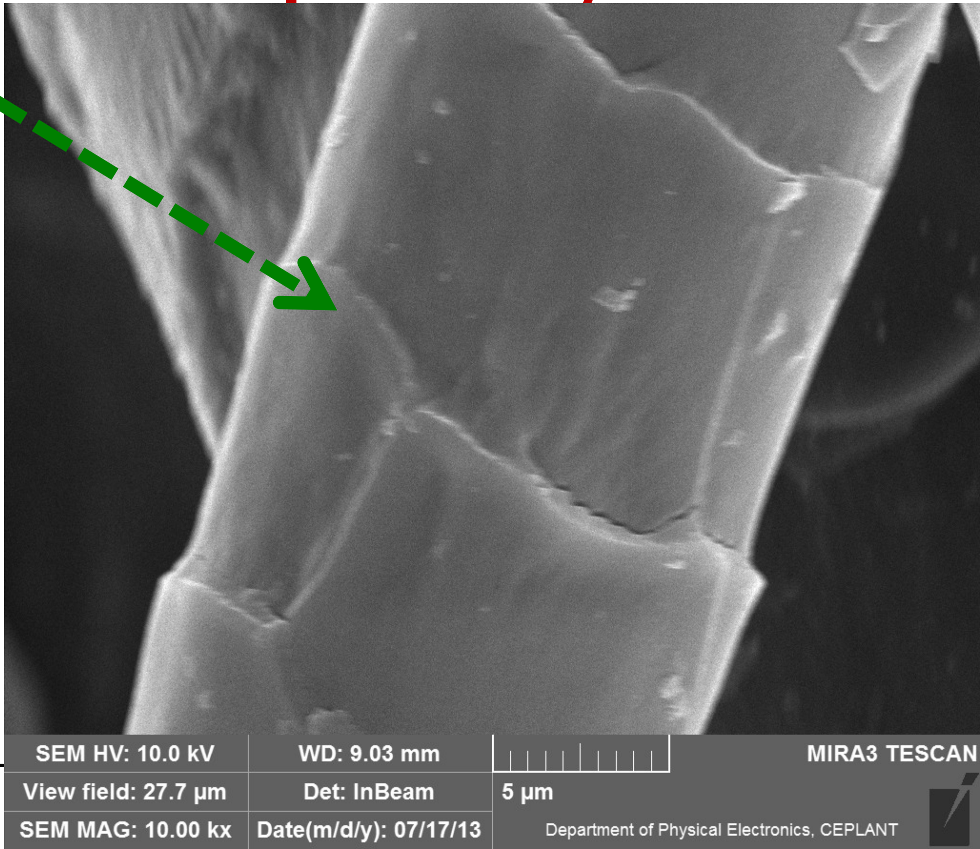
SEM – by Courtesy of Miss Mgr. Gabriela Vyskočilová

Typical SMALL SCALE on the Surface



Treatment of the Sheep's Wool

- **WOOL CARBONIZATION** – removal of Dirt from the Wool using concentrated H_2SO_4
- Modification against Felting up (Removing of the **SMALL SCALE on the Surface** by Oxidation and Mechanical Separation)
- ……………….



WOOL CARBONIZATION is the chemical Process, which Reason is removal from the Sheep's Wool all the Plant (vegetable) Impurities

E.g. Straws and Culms, Leafs, Grass etc. WOOL CARBONIZATION can be done at Dry or at Wet Conditions.

Wet Process

The strong inorganic Acid is used most frequently, e.g. (H_2SO_4 or HCl) or the Salt with acid Reaction, e.g. $(NH_4)_2SO_4$). The Wool is resistant for short Time even at high temperature, e.g. Approx. 15 minutes at 90 -110 °C. The Plant (vegetable) Impurities (Cellulose based material) are carbonised and change to Brittle State. The Products arisen are easy to crush and the remove. It is possible and mostly done to carbonise both Fabric and Flocks.

Dry Process

The Vapour of HCl is mostly used for this technology. This Procedure is employed less frequently then the **Wet Process,** despite it is Efficient and fast. The Machinery is expensive , because of Corrosiveness of the HCl , which is also Hazardous Chemical.

2. LANOLIN

LANOLIN

LANOLIN is further purified for the Cosmetic use to be Colourless

Raw Sheep's Wool from one Sheep (one cutting) contains approx. 100 – 300 ml of Lanolin

It is nothing special on the first Sight

It is NOT a Glyceride!

