NATURAL POLYMERS

Polysaccharide II

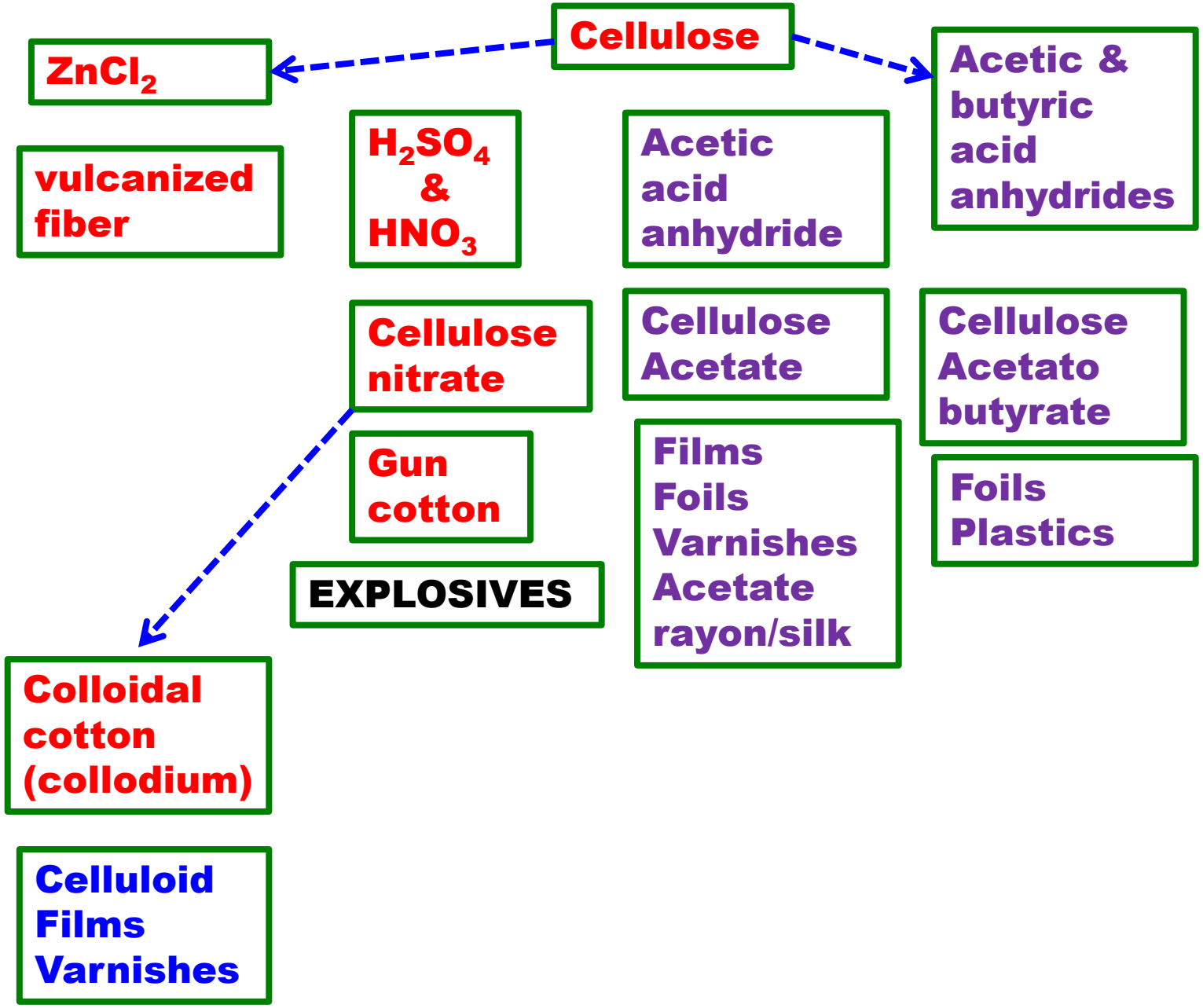
CELLULOSE 3

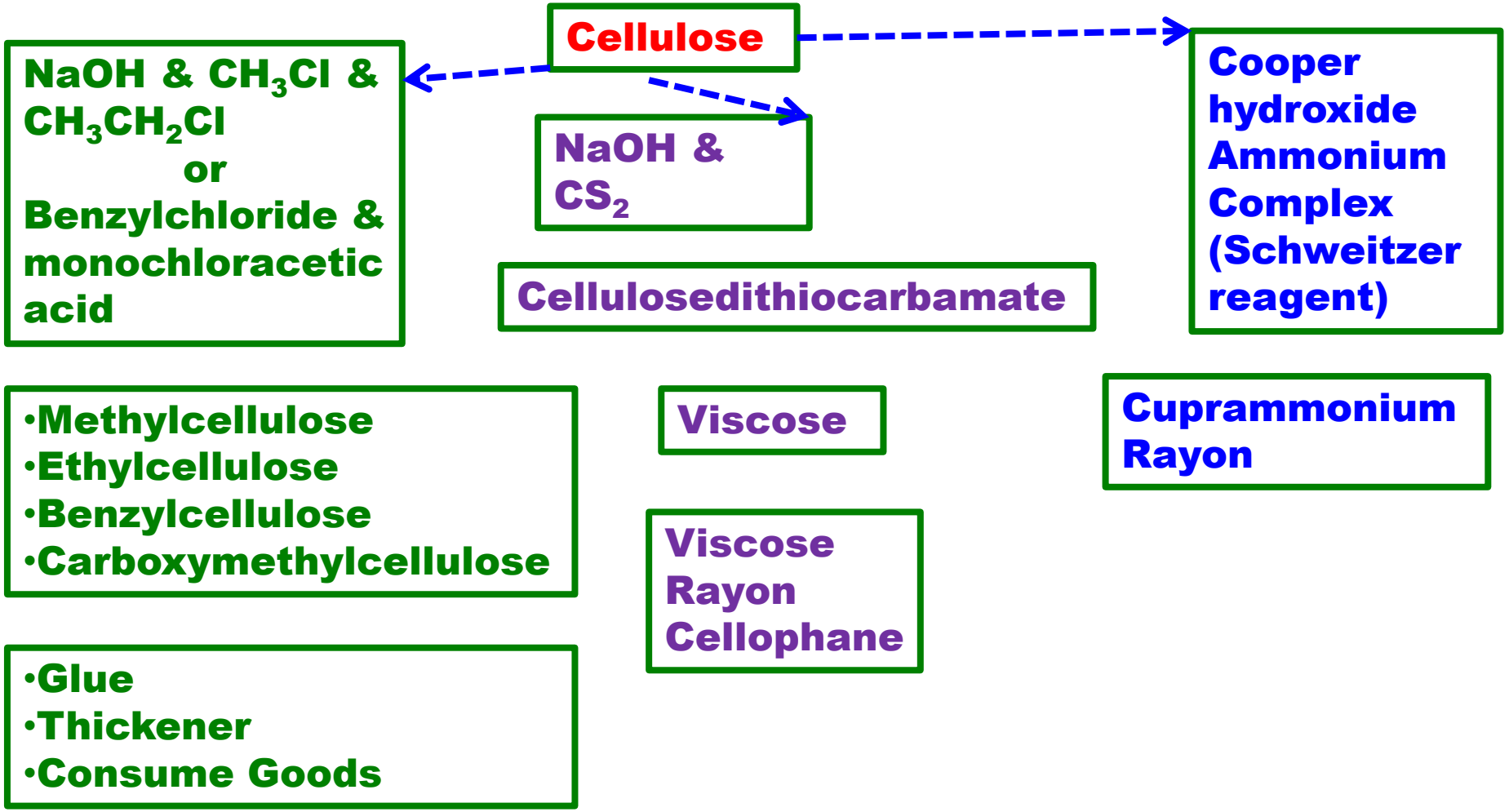
Cellulose is the most widespread BIOPOLYMER on Earth, up to $1,5 \times 10^9$ tons per annum is arising

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 – 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


Cellulose
$ZnCl_2$
vulcanized fiber
H_2SO_4 & HNO_3
Acetic acid anhydride
Acetic & butyric acid anhydrides
Cellulose nitrate
Gun cotton
EXPLOSIVES
Cellulose Acetate
Films
Foils
Varnishes
Acetate rayon/silk
Cellulose Acetato butyrate
Foils
Plastics
Colloidal cotton (collodium)
Celluloid
Films
Varnishes


Cellulose
NaOH & CH_3Cl & CH_3CH_2Cl
or
Benzylchloride & monochloracetic acid
NaOH & CS_2
Cellulosedithiocarbamate
Cooper hydroxide Ammonium Complex (Schweitzer reagent)
•Methylcellulose
•Ethylcellulose
•Benzylcellulose
•Carboxymethylcellulose
Viscose
Cuprammonium Rayon
Viscose Rayon Cellophane
•Glue
•Thickener
•Consume Goods

Cellulose Modification I

PRODUCT	PROPERTIES	USE
Regenerated Cellulose		
Viscose	Similar to native Cellulose	Fibres
Cellophane	Transparent, colourless	Foils for Foodindustry and technical Use
Cellulose Acetate	Transparent, colourless, soluble in organic Solvents	Varnishes ,Glue, Foils , Cine-film (HISTORY), Fibres , ……
Cellulose Propionate	Similar to Cellulose Acetate, but higher temperature Resistance and Strength	Thermoplastic for engineering Parts and electrotechnics
Cellulose Acetobutyrate	Gloss, dimensional Stability, Light exposure Resistance	Varnishes, Injection Moulding (Glasses Frames, Furnace handles etc.)

Cellulose Modification II

PRODUKT	VLASTNOST	POUŽITÍ
Cellulose Nitrate	Nitration level accordingly, e.g. Camphor plasticized > **Celluloid**	Varnishes, Foils , Thermoplastic, **EXPLOSIVES**
Methylcellulose, ethylcellulose	Methylation level accordingly soluble in organic Solvents or in Water also, film forming, emulsifying Agent	Glues, emulsifying Agent, textile Sizing
Benzylcellulose	As the Methylcellulose and ethylcellulose	Varnishes, Electroinsulation
Carboxymethylcellulose	Colloidal and emulsifying Properties, soluble in hot Water, Sodium salt is soluble in the cold Water also	Glues, textile Sizing, protective Colloid, Thickener

Cellulose Modification III

PRODUKT	VLASTNOST	POUŽITÍ
Hydroxyethylcellulose	Film forming, soluble in Water and in the Mixtures Water + ethanol	Hair spray, Thickener for Paints (THIXOTROPIC EFFECT)

Cuprammonium Rayon

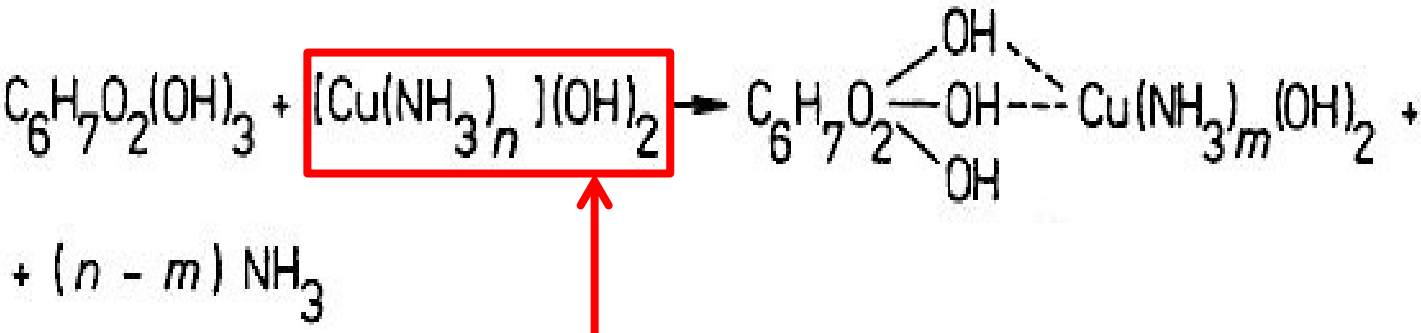
- α **Cellulose Content must be very high, > 95 %w/w and more**
- **So that so called LINTRES (Cotton) having the** α **Cellulose Content up to 99 % w/w are used for this Technology**

$$Cu(OH)_2 + 4\,NH_3 \rightarrow [Cu(NH_3)_4](OH)_2$$

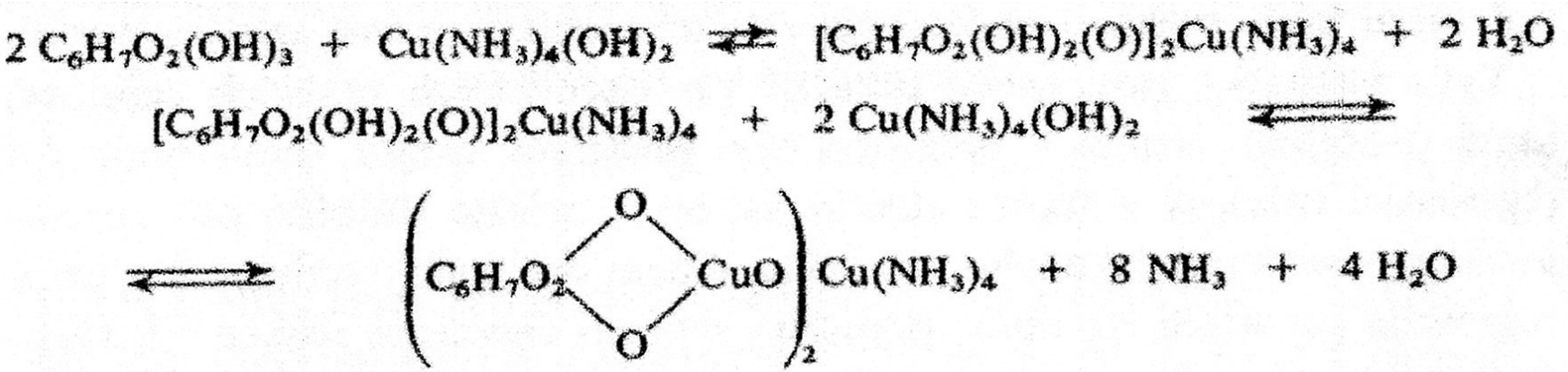
The Substance $mCuSO_4.nCu(OH)_2$ is used as the basic Salt and is prepared as follows:

$$4\,CuSO_4 + 6\,NaOH \rightarrow CuSO_4.3\,Cu(OH)_2 + 3\,Na_2SO_4$$

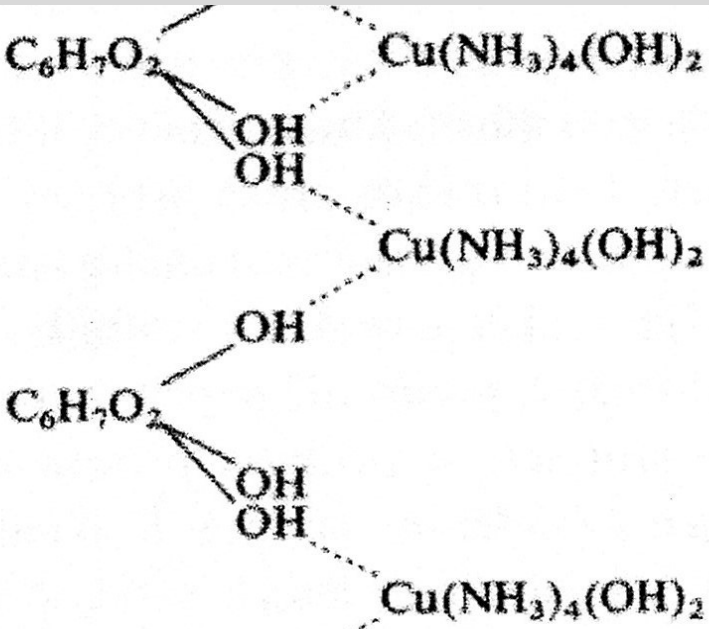
The following Reaction course is supposed during Dissolution of Cellulose in the Cooper hydroxide Ammonium Complex (Schweitzers reagent):



