

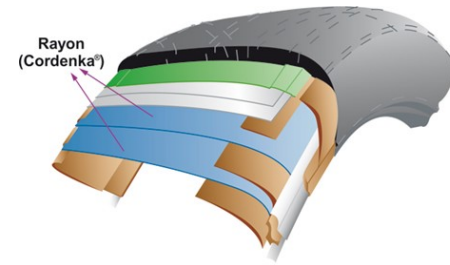
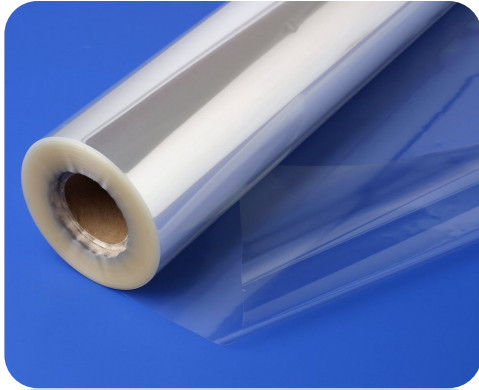


Aalto University
School of Chemical
Engineering

Cellulose: Regeneration

CHEM-E2140 - Cellulose Based Fibres
Michael Hummel

Cellulose products

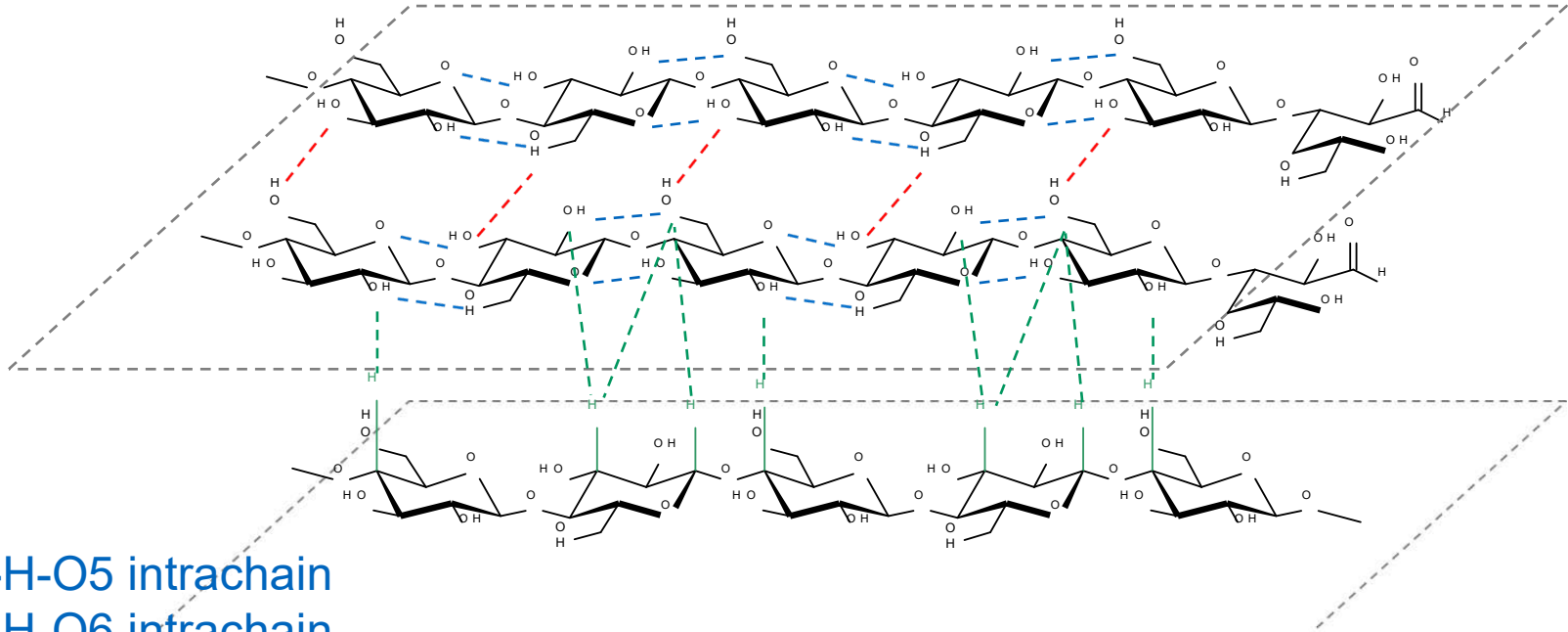