Lanolin also called **wool wax** or **wool grease**, is a wax secreted by the sebaceous glands of wool-bearing animals. Lanolin used by humans comes from domestic sheep breeds that are raised specifically for their wool. Historically, many pharmacopoeias have referred to lanolin as wool fat (*adeps lanae*); however**, as lanolin lacks Glycerides (glycerol esters), it is NOT a true fat**. Lanolin primarily consists of sterol esters instead. Lanolin's waterproofing property aids sheep in shedding water from their coats. Certain breeds of sheep produce large amounts of lanolin. There is an inverse correlation between wool fiber diameter and lanolin content.

Lanolin's role in nature is to protect wool and skin from climate and the environment; it also plays a role in skin (integumental) hygiene. Lanolin and its derivatives are used in the protection, treatment and beautification of human skin.

A typical high-purity grade of lanolin is composed predominantly of long chain waxy esters (approximately 97% by weight) the remainder being lanolin alcohols, lanolin acids and lanolin hydrocarbons

An estimated 8,000 to 20,000 different types of lanolin esters are present in lanolin, resulting from combinations between the 200 or so different lanolin acids and the 100 or so different lanolin alcohols identified so far.

Lanolin and its many derivatives are used extensively in both the personal care (e.g., high value cosmetics, facial cosmetics, lip products) and health care sectors such as topical liniments. Lanolin is also found in lubricants, rust-preventive coatings, shoe polish, and other commercial products.

Lanolin, when mixed with ingredients such as neatsfoot oil, beeswax and glycerine (glycerol), is used in various leather treatments, for example in some saddle soaps and in leather care products

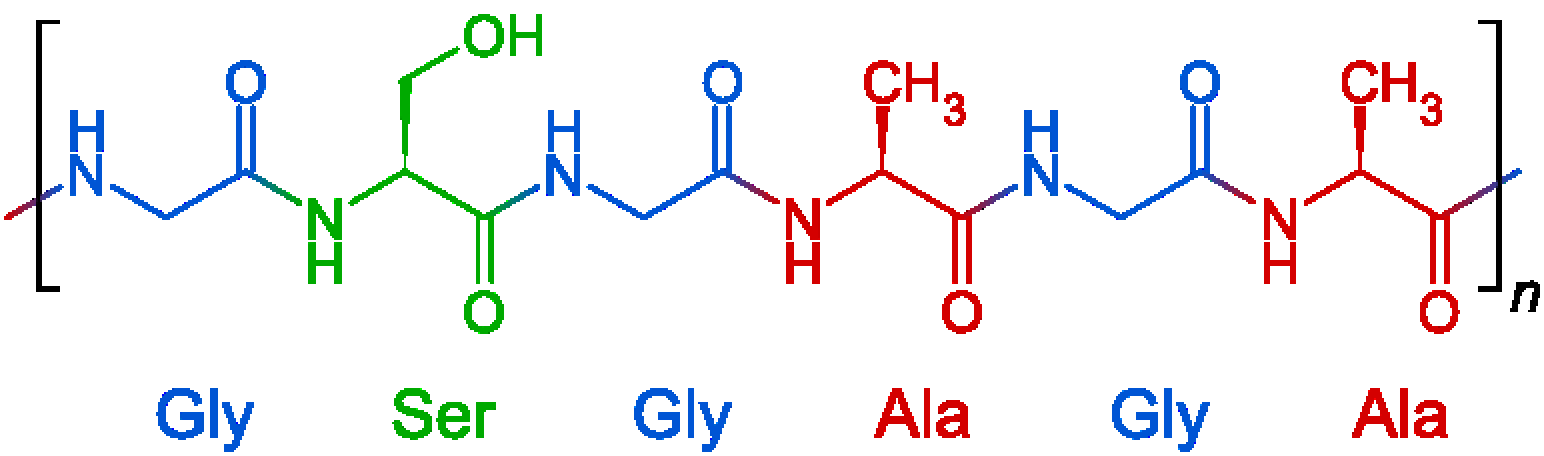
3. FIBROIN

Where can be found FIBROIN?