Schweitzers reagent = Kuamox

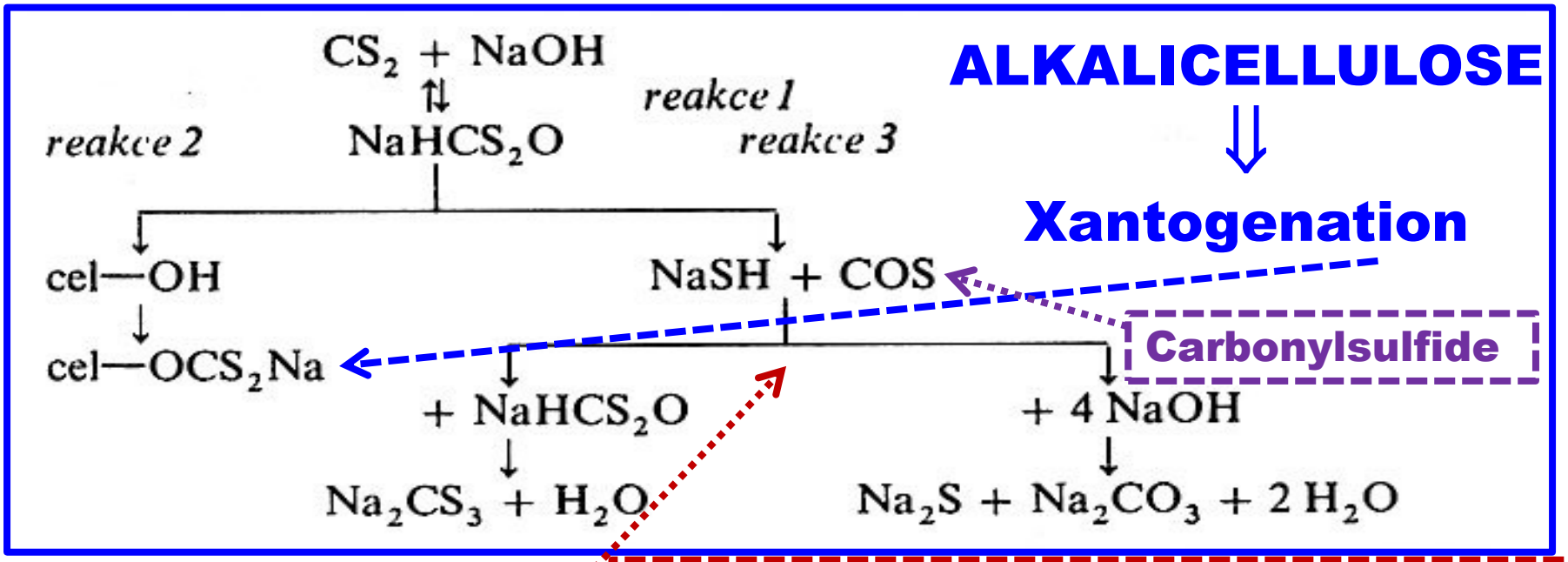


Another possibilities to express the Reactions course during Cellulose Dissolution are presented here (above & bellow)



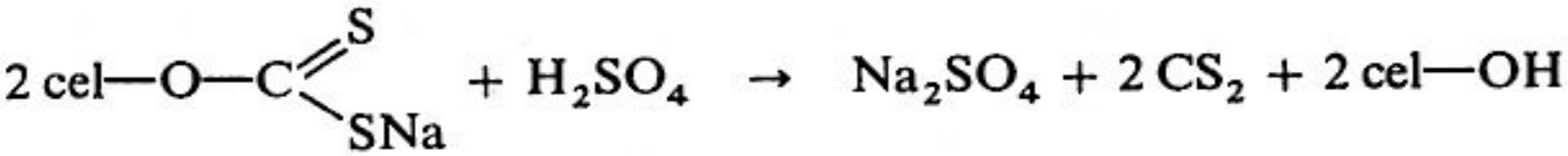
Viscose Fibre

1. **ALKALICELLULOSE** – β and γ Cellulose are separated by PRESSING > THE Rest is α Cellulose (*18 % w/w NaOH is used for this Process*)
   - NaOH is separated from Hemicelluloses and lower MW Celluloses by Dialysis
   - α Cellulose Content should be 90 – 92 %w/w for Rayon and > 95 % w/w for Tire cord fabric
2. **XANTOGENATION**
   - ALKALICELLULOSE + CS_2 > SOLUTION
3. Wet Spinning to Coagulant (Precipitant)



SIDE REACTIONS

$$6\,NaOH + 3\,CS_2 \rightarrow 2\,Na_2CS_3 + Na_2CO_3 + 3\,H_2O$$
$$6\,NaOH + CS_2 \rightarrow 2\,Na_2S + Na_2CO_3 + 3\,H_2O$$
$$Na_2S + CS_2 \rightarrow Na_2CS_3$$



$$Na_2CS_3 + H_2SO_4 \rightarrow Na_2SO_4 + CS_2 + H_2S$$
$$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S$$

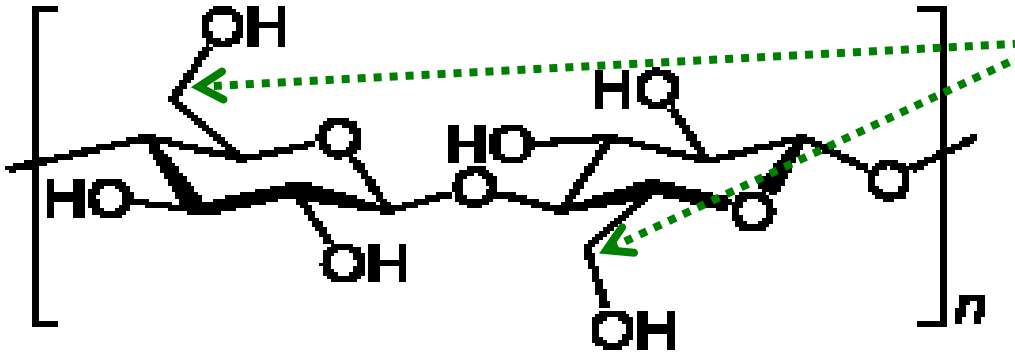
REGENERATION

The Reaction of NaOH with basic Cellulose Chain part (GLUCOSE) can go via two following Schemes:

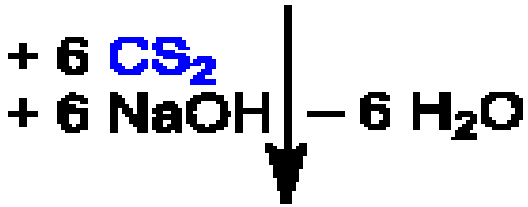
1. $C_6H_7O_2(OH)_3 + NaOH \longrightarrow C_6H_7O_2(OH)_2ONa + H_2O$

This Reaction accordingly Cellulose forms with NaOH chemical Compound of alcoholates Type, in this Case CELLULOSATE:

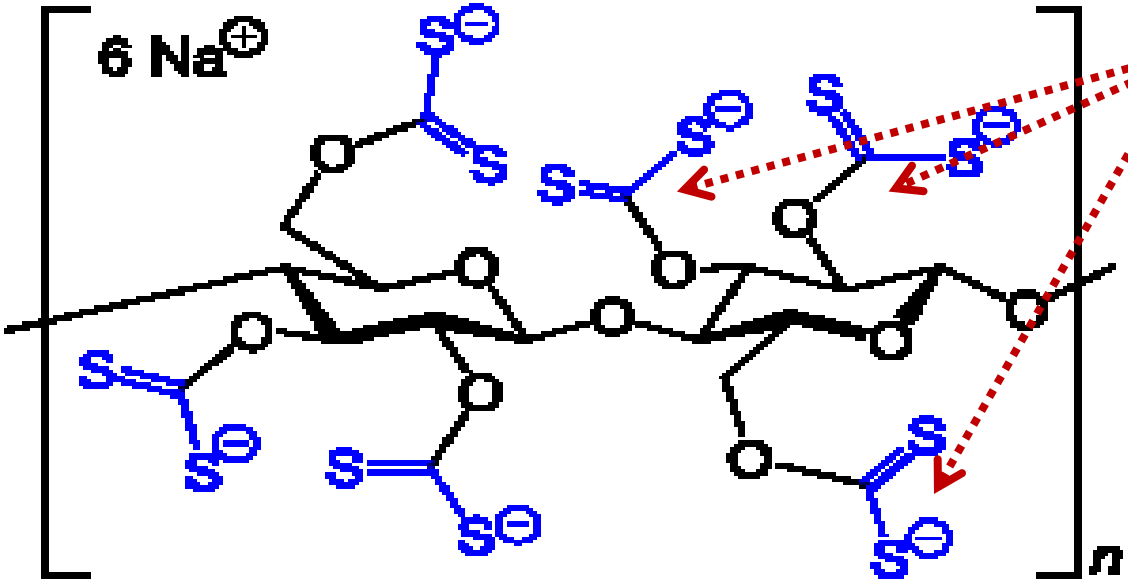
2. $C_6H_7O_2(OH)_3 + NaOH \longrightarrow C_6H_7O_2(OH)_2OH \cdot NaOH$



Carbons C6 are the most reactive, because having the lowest Steric Hindrance!

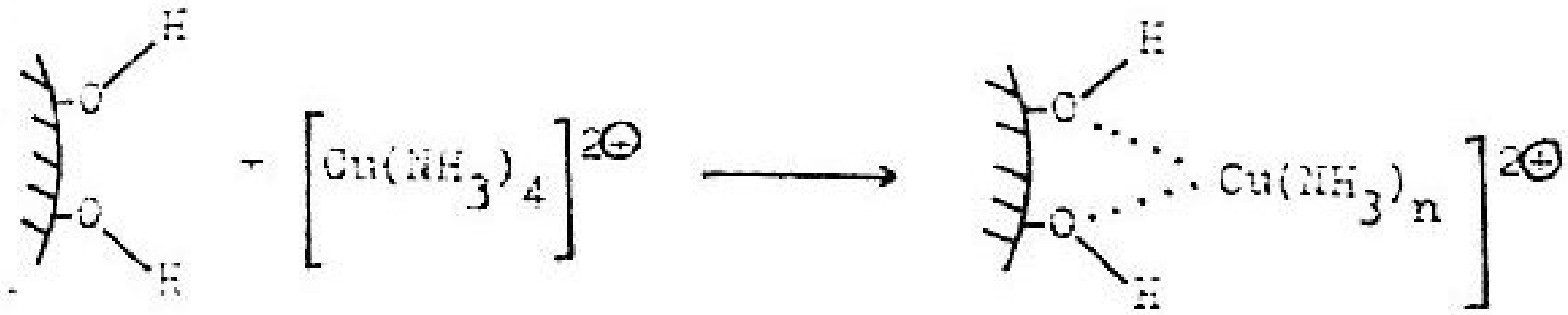


XANTOGENTION CELLULOSE



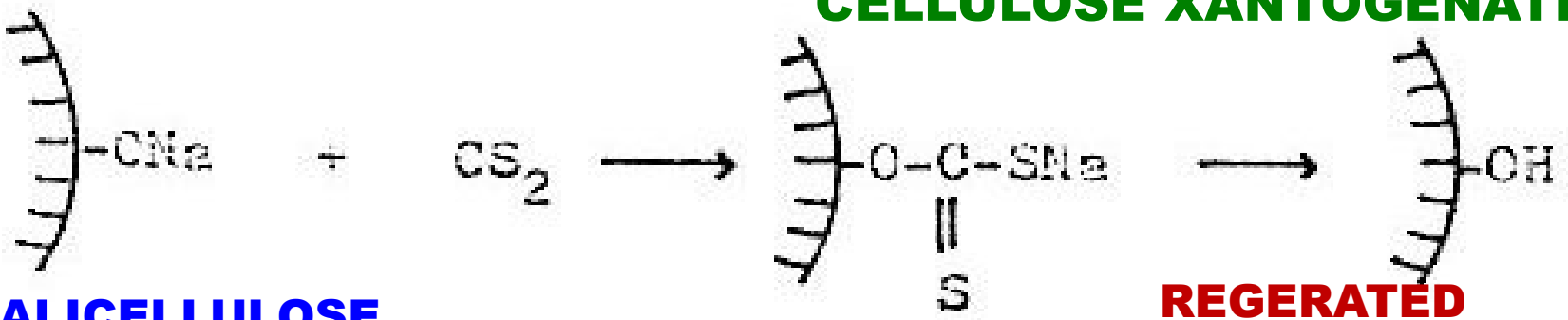
TRISUBSTITUTED Cellulose Derivatives is the maximal Substitution, because of Steric Hindrance of reaction possible Sites