Learning outcomes

After this lecture you know

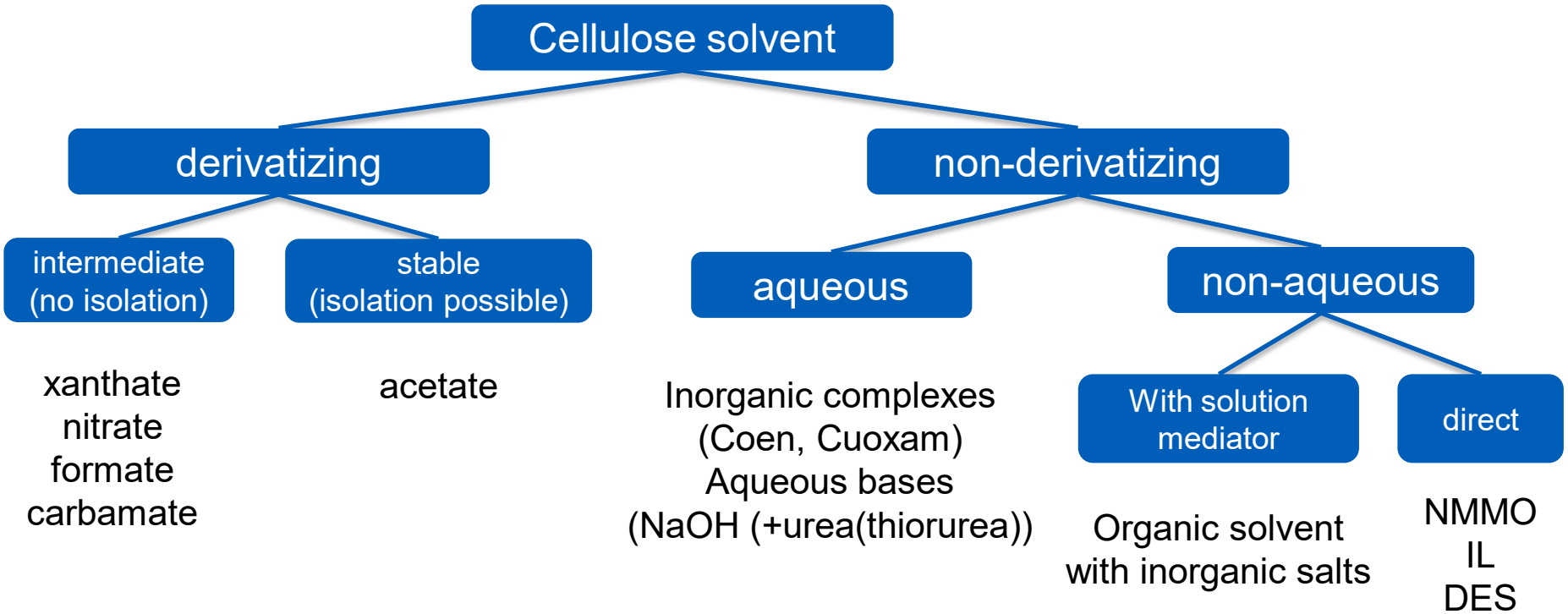
- a history of man-made cellulosic fibers
- different cellulose solvents
- how to classify the quality of a cellulose solvent
- difference between regeneration and coagulation