- **Natural/Genuine Silk produced by Silkworm**
- **Spider's is Protein Fibre from the Secret of Spiders Species *Argiope* and *Nephila***
- **Secret of the night Butterflies**

Natural/Genuine Silk

- **MOST OF THE Natural/Genuine Silk is gained from the Secret produced by Silkworm Moths. It is called „Endless“ natural textile Fibre**
- **This FIBROIN has the typical PRIMARY STRUCTURE, as shown bellow:**



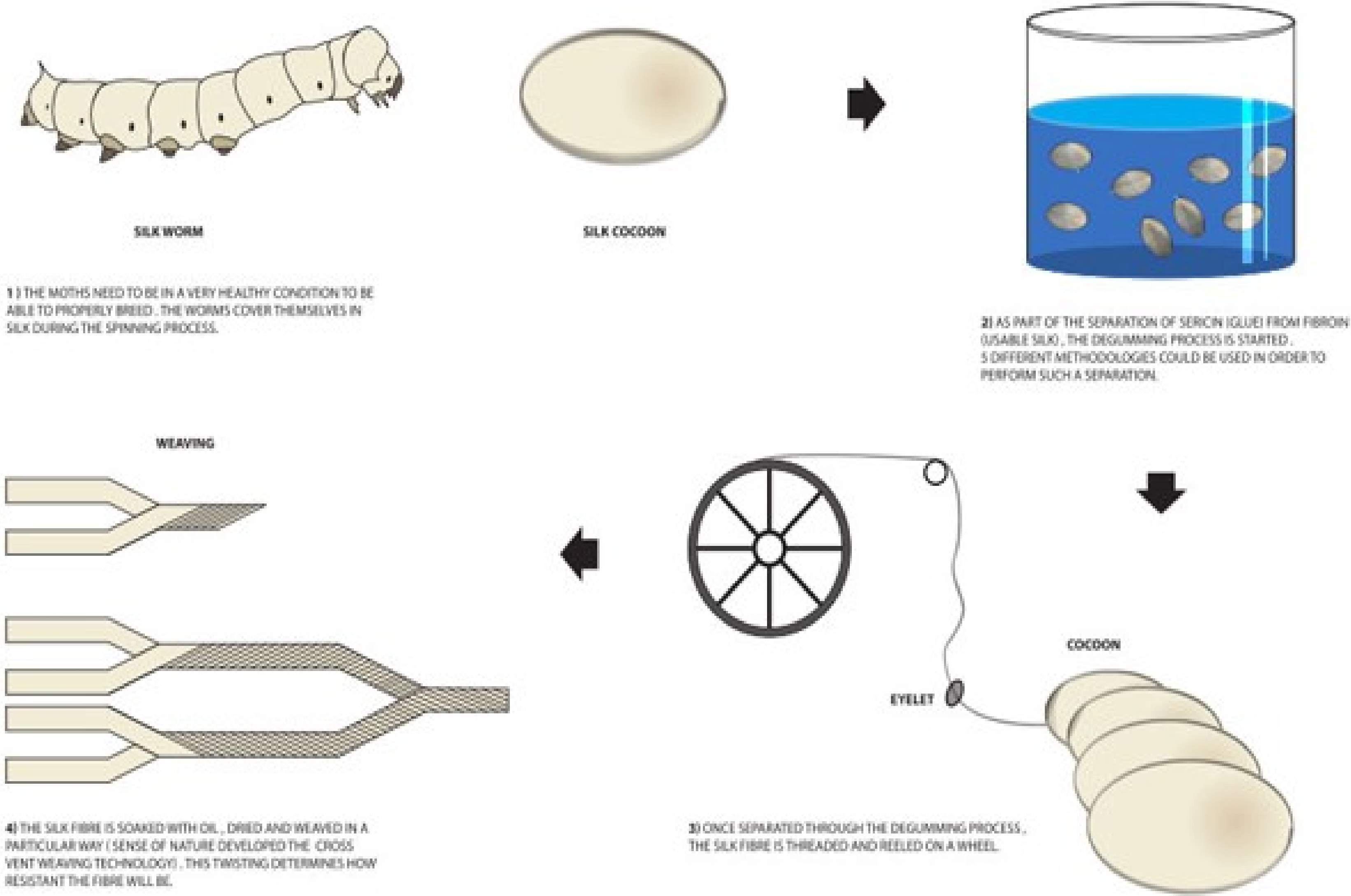
Fibre's Properties	Natural/ Genuine Silk	Polyamide (PA 6)	Polyester (PETP)	Viscose (CV)
Density (g/cm^3)	1,25	1,14	1,33	1,52
dtex	1,17	1,0	1,1	1,4
Strength DRY (cN/dtex)	3-5	3,6-7,5	3,8-7,2	1,8-3,0
Strength WET (% of the DRY)	85	85	95-100	60
Elengation (%)	24	23-55	50-70	15-30
Water uptake (%)	30	3-4,5	0,3-0,4	28
World Consumption approx. (1000 t)	107	3.500	14.500	500

TYPICAL FIGURES ARE GIVEN IN THIS TABLE!