Comparision of Cuprammonium Rayon and Viscose Fibre



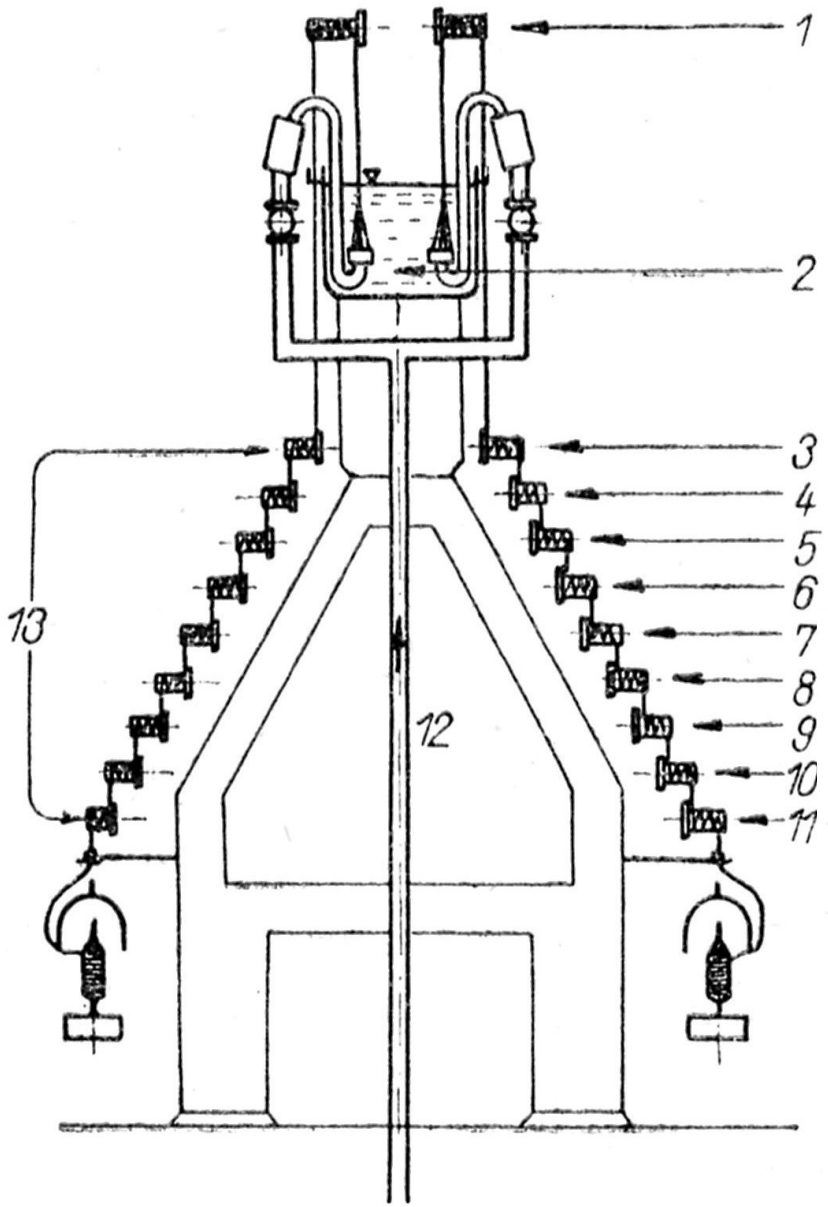
Schweitzers Reagent

CELLULOSE XANTOGENATE



ALKALICELLULOSE

REGERATED CELLULOSE



It was approx. 50 years ago:

- **Viscose Fibre was the Dominant Manmade type**
- **Technology was developed up to almost Perfection**

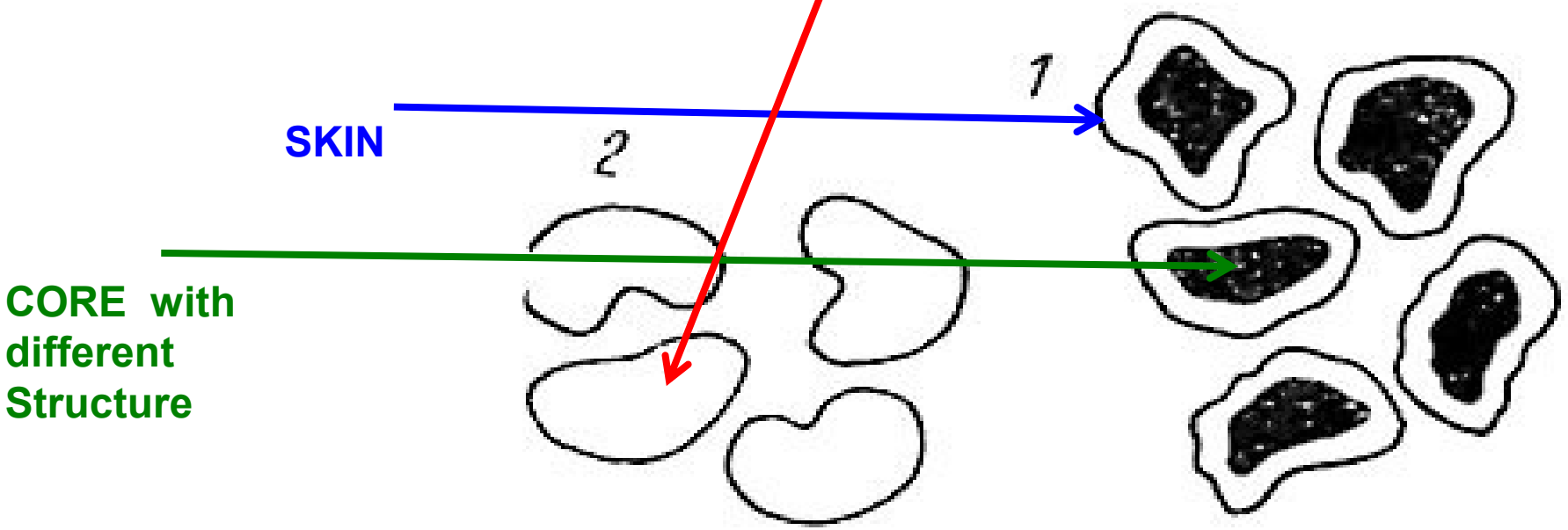
Why is it today the only minor Fibre one?

Technology INDUSTRIAL RAYON Scheme of the Continuous Spinning of Viscose

Why is it today the only minor Fibre one?

- **Technological demanding character**
  - Too much Technological production Steps
  - Time consuming, Process is very long-lasting
  - Solvents' Regeneration is necessary
- **Expences**
  - Technology has many complicated Machines
  - Solvents' Regeneration
- **Environment Protection**
  - CS_2
  - Europe didn't invest to e.g. Multi-skin Buildings and/or CS_2 Adsorption or Absorption

Slowly Precipitation (Coagulation) > uniform Structure in Fibre Crosscut > HIGHER TENSILE STRENGHT > TIRE CORD

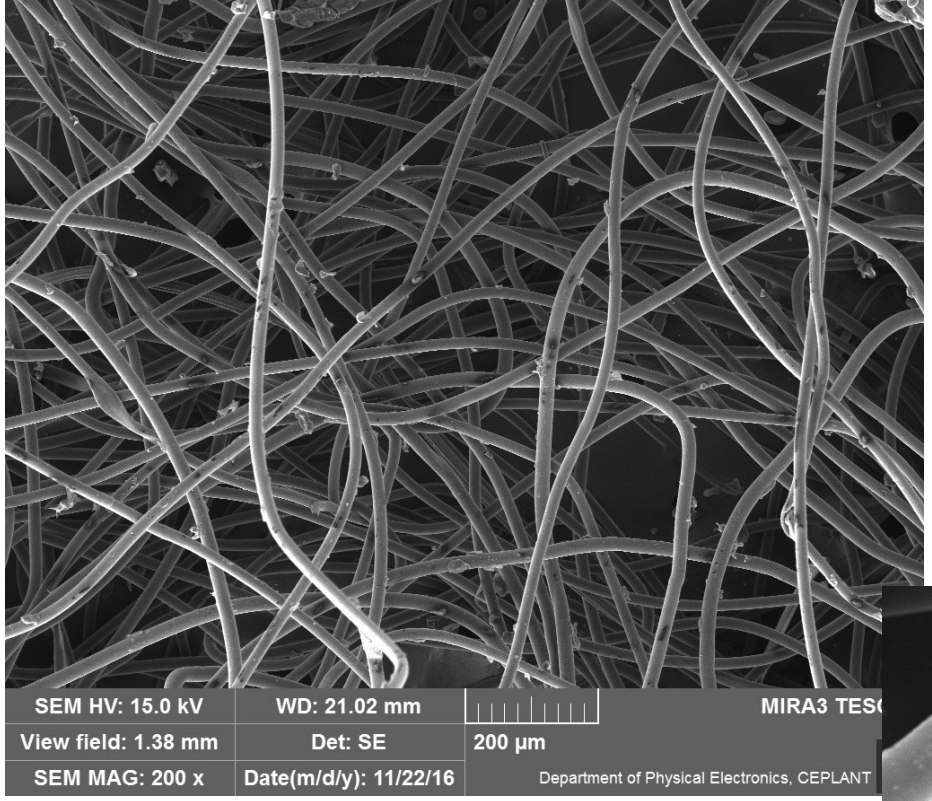


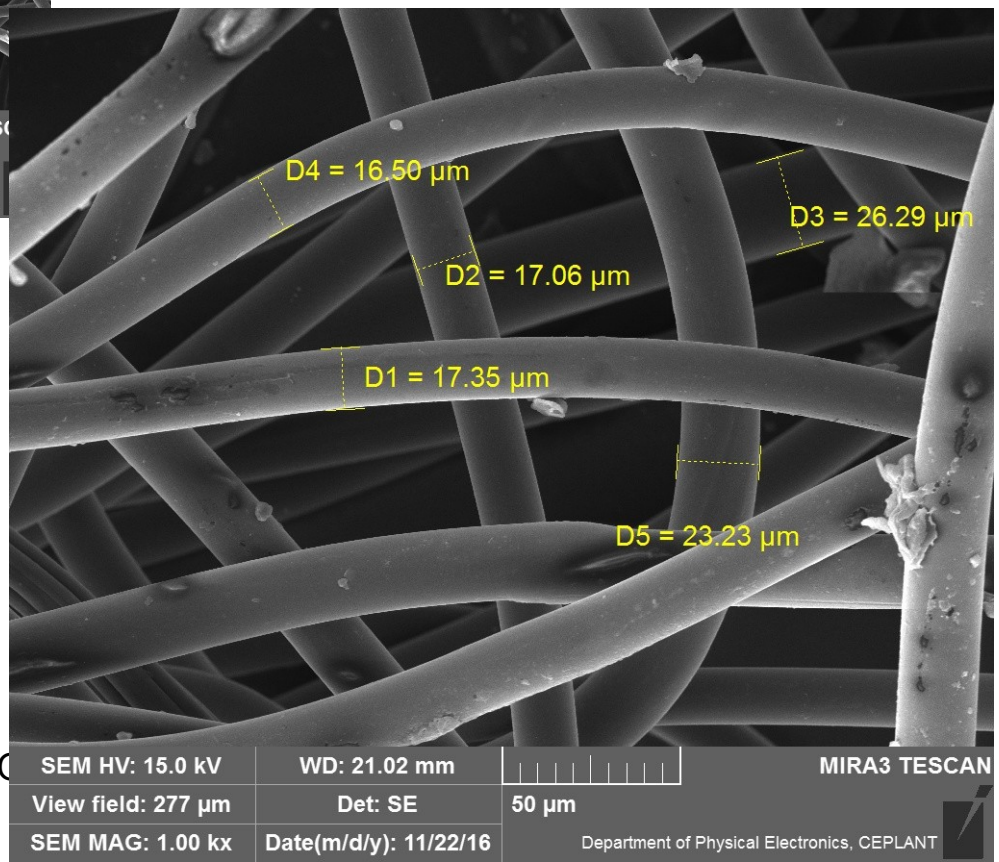
Fibre Crosscut Scheme:
1. Fibre with Core
2. Fibre WITHOUT CORE

Current us of VISCOSE CORD

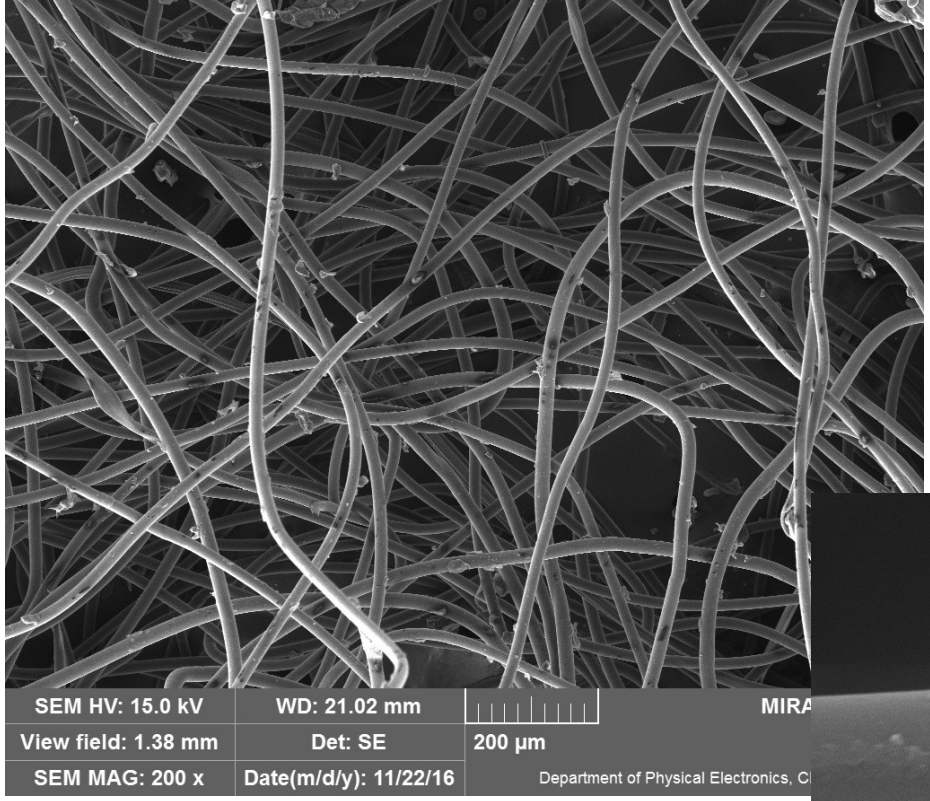
- **CORD** = Rayon of extremly high **TENSILE STRENGHT**
- **Manufacture of CARBON FIBRES:**
  - **PAN (polyacrylonitrile) – the main Raw Material today**
  - **Black Coal-tar pitch (By-product in Production of Coke (Coking plant)) – the minor Raw Material today**
  - **Viscose Cord – the IGNORED Raw Material today**
- **Viscose Cord – Tire carcass (formerly)**

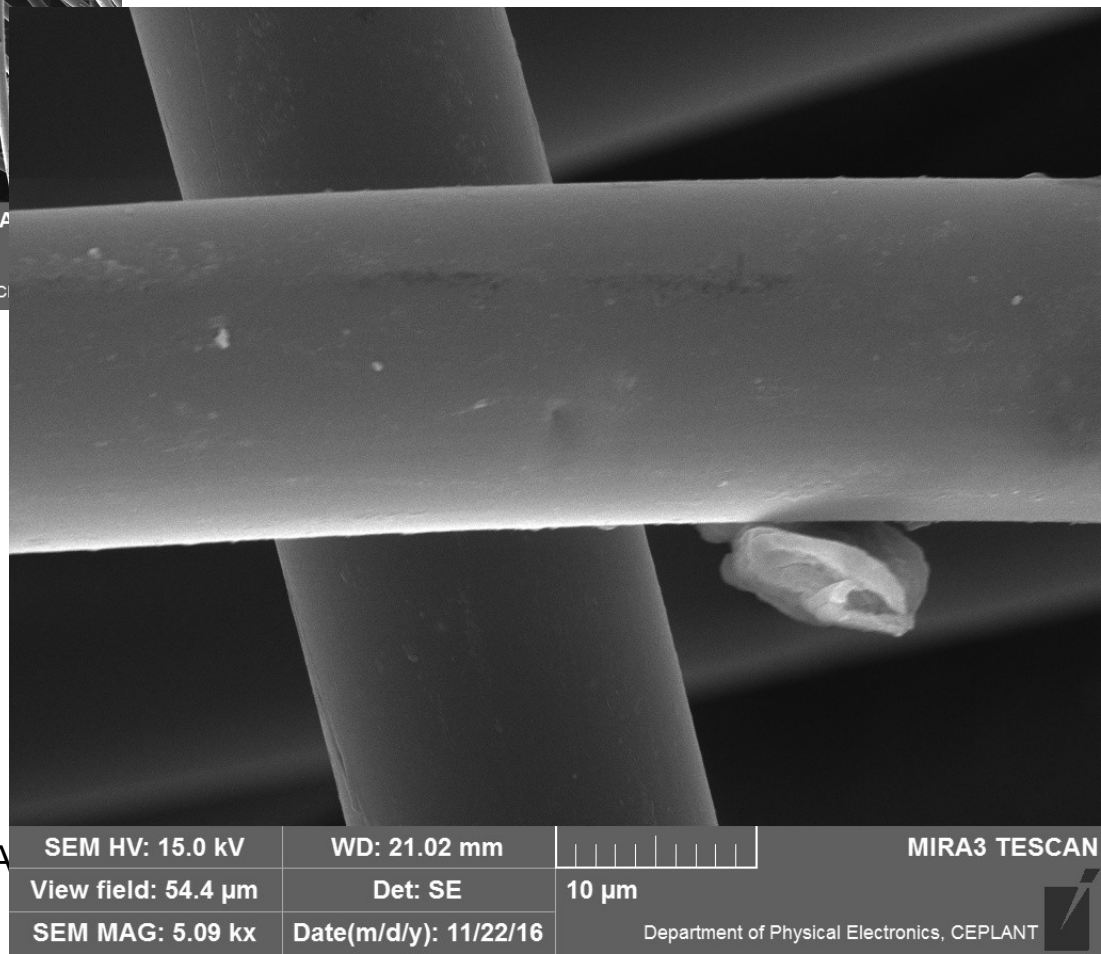
Viscose Rayon Nonwoven Textile





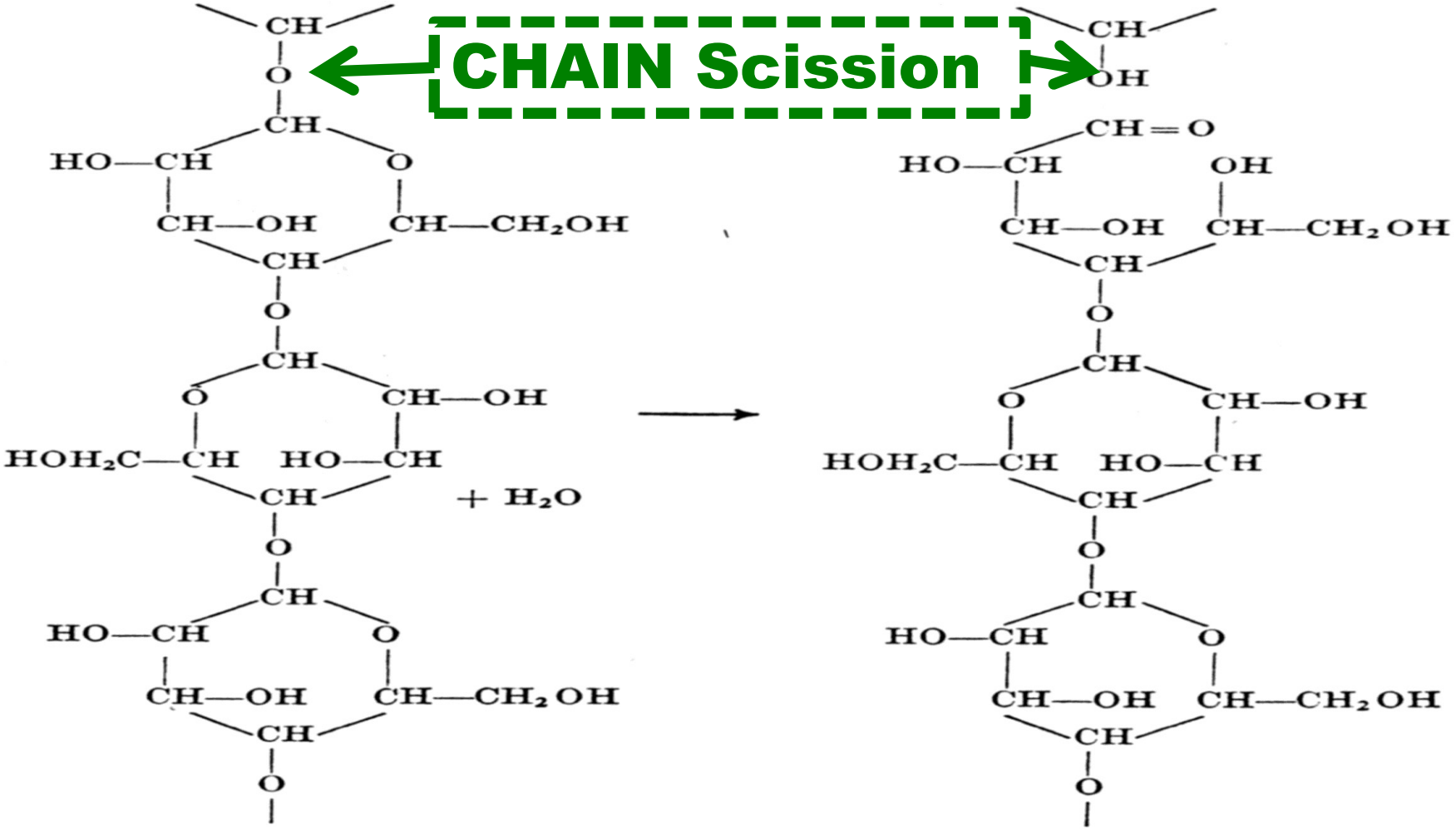
Viscose Rayon Nonwoven Textile





Cellulose hydrolysis 1

Catalysed mainly by INORGANIC ACIDS (HCl, H_2SO_4)



Cellulose hydrolysis 2

Catalysed mainly by INORGANIC ACIDS (HCl, H_2SO_4)

It is sufficient to prepare Cellulose by 1 % Solution of these Acids and dry at 60 – 70 °C

The Result is so called HYDROCELLULOSE, having the lower MW > *the Reaction see the last Picture*

HYDROCELLULOSE has other Properties:

- **It gives the REDUCING SACCHARIDES REACTION > the ENDGROUPS after Scission are ALDEHYDES**
- **It has higher Solubility in Alkalis (NaOH), MW accordingly**

Cellulose Solvents

The Derivatives of Cellulose are presented in this Table mostly!

This was found out be me in the Original literature only!

Dissolved Substance	Solvent
Celulóza	Schweitzerovo činidlo
Celulóza	NaOH
Celulóza	$Ca(CNS)_2$
Celulóza	tetraetylammoniumhydroxid
Celulóza	etylendiamin
Nitrát celulózy	aceton
Nitrát celulózy	butylacetát
Triacetát celulózy	m-kresol
Triacetát celulózy	chloroform
Xantogenát celulózy	
s 10 % S	2N NaOH
s 15 % S	2N NaOH
s 20 % S	2N NaOH
s 23 % S	2N NaOH

The latest Trends:

- **IONIC LIQUIDS,**
- **METLS OF SOLTS (e.g. $ZnCl_2 . 4H_2O$.**

What were the REASONS to start the Production of Viscose Rayon?

- ENDLESS FIBER
- Substitution of the Natural Silk
- It can coloured in Mass
- Possibilities of the various Diameters
- Possibility to control the Mechanical Properties by Drawing etc.
- Utilisation the other sorts of Cellulose then the Cotton only
- ??????????????

Oxidised Cellulose

- **Company SYNTHESIA Pardubice (Czech Republic) > Trade name OKCEL**
  - POWDER
  - TEXTILE
- **Use**
  - **Medicine – haemostatic (styptic) agent, absorbable Covering of the open wound**
  - Technical –Varnishes, foils (films), ……..
- **Production Technology**
  - **Cotton Oxidation**
    - **H_2O_2, HNO_3, Hypochlorite, …**
- **Oxidised Cellulose Types (Kinds)**
  - **Changes of the main Chain done by Oxidation**
  - **Different Solubility in Water and in NaOH water Solution**

OKCEL: Humane Medicine and Surgery

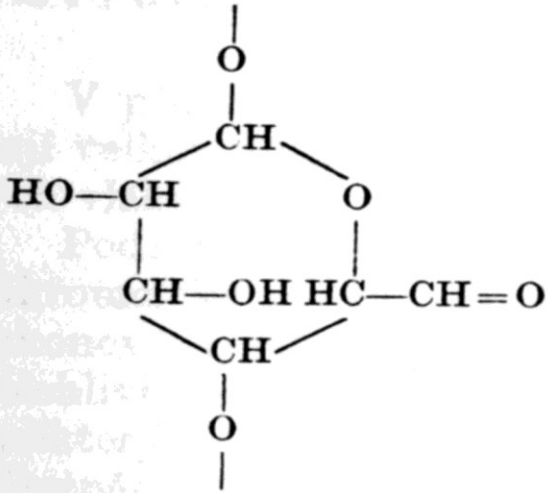
OKCEL® is a quality oxidized cellulose based haemostat designed for controlling internal bleeding during surgical procedures, includig minimally invasive procedures. It is perfectly accepted by organism and fully absorbed. Thanks to protection against infection, OKCEL® products help with the tissue regeneration and thus enhance the healing effect. OKCEL® products are available in various sizes and shapes and can be customized to meet individual customer requirements.

OKCEL® H-T
heavy duty textile form of oxidized cellulose
OKCEL® H-D
cotton wool form of oxidized cellulose
OKCEL® F
cotton wool form of oxidized cellulose

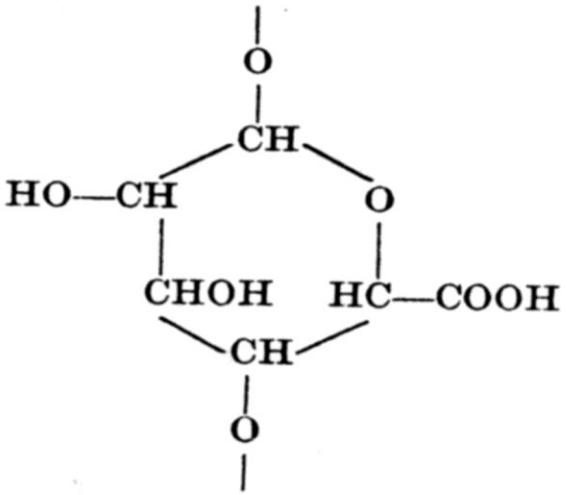
Oxidised Cellulose – basic Description of Oxidation Process 1

1. Oxidation of the hydroxyl Group (-OH) on the sixth Carbon to aldehydic Group (-CH=O), the Oxidised Cellulose of the so called REDUCTION TYPE is arising
2. Oxidation of the aldehydic Group (-CH=O) on the sixth Carbon to carboxylic Group (-COOH), the Oxidised Cellulose of the so called ACIDIC TYPE is arising
3. Oxidation of the hydroxyl Group (-OH) on the second and third Carbons to aldehydic Groups (-CH=O), without an Opening of the Glucopyranose Cycle, the Oxidised Cellulose of the so called HIGHLY REDUCTION TYPE is arising
4. Oxidation of the hydroxyl Group (-OH) on the second and third Carbons to aldehydic Groups (-CH=O), WITH an Opening of the Glucopyranose Cycle, the Oxidised Cellulose of the so called REDUCTION TYPE is arising
5. Oxidation of the aldehydic Group (-CH=O) the Step 4) accordingly to the Oxidised Cellulose of the so called ACIDIC TYPE is arising
6. Oxidation on the first Carbon is negligible, it concerns the aldehydic Group (-CH=O) on the Macromolecular Chain only

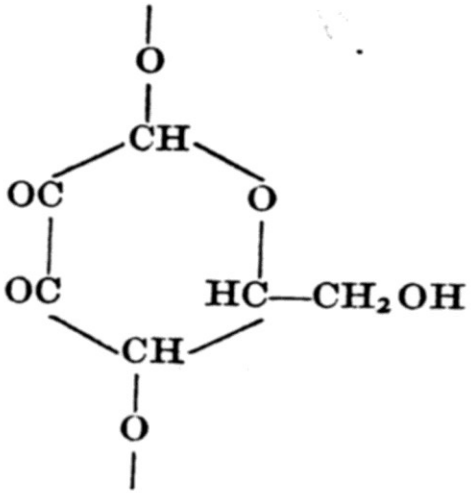
Oxidised Cellulose – basic Schema of Oxidation Process 2