AMINO ACIDS COMPOSITION of some grades ot the Natural/Genuine Silk (the very minor Amino acids are not given)

AMINO ACID	Bombyx mori	Tussah Caligula	Tussah II	Anaphe	Chrasopha flava
Glycine	**43.6**	**23.6**	**23.9**	**41.7**	**23.5**
Alanine	**29.6**	**39.4**	**47.2**	**52.1**	**50.2**
Serine	**11.7**	**10.5**	**14.8**	**-----**	**40.7**
Asparagic acid	1.4	4.2	7.5	-----	-----
Glutamic acid	-----	-----	1.5	-----	-----
Tyrosine	4.8	4.4	10.6	-----	-----
Histidine	0.4	2.2	1.6	-----	-----
Arginine	1.7	9.2	5.4	2.1	1.8
Proline	0.4	0.3	0.4	-----	-----
Tryptophan	0.4	2.0	2.7	-----	-----





SILK WORM
SILK COCOON
1) THE MOTHS NEED TO BE IN A VERY HEALTHY CONDITION TO BE ABLE TO PROPERLY BREED . THE WORMS COVER THEMSELVES IN SILK DURING THE SPINNING PROCESS.
2) AS PART OF THE SEPARATION OF SERICIN (GLUE) FROM FIBROIN (USABLE SILK) , THE DEGUMMING PROCESS IS STARTED .
5 DIFFERENT METHODOLOGIES COULD BE USED IN ORDER TO PERFORM SUCH A SEPARATION.
WEAVING
EYELET
COCOON
4) THE SILK FIBRE IS SOAKED WITH OIL , DRIED AND WEAVED IN A PARTICULAR WAY (SENSE OF NATURE DEVELOPED THE CROSS VENT WEAVING TECHNOLOGY) . THIS TWISTING DETERMINES HOW RESISTANT THE FIBRE WILL BE.
3) ONCE SEPARATED THROUGH THE DEGUMMING PROCESS , THE SILK FIBRE IS THREADED AND REELED ON A WHEEL.

Silk fibres are a continuous protein fibre created from natural processes and extracted from cocoons, which means that these fibres can retain the properties that are associated with the chemicals produced by the silkworm. When secreted by the silkworm, the natural state of the fibre is a single silk thread made up of a double filament of protein material (fibroin) glued together with sericin, an allergenic and gummy substance that is normally extracted during the processing of the silk threads.

EXTRACTING RAW SILK

The production process of silk can seem deceptively simple but indeed **has several steps**. In fact, the process of creating silk fibres of the highest quality take a few weeks to complete.