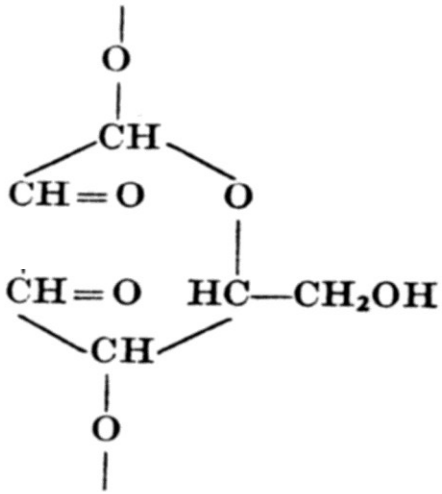
1a



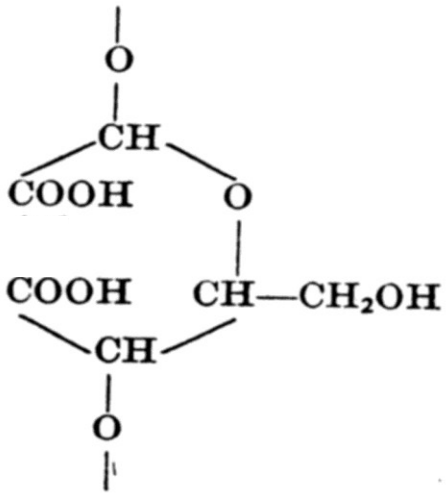
1b



2a

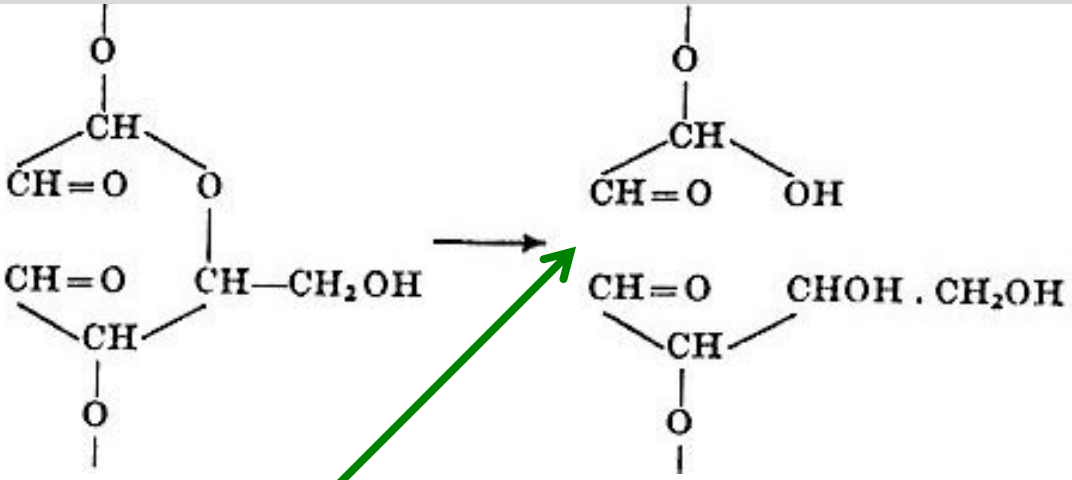


2b

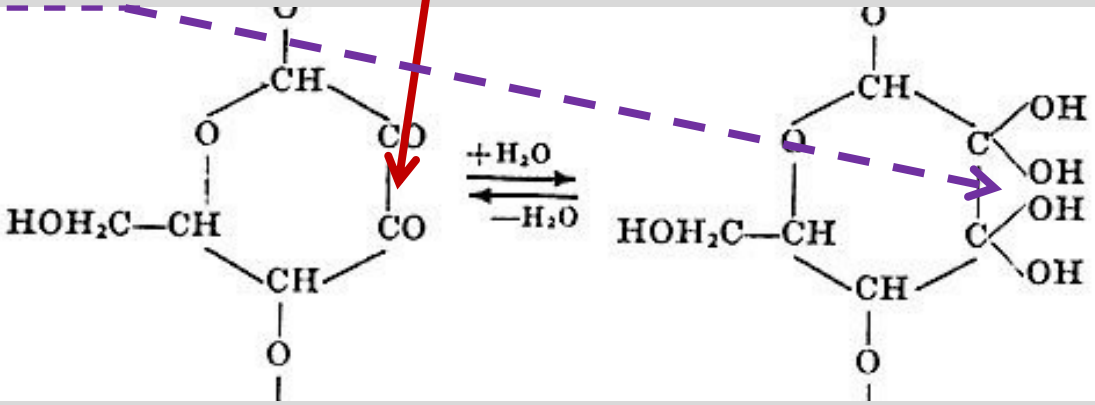


2c

Oxidised Cellulose with two to aldehydic Groups (-CH=O) in the Positions 2 and 3 is very easy to hydrolyse in the alkali Medium

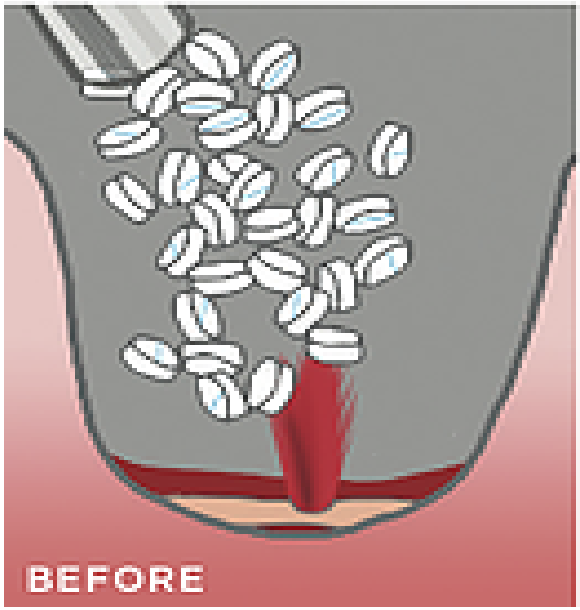


Diketonic Oxidised Cellulose is due to Conjugation of both Ketogroups yellow, the Water have effect on this Colour, which is dissipating. It could be caused by a reversible Hydratation.



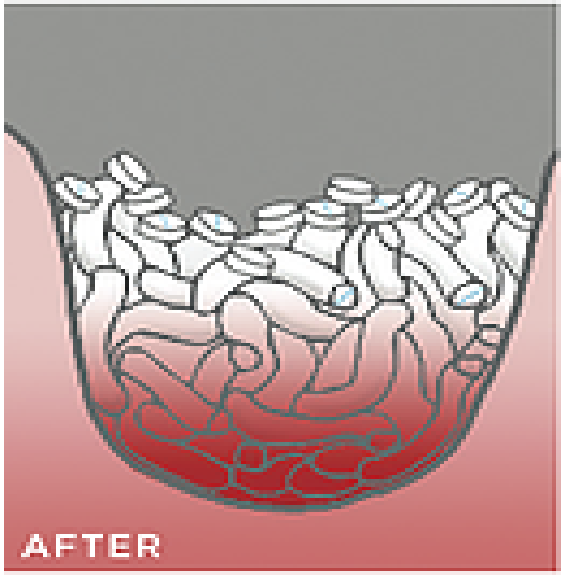
This type of the Oxidised Cellulose is also easy to hydrolyse.

Cellulose haemostatic (styptic) agent

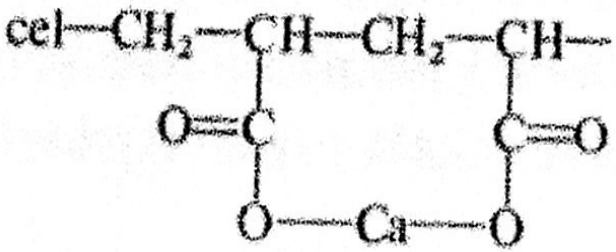


XStat® is a first-in-kind **hemostatic device** for the treatment of gunshot and shrapnel wounds. XStat works by injecting a group of **small, rapidly-expanding sponges into a wound cavity** using a syringe-like applicator. Each sponge contains an x-ray detectable marker. In the wound, the XSTAT sponges expand and swell to **fill the wound cavity within 20 seconds of contact with blood. This creates a temporary barrier to blood flow and provides hemostatic pressure.**

US Patent 8,828,050 B2



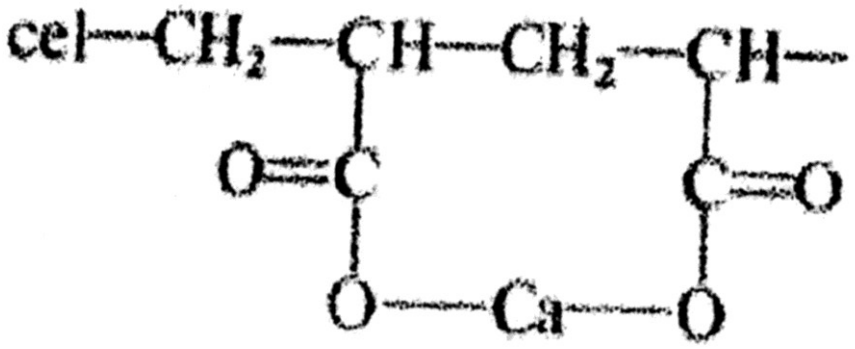
Obvazové tkaniny zastavující krvácení se připravují roubováním celulosy vápenatou solí kyseliny akrylové:



Podrobný popis výrobku Kompres Medicomp nester.10x10cm/100ks 4218251
Kompres z netkaného textilu Medicomp může být v mnoha oblastech na oddělení i v ambulanci vhodnou alternativou ke klasickému mulovému kompresu.
Kompresy z netkaného textilu Medicomp z **60 % viskózy a 34 % polyesterových vláken** mají otevřenou, mulu podobnou strukturu. Proto mají velmi dobrou savou schopnost, jsou měkké a prodyšné. Netkaný textil je čistě mechanicky stabilizován a bez pojidel i optických bělicích látek. Pro hospodárné použití jsou k dispozici kompresy z netkaného textilu Medicomp s různým počtem vrstev a s rozdílnými rozměry, sterilizované pro přímé použití i nesterilizované. Speciálně k ošetření ran s drenáží, při tracheotomiích a extenzích i jako ochrana při aplikaci kanyl a sond jsou k dispozici kompresy z netkaného textilu Medicomp Drain ve tvaru Y.
Ke všeobecnému ošetření ran; jako tampon a jako kompres při ambulantních a stacionárních zásazích.

Cellulose GRAFTING to get Haemostatic (styptic) agent

Cellulose GRAFTING by ACRYLIC ACID



The Haemostatic (styptic) is done by influence of Ca^{+2} Salt of the Acrylic Acid

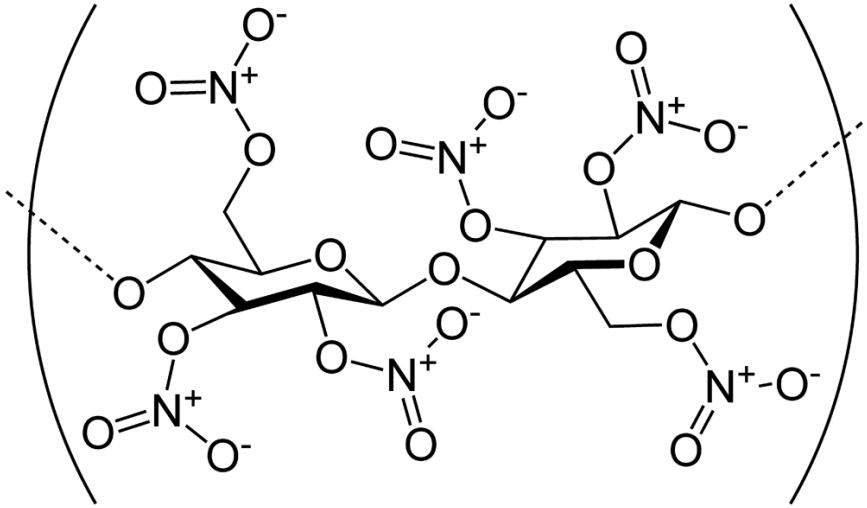
Nitrocellulose 1

- **Company SYNTHESIA Pardubice (Czech Republic) > an Example >>>**
- **Industrial nitrocellulose type A**
  - Nitrocellulose type A with nitrogen content 10,6-11,3% is characteristic with good solubility in alcohol-type solvents and good solubility in ethyl alcohol (up to 100 %). It forms films with *Available wetting agents:* ***ethanol, isopropanol, water – 30 or 35%.*** *thermoplastic and good mechanical properties*
- **Use**
  - *Explosives*
  - **Civilian – Plastics, Varnishes, Foil, ……..**
- **Manufacture Technology**
  - **Oxidation of Wood Pulp or Cotton**
  - **HNO_3**
- **They are ideal for wood finishing, metal, leather, coating lacquers, for production of printing inks, nail varnishes and membranes.**
- **The manufacturing programme consists of two basic type ranges of industrial nitrocellulose, differing in their nitrogen content, viscosity, solubility in solvents and resulting nature of the film.**

Nitrocellulose 2

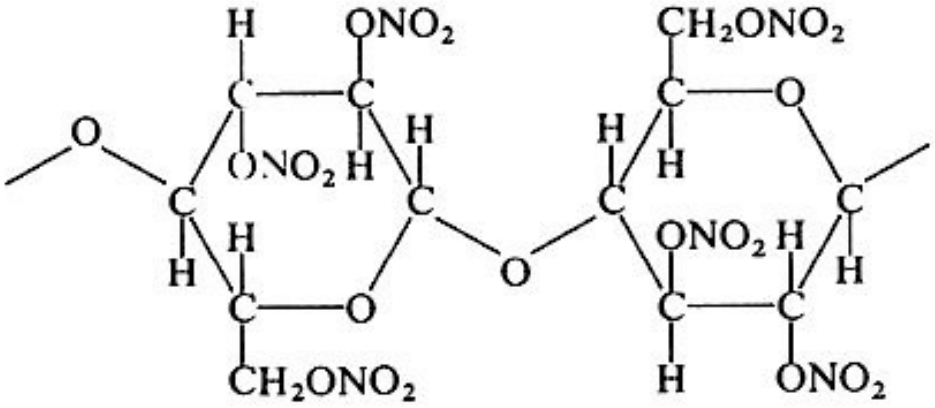
Collodium is a Solution of **Nitrocelluose** in **ether** and **ethanol**, **having a** syrup like Consistency used in Surgery as a **„Liquid bandage"** and for a Holding of a Covering on a given Place. Applied on the Skin, it forms the dry elastic Cellulose Film.

The ACRYLATES are currently used for this Purpose as the Spray also.



Nitrocellulose having high nitration Level

Pyroxylin = another E*NGLISH name for* Nitrocellulose



(21.7)

The currently used Nitrocellulose has the Nitrogen content lower. Approx. 13,5 % w/w for the Explosive and 10,5 – 12,5 % w/w for the Civilian use.