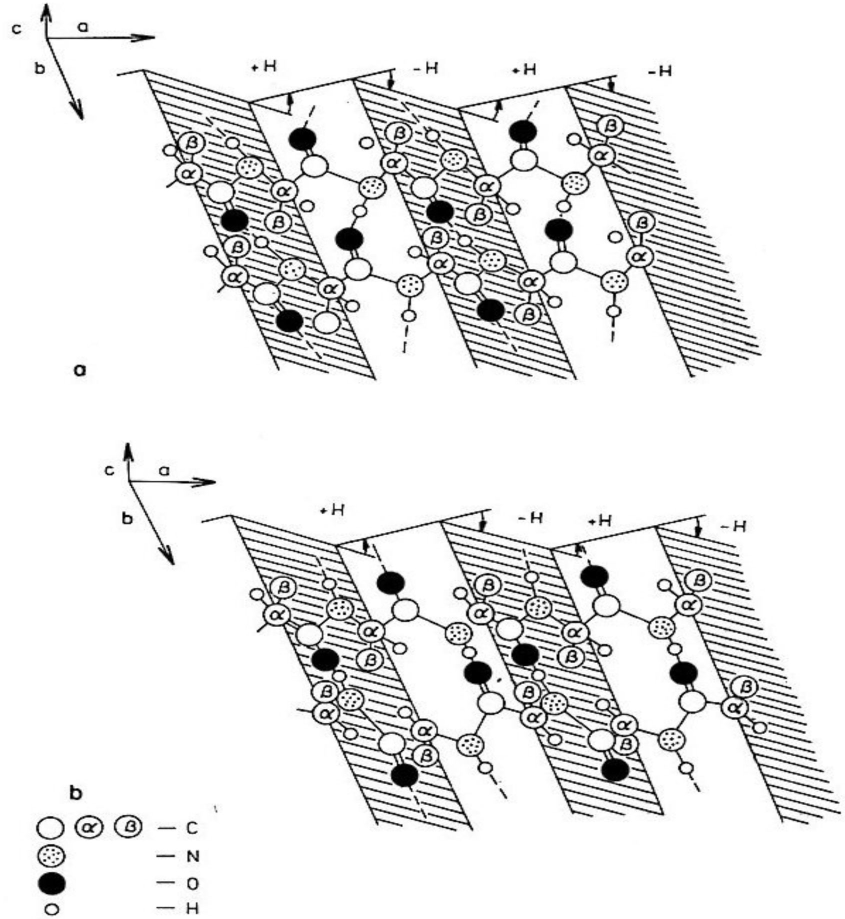
1. **First**, the new born larvae of the **silkworms are kept in a warm and stable environment** and given plenty of mulberry leaves, their favourite diet.
2. The **silkworms naturally produce cocoons** around themselves to pupate. This process is done through "spinning": the worm secretes a dense fluid from its gland structural glands, resulting in the fibre of the cocoon.
3. The **cocoons are sorted** carefully according to size and quality.
4. Boiling water with soap is used **unravel the silk fibres from the cocoon**. This is known as the degumming process.
5. The outer shell of **the cocoon is fed into into the spinning reel**, which is still often operated manually
6. **The long fibre** thread that are extracted from the cocoon **are then cleaned and stripped** from any deficiencies.

The degumming process

- The Fibre is connected by Sericine in the **COCOONS**, which is the SOLUBLE GLYCOPROTEINE „guarding“ (protecting) the FIBROIN
- SERICIN is dissolved in the boiling Water and so are the Fibres released
- The Fats and Waxes are dissolved also
- The only approx. 1 % w/w is the Ash (inorganic Materials) in the Fibre, the Rest are Proteins.

Natural/Genuine Silk SECUNDARY STRUCTURE

β Keratin folded (Pleated) Sheet



Schema showing the Protein's β Keratin Folded (Pleated) Sheet Structure

a) PARALEL arrangement

b) ANTIPARALEL arrangement

The Backbone is bonded by the Covalent Bonds in the a Axis Direction.

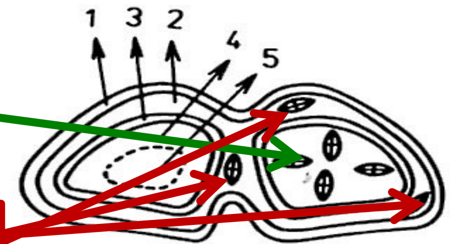
The Backbone is bonded by the Hydrogen Bonds in the b Axis Direction.

The Backbone is bonded by the Wan der Waals Forces in the c Axis Direction.

Natural/Genuine Silk Fibre is very COMPLICATED (COMPLEX) STRUCTURE

PRIMARY FIBRES

SECUNDARNÍ FIBRES



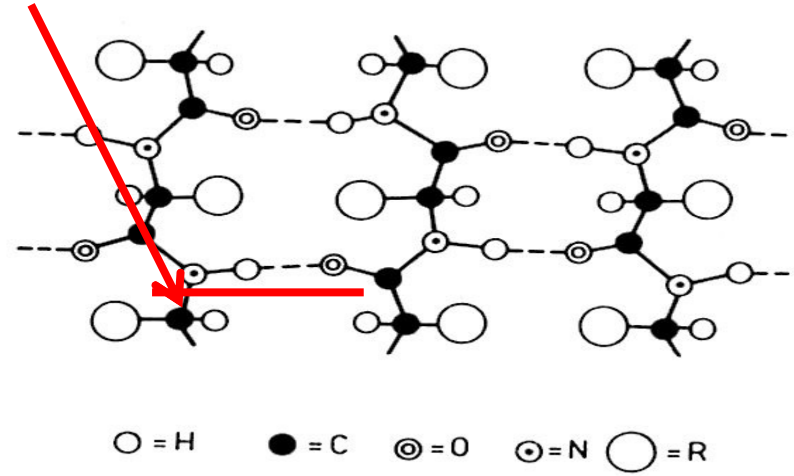
a)

b)

It is so called TWINFIBRE CONNECTED BY SERICINE (so called **Silk Glue**) of Length approx. 3000 – 4000 m

Hydrogen Bond of the FIBROIN's

—NH ··· O=C—



c)

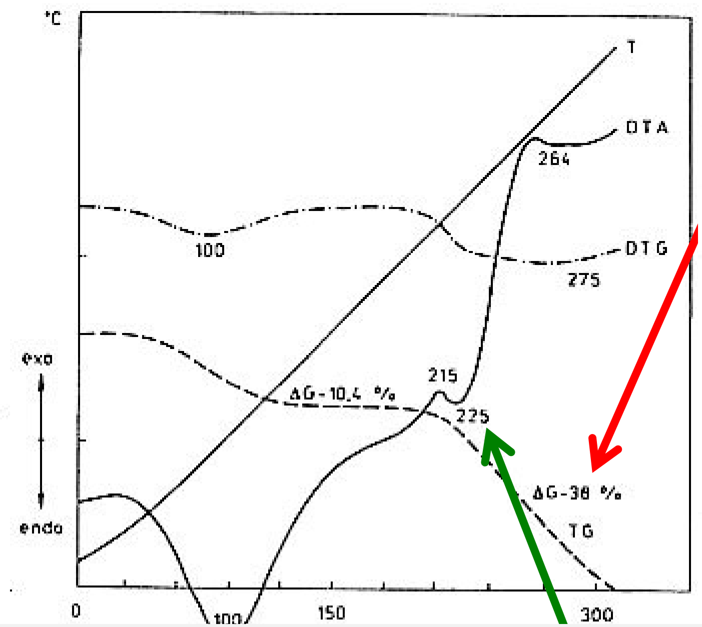
a) The Crosscut of the Natural/Genuine Silk Fibre
1. Sericine Skin
2. Sericine's Core
3. Fibroin's Fibre Cubicula
4. Fibroin's Fibre Core
5. Fibroin's Fibre central Part (Zone)

b) Longitudinal cut of the Natural/Genuine Silk Fibre
3. Fibroin's Fibre Skin
4. Fibroin's Fibre Core
5. Fibroin's Fibre central Part (Zone)

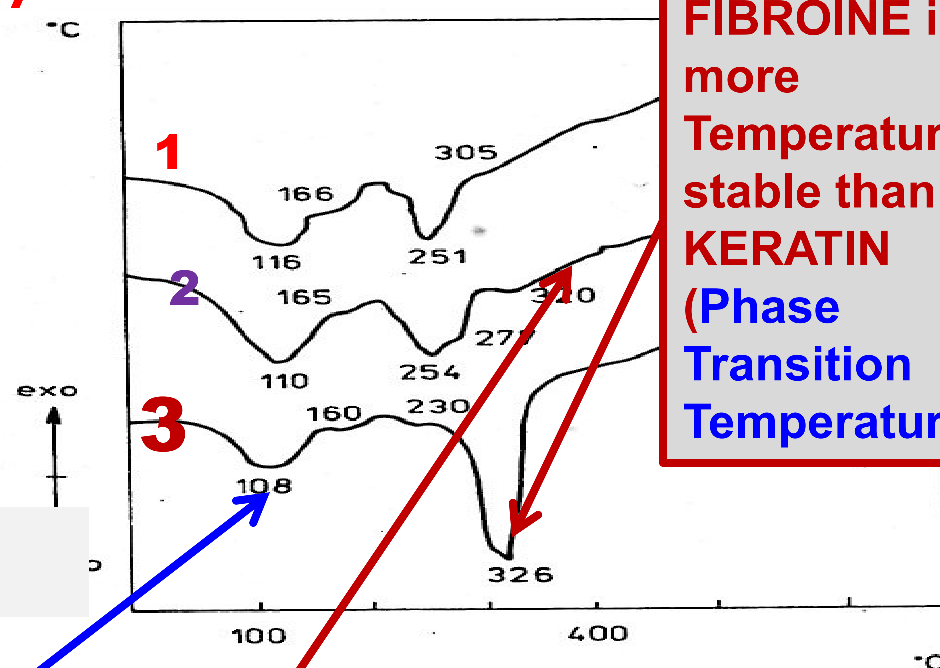
c) Polypeptide Chains of Fibroine in the ANTIPARALEL CONFORMATION