Dividing of the Nitrocellulose based on the Nitrogen content (An EXAMPLE ONLY!)			
Nitrocellulose Type	Nitrogen content (% w/w)	Mostly used Solvents	Use
A	10,5 – 11,2	Ethanol	Celluloid, paints (Varnishes (lacquers))
M	11,2 – 11,7	Esters, ketons, mixture of diethylether - ethanol	Paints (Varnishes (lacquers))
E	11,8 – 12,5		
	12,0 – 13,5	---	Explosives

Nitrocellulose 3

- **Solvent Varnishes (LACQUERS)**
- **The lower Nitrogen Content > Solubility in EtOH and Aromatics > POLISHES**
- **The middle Nitrogen Content > Solubility in ethylacetate & butylacetate > NITROCELLULOSE LACQUER > quick-drying >Hard layer**
  - **If a more elastic film is necessary > ELASTIC AFTER ADDITION OF PLASTICIZERS > PTHALATE PLASTICIZERS**

FORMER USE WAS ALSO:

- **Car organic Solvent Varnishes (LACQUERS) > WATER BASED MATERIALS NOW**
- **Ski Runner organic Solvent Varnishes (LACQUERS)**

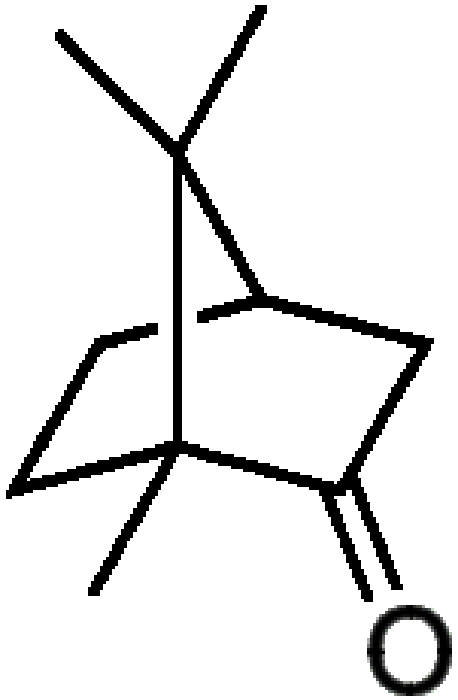
Nitrocellulose 4/1 - CELLULOID

Nitrocellulose wetted by Alcohol (100 weight Parts) s mixed in a kneading Mixer with Camphor (27 to 33 weight Parts) and the other Ingrediens (Plasticizers, Pigments, Colouring agents, Stabilizers) are added and this all is further mixed. To get good homogeneity, some Ethanol is further added. It is mixed at 40 – 50 °C for several Hours. The Filtration is the next Step. The Ethanol is evaporated during kneading at two Roll mill, at which the Homogenisation is finished. The Matter is then fully Gelantioned. The Calendered Sheets are hot pressed to a desired Thickness and after it are dried at 30 – 50 °C for several Hours to remove the Rest of the Ethanol. The last Manufacture step is a Polishing.

An Advantage of the Celluloid is very good colourability, possibility of do various Graving and easy Processing. A Disadvantage is Flammability and the Manufacturing labour intensity. The freshly made Celluloid has the Camphor smell, which is lowering in the course of time. The Celluloid is soft and mouldable after heating to approx. 70 – 100 °C (Thermoforming). It is decomposed at temperatures over approx. 170 °C. Its Importance and Production volume is lowering steadily.

Made of Celluloid: Combs,Table tennis Balls, Art Products etc.

Nitrocellulose 4/2 - CELLULOID

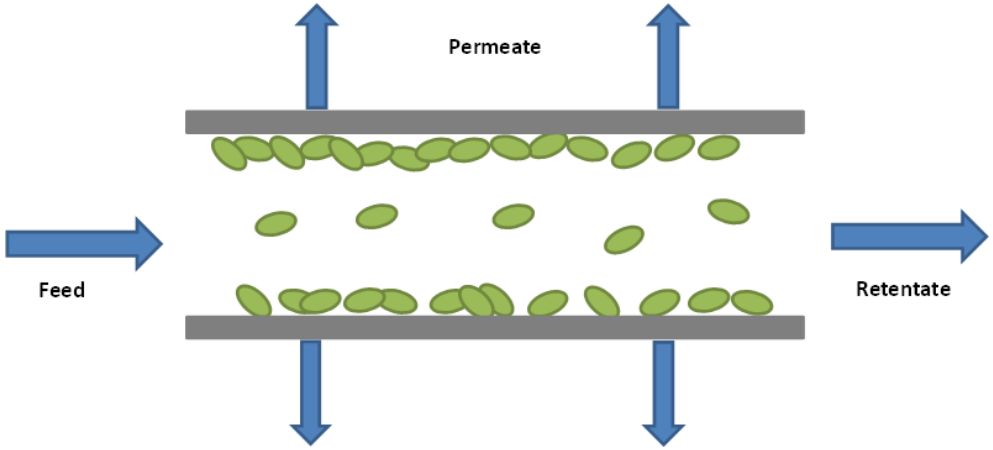


Camphor

GENERAL	
Systematic name	1,7,7-trimethylbicyklo[2.2.1]heptan-2-on
Anglický name	**Camphor**
Summary **formula**	$C_{10}H_{16}O$
Appearance	White crystalsy, aromatic smell
Identification	
Registration number CAS	76-22-2
properties	
Molecular weight	152,23 g/mol
Mlting point	175-177 °C
Boliling temperature	204 °C
Density	0,990 g/cm^3
Solubility in water	1,2 mg/l

Nitrocellulose 5 - ULTRAFILTRATION

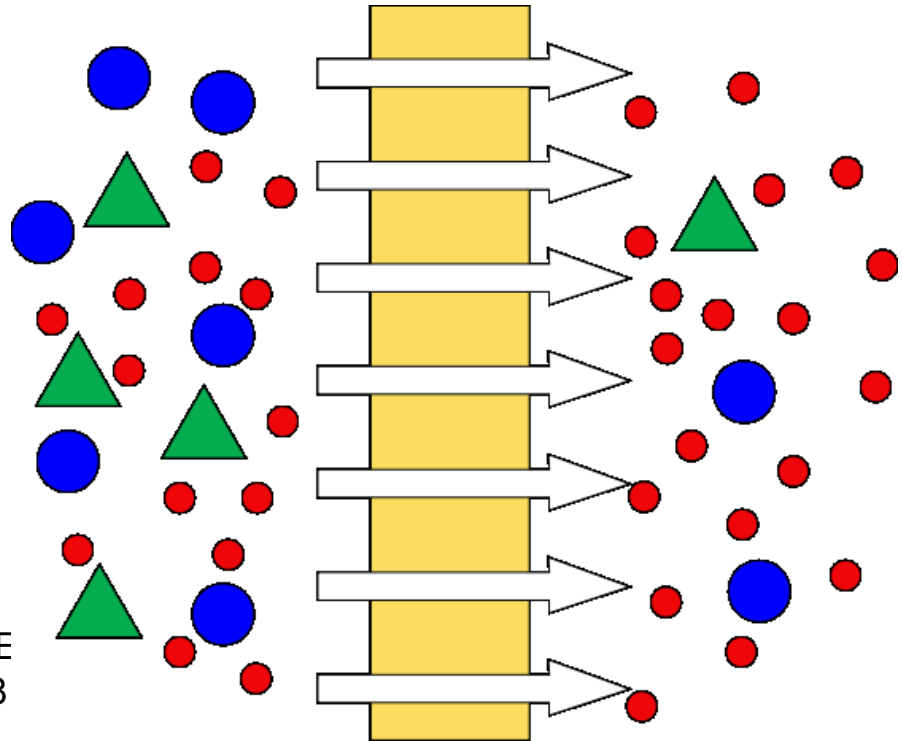
ULTRAFILTRATIONS, so called also as **MEMBRANE FILTRES**, are the Micro porous films manufactured by Casting of the Nitrocellulose Solution. Their filtration Efficiency is done by the presence of the Ultrafine pores, being of 0,1 – 5,0 mm.



An Example

Pores diameter (μm)

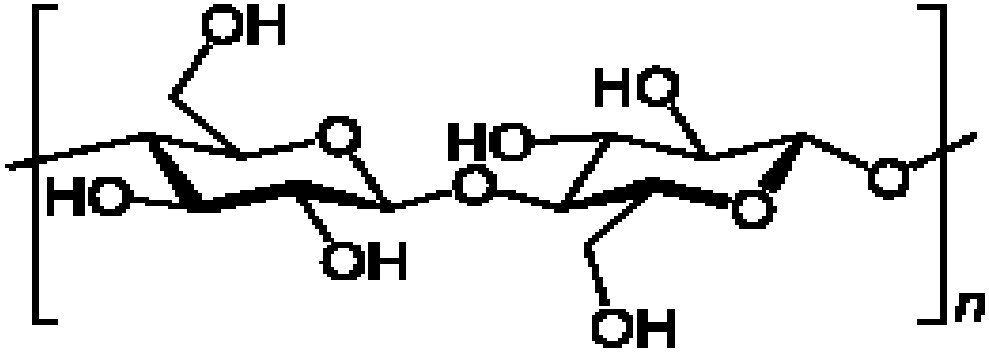
Diameter range (μm)	Diameter mean Value (μm)
0,1 – 0,3	0,25
0,3 – 0,5	0,40
0,6 – 0,9	0,85
1,0 – 1,2	1,1
2,0 – 5,0	---



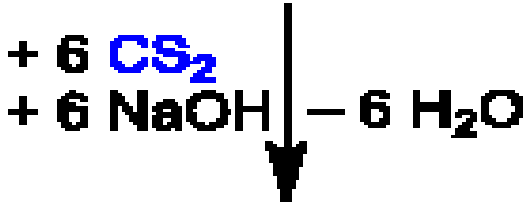
OLYME
2018

CELLOPHAN

- **Manufacturing similar to Viscose Rayon, it is from Solution, but by Casting from the flat Die to the Precipitant**
- **Film is brittle > so it is plasticized by Glycerol (approx. 10 – 15 % w/w)**
- **It is often surface treated by Nitrocellulose Varnish > Food Wrap and Cigarette Wrap (BOPP now)**
- **It is mouldable after Moistening > Capping of the Glasses etc.**
- **Water Vapour permeable after Moistening SEMIPERMEABLE MEMBRANE > HEMODIALYSIS (*Formerly*)**

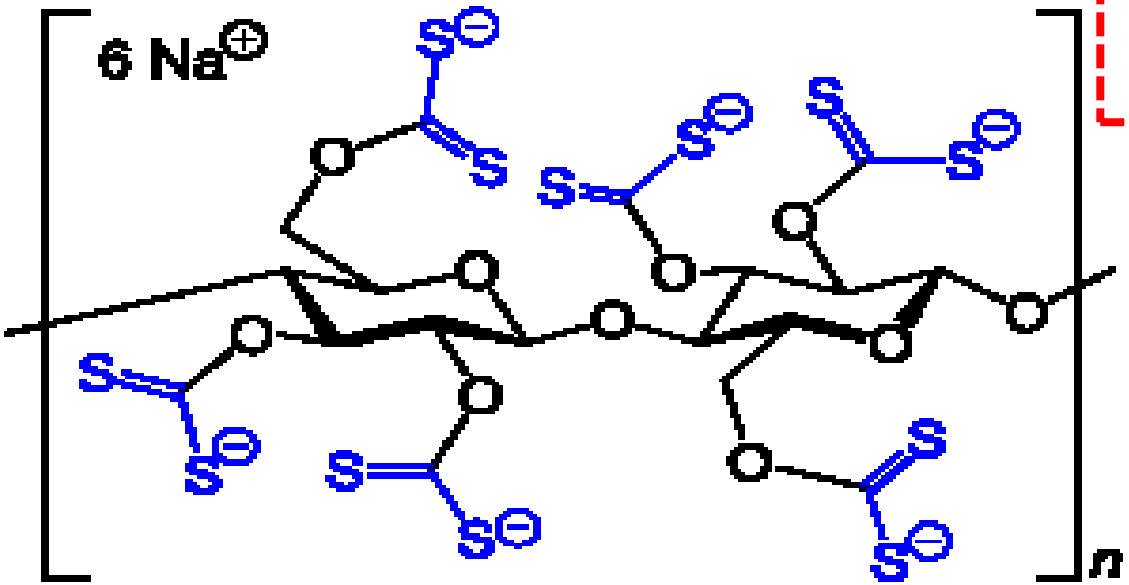


α **Cellulose Content must be high, approx. 89 – 90 %w/w for the Manufacture of CELOPHANE**