Phase Transitions of KERATIN & FIBROIN 2

On Air > OXIDATION > Burning already at approx. 230 °C



DTA and TG Curves 100 % w/w of Wool heating up to 300 °C in Air



FIBROINE is more Temperature stable than KERATIN (Phase Transition Temperature)

α Keratin (**Coil**) > β Keratin (Folded (**Pleated**) Sheet)

DTA Curves in the NITROGEN: 1) Human Hair, 2) Mohair Wool, 3) Natural/Genuine silk

Evaporation of the Water

Decomposition in NITROGEN is only at higher Temperature and is more slowly

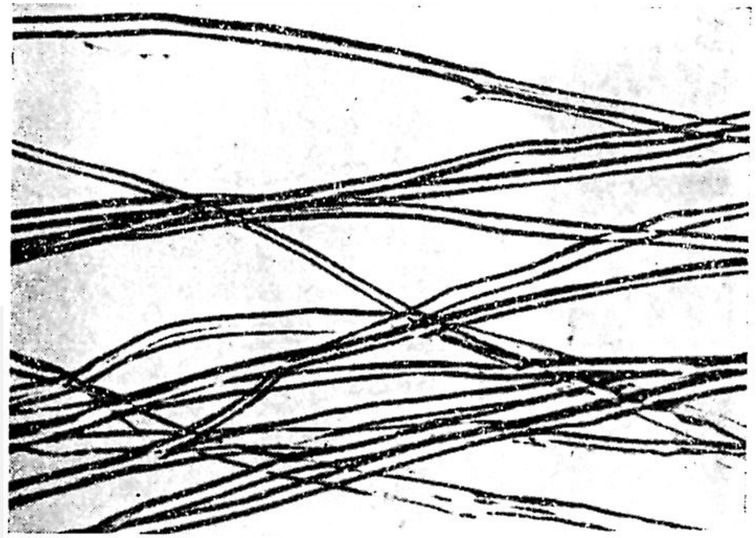
CHEMICAL REACTIONS AND SOLUBILITY OF THE FIBROIN 1

- **Decomposition by Acids (more Efficient) and Alkali**
- **OXIDATION (Chlorine)**
- **ACETANHYDRIDE, ALKALIC METALLS AND ALKALIC EARTH SALTS**
- HEAVY METALLS SALTS, MAINLY STANNUM (TIN) > **Natural/Genuine Silk takes up** 100 % w/w > **„WEIGHTING“ of the Natural/Genuine Silk**
- **Formation of the Cross Bonds**

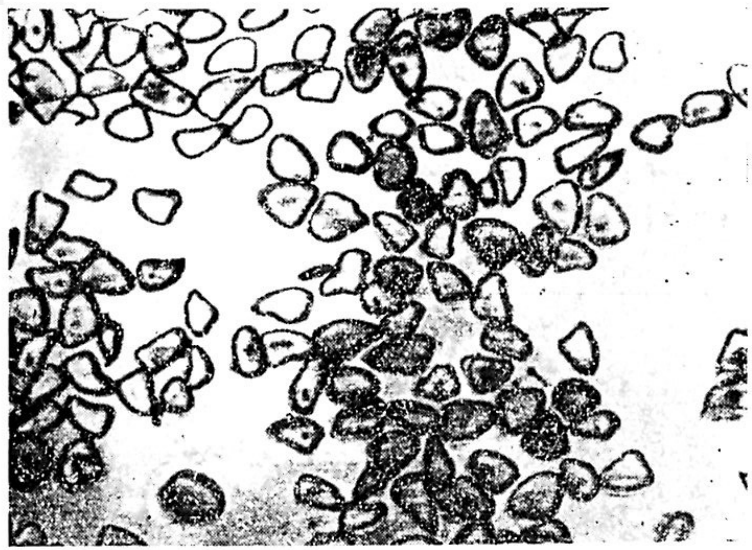
CHEMICAL REACTIONS AND SOLUBILITY OF THE FIBROIN 2

- **Decomposition by Acids (more Efficient)** – *hot concentrated **HCl dissolves*** **Natural/Genuine Silk in** ***30 minutes QUANTITAVELY***
- OXIDACTION – H_2O_2, $KMnO_4$ at higher concentration damages **Natural/Genuine Silk**
- CHLORINE
- ACETANHYDRIDE, **ALKALIC METALLS and ALKALIC EARTH SALTS and also e.g.** ***$ZnCl_2$ dissolves*** **Natural/Genuine Silk** ***(similar as the PA6)***
- **Formation of the Cross Bonds – via more complex organic Substances**