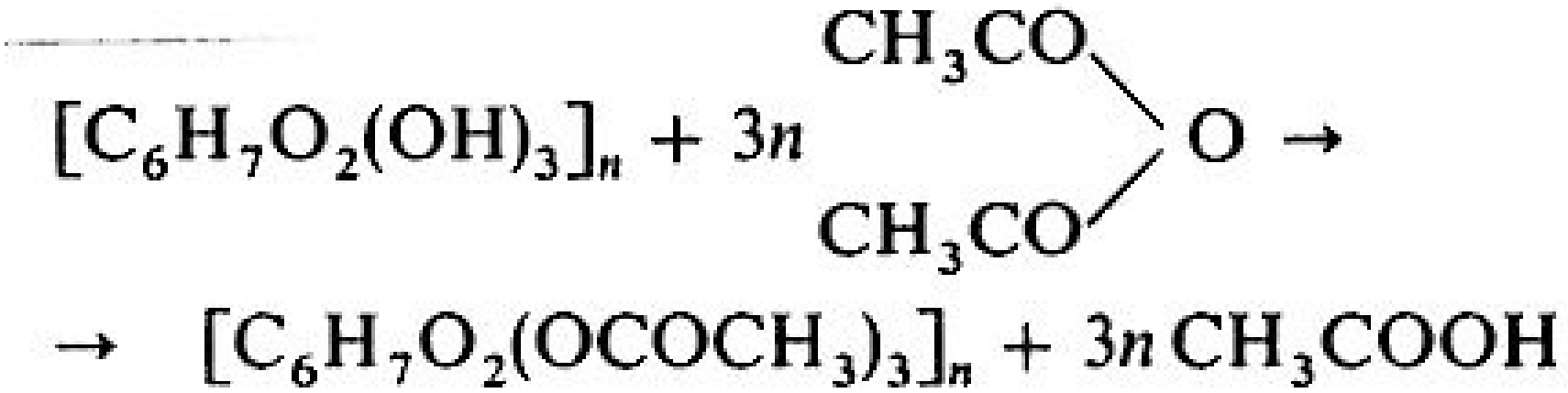


CELULOSE XANTOGENATION

Once more this Schema



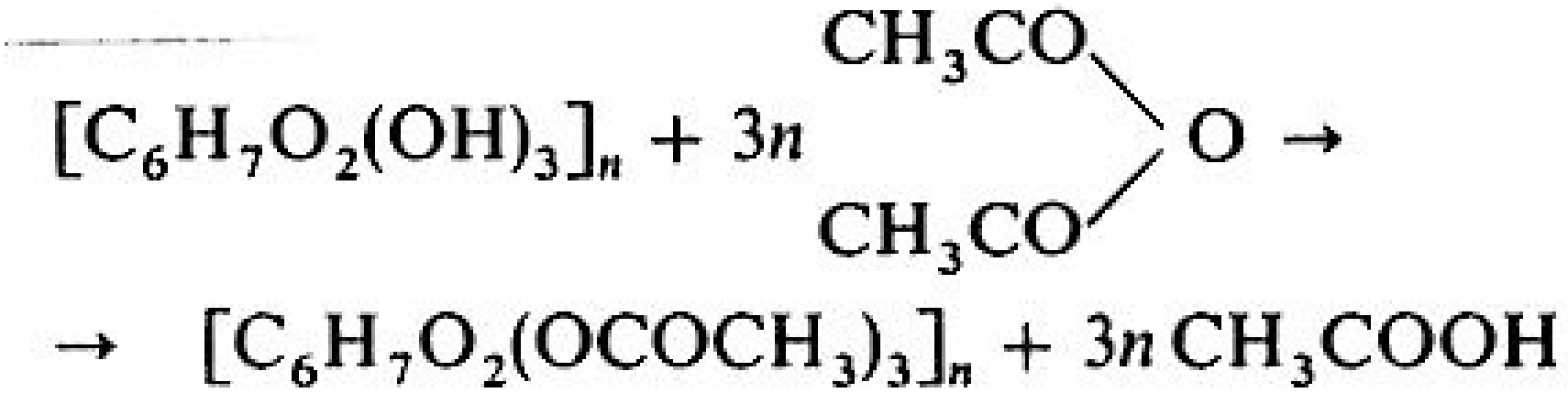
Acetát celulózy > vlákna, plasty



Kdysi vyráběla SYNTHESIA Pardubice

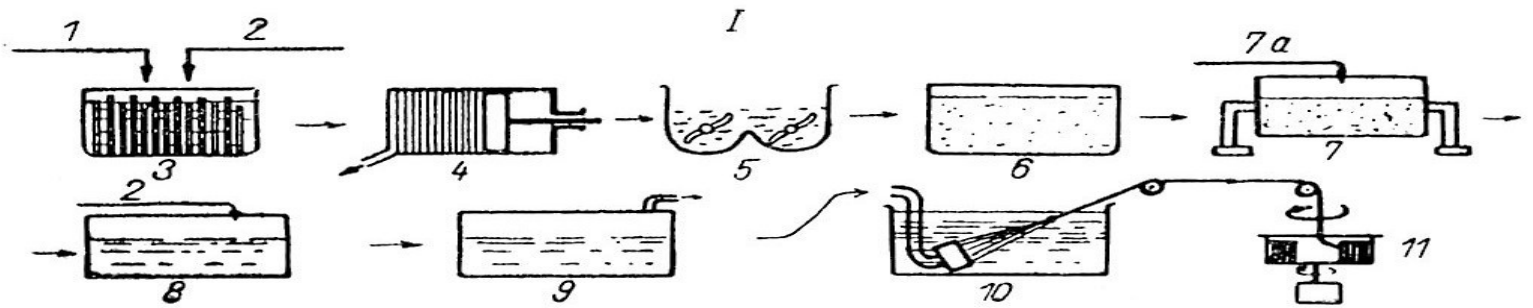
Nyní např. www.mazzucchelli.it > pro designové výrobky, např. brýle

Cellulose Acetate > Fibers, Plastics

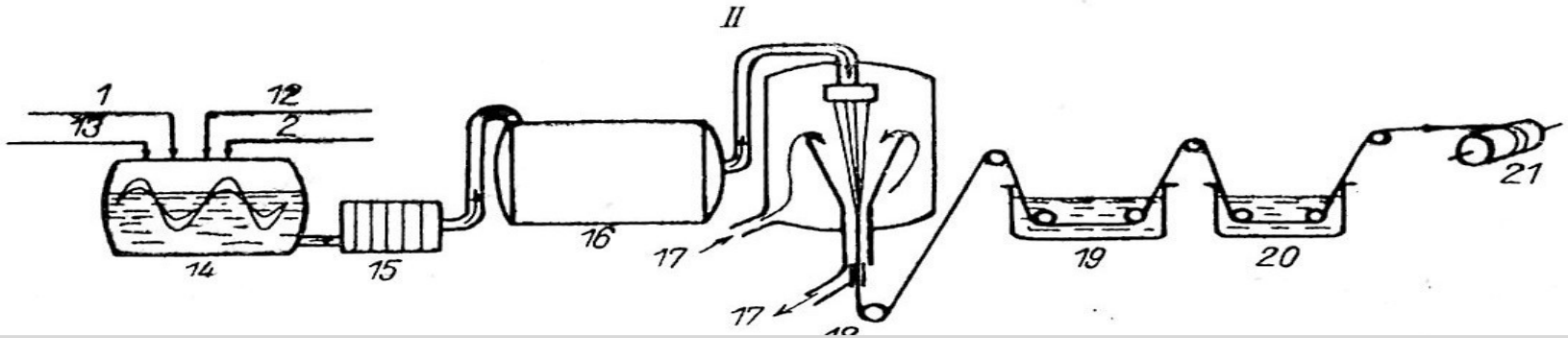


A Current producer e.g. www.mazzucchelli.it > for design Products, e.g. Glasses Frames

Cellulose based Fibres – Manufacture Schemas I



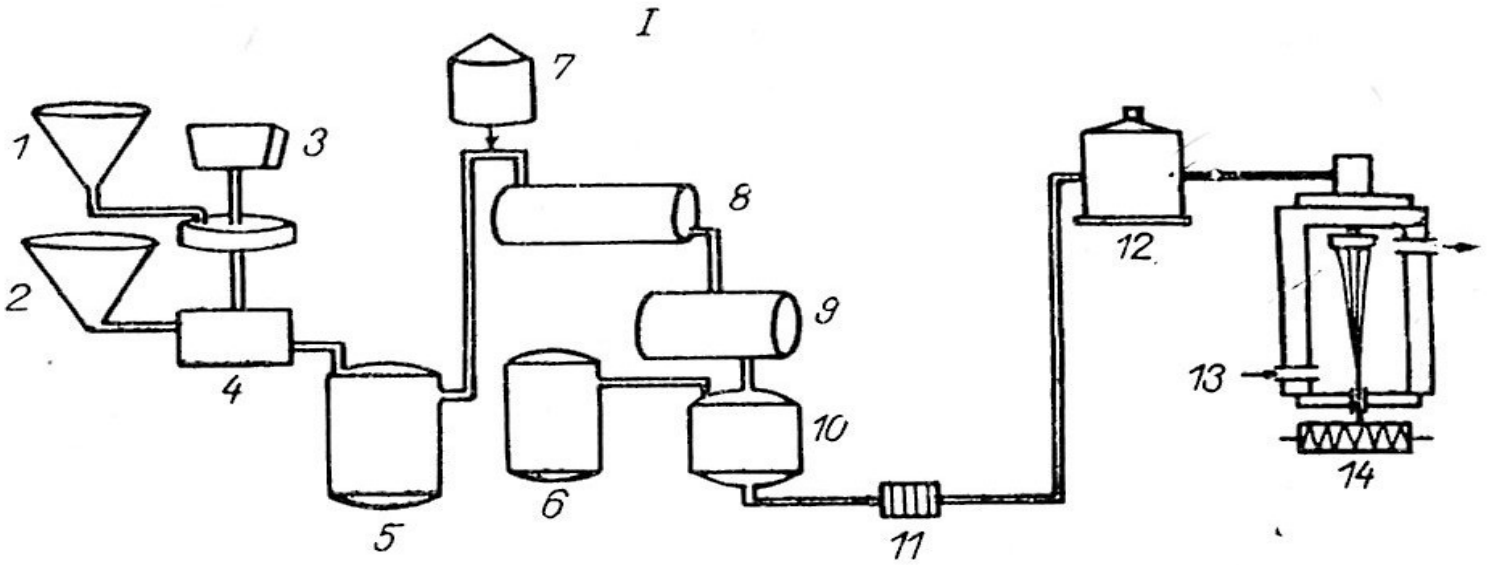
VISCOSE Rayon Manufacture



Cuprammonium Rayon Manufacture

1) Cellulose, 2) NaOH Solution, 3) Caustic dip, 4) Pressing, 5) Fibrillation, 6) Alkalicellulose Maturing, 7) Sulfidation, 7a) CS_2, 8) Dissolving Carboxymethylcellulose to VISCOSE, 9) Deaeration and Carboxymethylcellulose Maturing, 10) Spinning, 11) Filament Winding, 12) $CuSO_4$, 13) NH_3, 14) Cellulose Dissolving, 15) Filtration, 16) Tank, 17) Water, 18) Drawing Spinning, 19) Acid Liquor, 20) Washing, 21) Filament Winding

Cellulose based Fibres – Manufacture Schema II

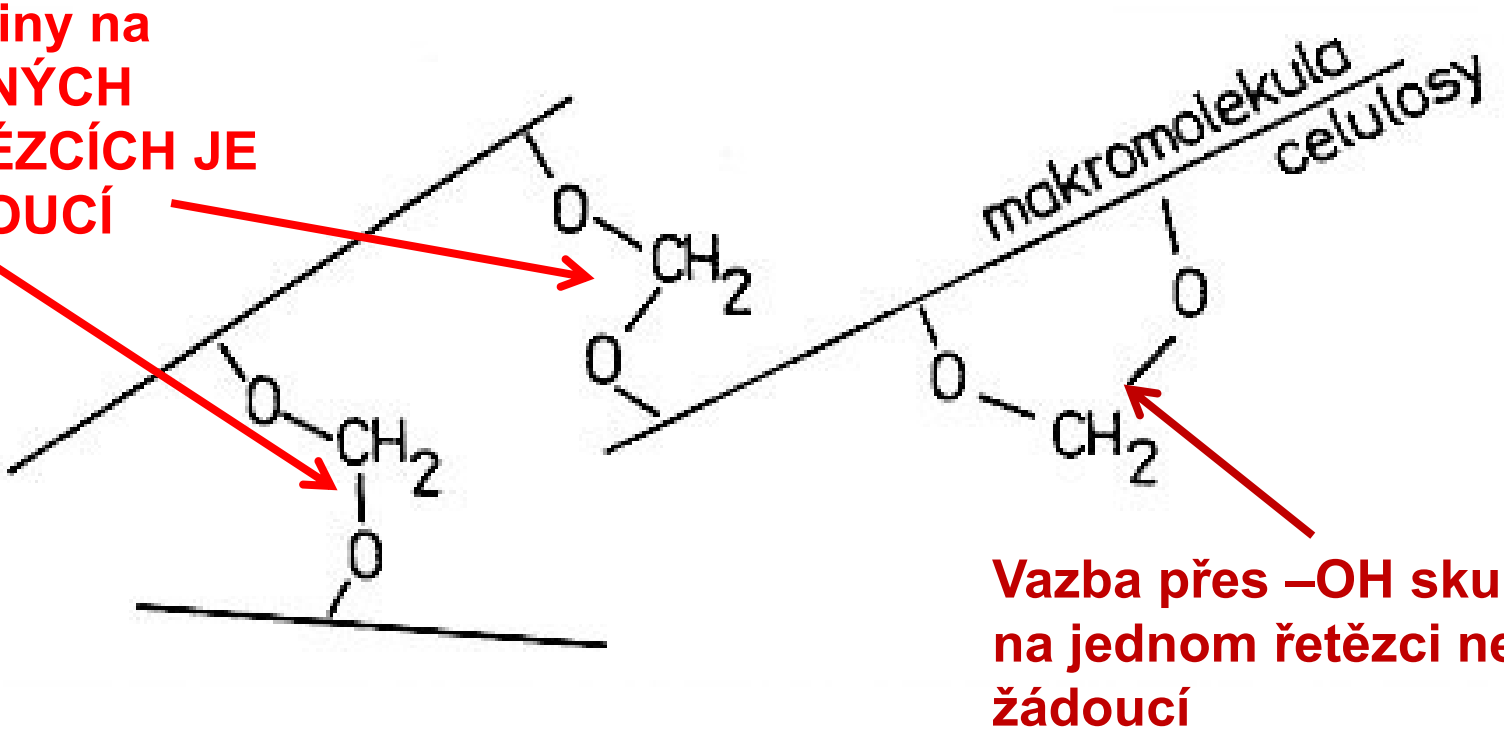


Cellulose Acetate Rayon Manufacture

1) Acetic Acid, 2) Acetanhydride, 3) Cellulose, 4) Kneading, 5) Triacetate tank, 6) Acetone, 7) Water, 8) Precipitation, 9) Hydrolysis, 10) Dissolving of the Secondary Acetate, 11) Filtration, 12) Tank for the Spinning Solution, 13) Hot Air, 14) Spinning & Winding

Vazba molekul celulózy > sesíťovaná vlákna

Vazba přes –OH skupiny na RŮZNÝCH ŘETĚZCÍCH JE ŽÁDOUCÍ



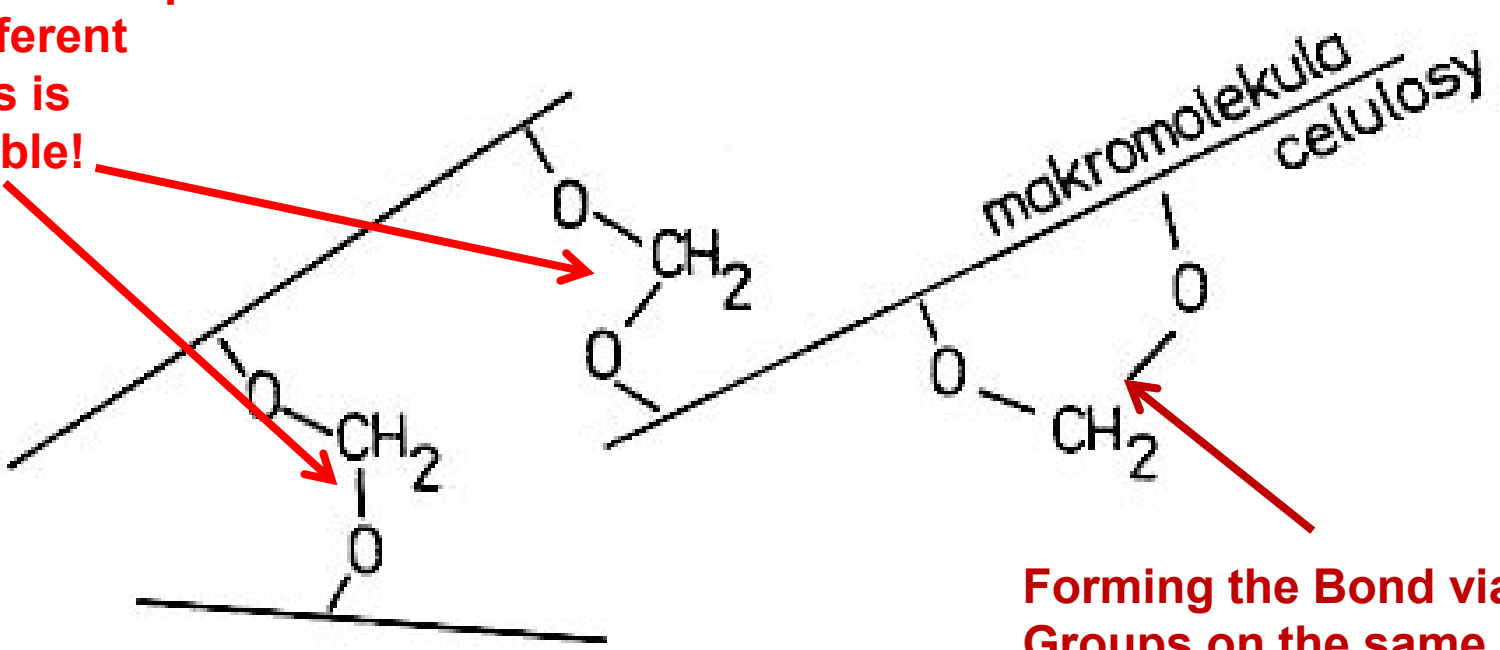
Vazba přes –OH skupiny na jednom řetězci není žádoucí

Umělý pergamen – H_2SO_4 > balení tuků

Vulkánfíbr – $ZnCl_2$ > kufry, složky

Fibers Crosslinking – molecular Schema

Forming the Bond via –OH Groups on Different Chains is desirable!



Forming the Bond via –OH Groups on the same Chain is Undesirable!

Artificial Parchment paper – Treatment by H_2SO_4 > Packaging of Fats
Vulcanized fibre – Treatment by $ZnCl_2$ > Luggage, Office letter folder

Microcrystalline Cellulose

- Inertní látka pro přenos účinné látky léčiv a potravinových doplňků
- Nakypřovací prostředek v potravinách
- Vláknitá přísada do potravin

Cellulose Derivatives in Pharmacy

Neutral and Additive Substances based on the CELLULOSE

Složení:
Glukosamin sulfát.2KCl (**z korýšů**), plnidlo (mikrokrystalická celulóza, sodná sůl karboxymethylcelulózy, hydroxypropyl-methylcelulóza), výtažek z plodů jírovce maďalu, protispékavá látka (stearan hořečnatý), kyselina askorbová, potahovací látka (hydroxypropylmethylcelulóza, mastek), barvivo (oxid titaničitý).

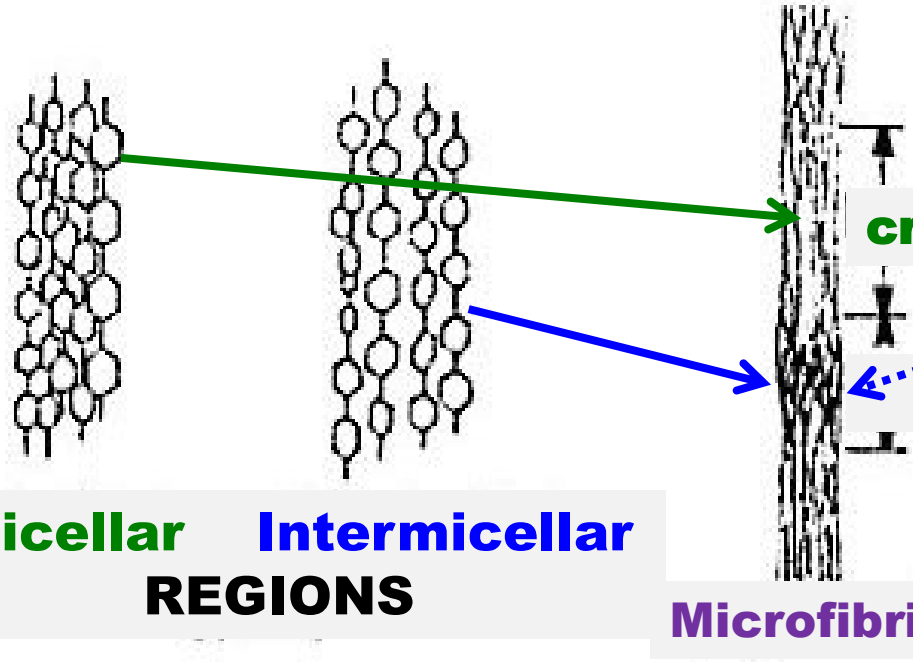
Nanocellulose

Nanocellulose, or microfibrillated cellulose (MFC) is a material:

composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). Typical **lateral dimensions are 5–20 nanometers** and **longitudinal dimension is in a wide range from tens of nanometers to several micrometers**. It is pseudo-plastic and exhibits the property of certain gels or fluids that are thick (viscous) under normal conditions, but flow (become thin, less viscous) over time when shaken, agitated, or otherwise stressed. This property is known as thixotropy. When the shearing forces are removed the gel regains much of its original state. The fibrils are isolated from any cellulose containing source including wood-based fibers (pulp fibers) through high-pressure, high temperature and high velocity impact homogenization (see manufacture below).

Nanocellulose can also be obtained from native fibers by an acid hydrolysis, giving rise to highly crystalline and rigid nanoparticles (generally referred to as **nanowhiskers) which are shorter (100s to 1000 nanometers) than the** nanofibrils obtained through the homogenization route. The resulting material is known as **nanocrystalline cellulose** (NCC).

Supermolecular Structure of Cellulose I



Space between the Microfibrils is filled by HEMICELLULOSE & LIGNIN

Fibrils are selectively broken in the AMORPHOUS REGIONS > *CRYSTALLINE NANOPARTICLES ARE RESULTING*

AMORPHOUS CELLULOSE:
- **easy to swell**
- **is more reactive than the crystalline one**

Hierarchy of STRUCTURES in CELLULOSE:
- **Macromolecule,**
- **Microfibril,**
- **Fibril,**
- **LAMELAE.**

Nanocelulóze je věnována pozornost již MINIMÁLNĚ 10 let, hlavně ve Švédsku, Finsku a Norsku

Cellulose Nanocrystals and Nanocomposites

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Duane Priddy Sr. - Jul 25, 2011

Technical Paper - Aqueous suspensions of cellulose nanocrystals can be obtained by hydrolysis of lignocellulosic fibers. Cellulose nanocrystals correspond to defect-free rod-like nanoparticles that present remarkable properties such as light wt., low cost, availability of raw material, renewability, nanoscale dimension, and unique morphology. Because of these properties, cellulose nanocrystals have been largely applied as reinforcing fillers in nanocomposites materials. This article discusses the preparation, morphology features, and physical properties of cellulose nanocrystals, as well as their incorporation in tough and renewable nanocomposite materials.
More information on: http://www.tappi.org/...

Source : Ramires, Elaine C.; Dufresne, Alain. The International School of Paper, Print Media and Biomaterials, Grenoble Institute of Technology, Fr. Tappi Journal (2011), 10(4), 9-16. Publisher: TAPPI Press

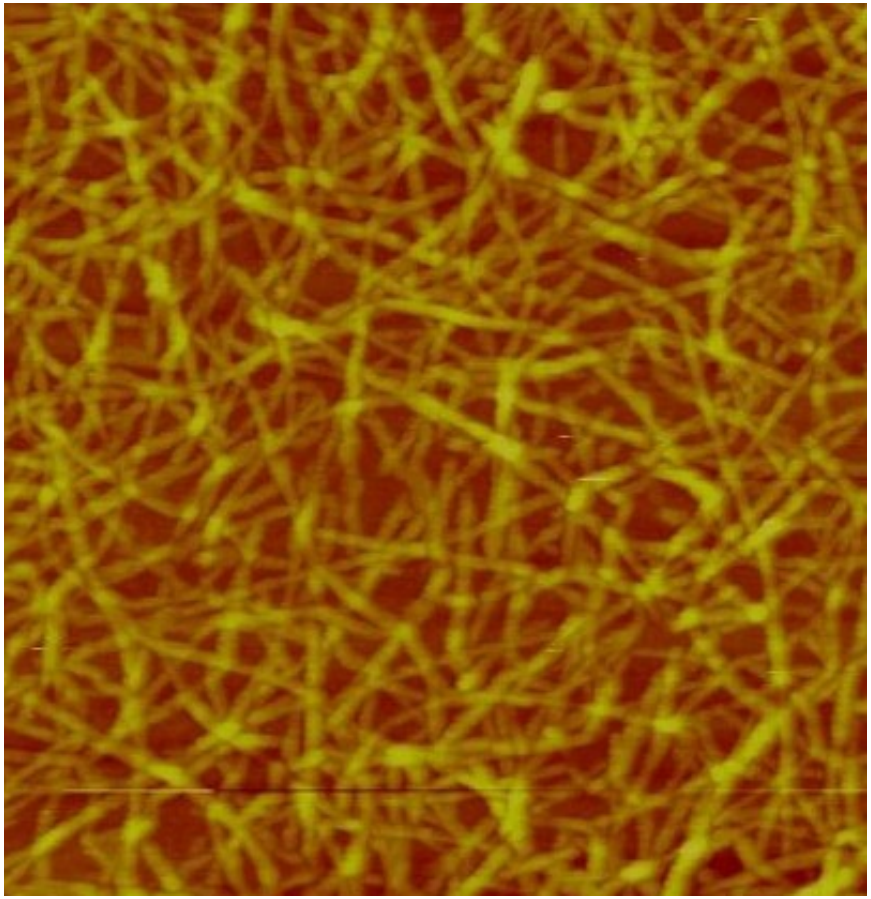
Source : Yang, Han-Seung; Gardner, Douglas J. AEWC-Advanced Structures and Composites Center, Forest Bioproducts Research Institute (FBRI), University of Maine, Orono, ME, USA. Wood and Fiber Science (2011), 43(2), 143-152. Publisher: Society of Wood Science and Technology

Mechanical Properties of Cellulose Nanofibril-filled PP Composites

Duane Priddy Sr. - Jul 22, 2011

Technical Paper - Cellulose nanofiber (CNF), microfibrillated cellulose (MFC), and microcrystalline cellulose (MCC) filled-polypropylene (PP) composite samples were manufactured using a melt mixing technique. Mechanical testing was conducted to investigate tensile and flexural properties of the composites at different filler loading levels. Test results showed that in the case of cellulose nanofibril fillers, the composites sustained considerable tensile strength up to 10% (w/w) filler loading whereas the tensile strength of the MCC-filled composites decreased continuously. Moreover, tensile modulus increased as filler loading increased for all cellulose fillers. CNF and MCC-filled composites demonstrate plastic deformation and longer elongation at break than MFC-filled composites while MFC-filled composites exhibited a quasi-brittle behavior under tensile deformation. Flexural strength of cellulose nanofibril-filled composites decreased slightly as a function of filler loading up to 6% (w/w) and increased beyond 6% (w/w). The 10% (w/w) cellulose nanofibril-filled composite samples exhibited sustained flexural strength as compared with neat PP. The trend of increased flexural modulus of elasticity behavior was identical to the tensile modulus of elasticity behavior.
More information on: http://swst.metapress.com/...

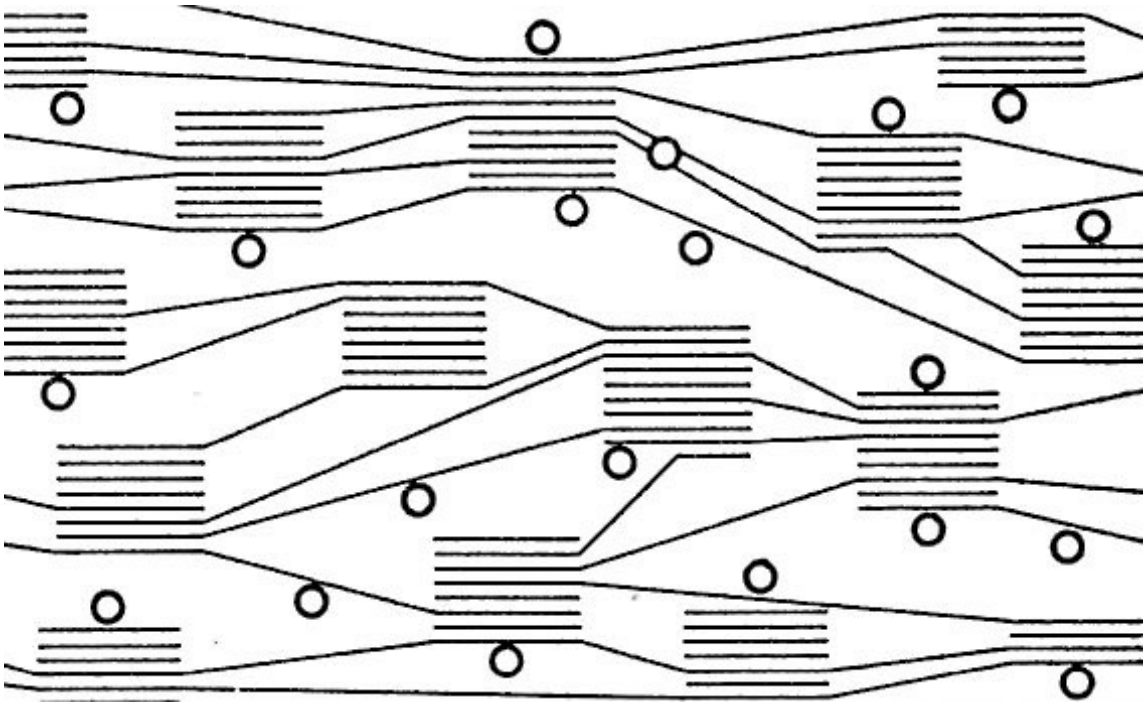
Nanocellulose



AFM height image of carboxymethylated nanocellulose adsorbed on a silica surface. The scanned surface area is 1 μm^2 >

FIBRES HAVE DIAMETER approx. 80 – 100 nm

Cellulose as the IONEXCHANGER



Microstructure Schema of the Cellulose Fibres based Ion exchanger

Lines – Cellulose Chains, Circles - Ion exchanging Groups