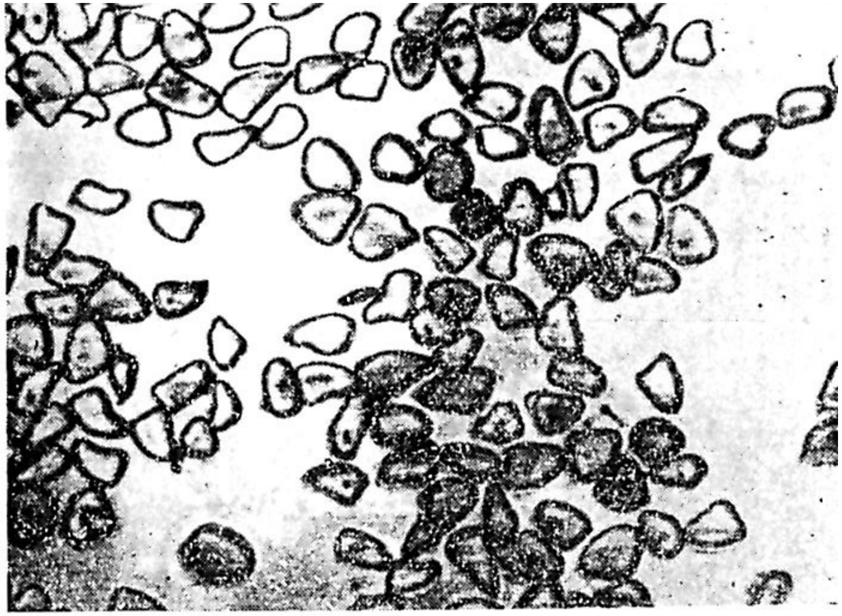
Natural/Genuine Silk Fibre
OPTICAL MICROSCOPY



Natural/Genuine Silk Magnificatin 180 x

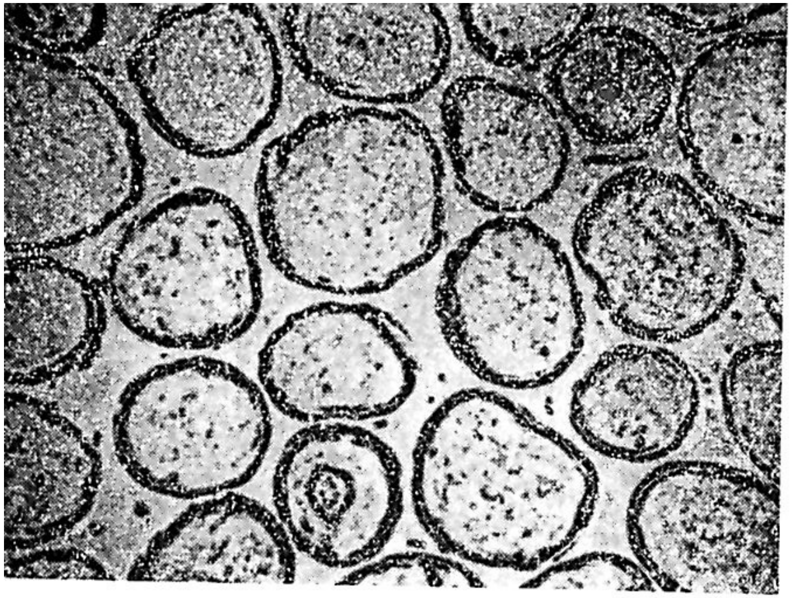


Natural/Genuine Silk (CROSS CUT) Magnificatin 500 x



Natural/Genuine
Silk
Magnificatin
180 x

Fibre's Thickness of the Sheep's Wool and Natural/Genuine Silk at the same Magnification



Sheep's Wool
Magnificatin
180 x

SUROVINOVÝ VÝZNAM Natural/Genuine Silk Fibre

- **Natural/Genuine Silk is the very exclusive textile raw Material**
- **Annual World Production is only approx. 300 000 t/annum**
- **China is the principal Producer now**
- ***There were many Attempts to start the* Natural/Genuine Silk *Production in Europe, but they ended unsuccessfully***