Non-covalent bonds in cellulose



O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond

Cellulose dissolution - overview



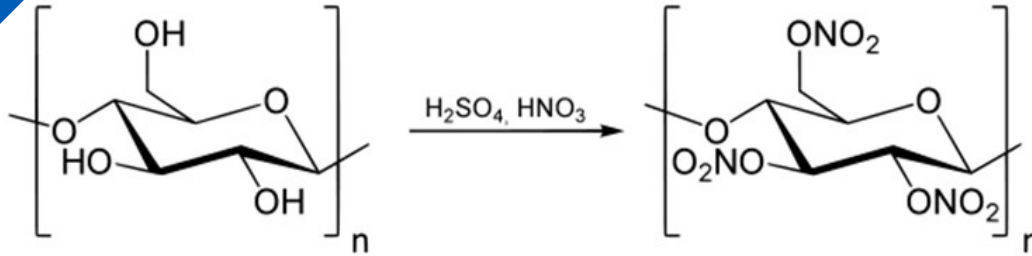
Regeneration

Coagulation

History of cellulose solvents

1846: Cellulose nitrate

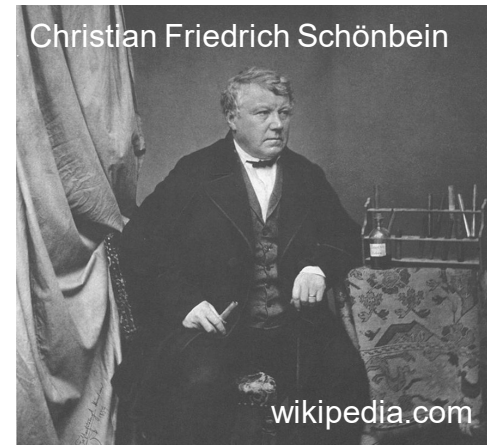
derivatizing



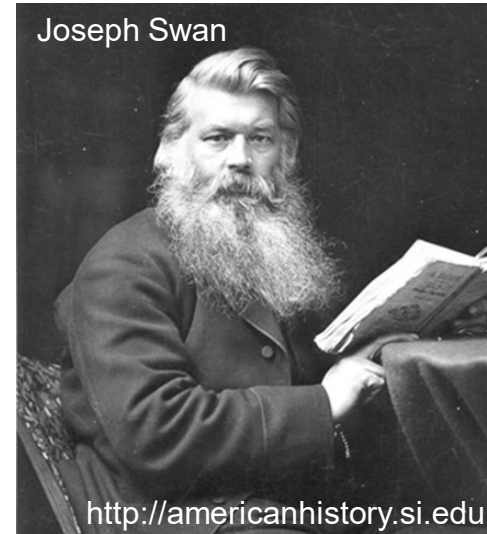
= guncotton, highly flammable

Swan developed the process to spin cellulose nitrate and de-nitrate the cellulose using ammonium bisulfate; yet he did not pursue this process further

Christian Friedrich Schönbein

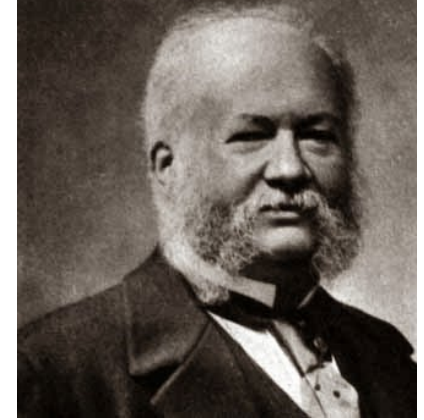


Joseph Swan



1889: Chardonnet silk

Hilaire de Chardonnet



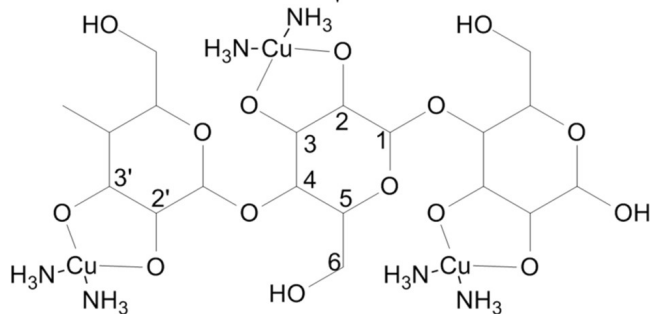
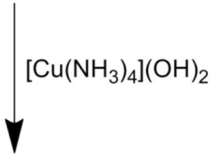
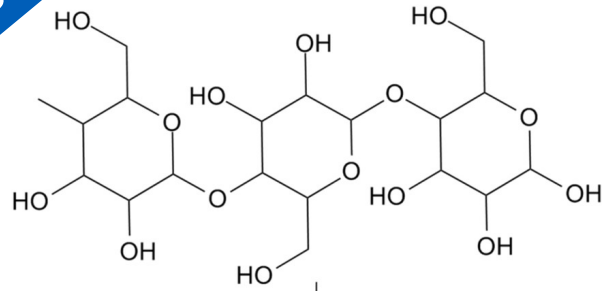
Cover illustration by Albert Edelfelt



Developed spinning of cellulose nitrate to a commercial level. Nowadays called the Father of “Father of Rayon” and the founder of the MMCF industry

1857: Schweizer's reagent

aqueous



wikipedia.com

Schweizer's reagent is an alkaline solution of copper sulfate in ammonia, $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2 \cdot 3\text{H}_2\text{O}$, named after Matthias Eduard Schweizer (1818-1860)

1934: direct dissolution

direct

Patented Jan. 9, 1934

1,943,176

UNITED STATES PATENT OFFICE

1,943,176

CELLULOSE SOLUTION

Charles Graenacher, Basel, Switzerland, assignor
to Society of Chemical Industry in Basel,
Basel, Switzerland

No Drawing. Application September 16, 1931,
Serial No. 563,218, and in Switzerland Sep-
tember 27, 1930

21 Claims. (Cl. 260—109)

This invention relates to new cellulose solutions and the application thereof for making various products chemically or mechanically, and necessary, with suitable anhydrous diluents or other suitable additions. As such additions may be named, for example, substances having a re-

Charles Graenacher: father of direct solvents:

organic solvents that are capable of dissolving cellulose without derivatization or additional solubilization-mediator

Types of cellulose (dissolution and) regeneration

Cellulose swelling: gross structure of cellulose as a moiety of particles, fibers, or a film (i.e., solid cellulosic phase) maintained, despite significant changes of physical properties and an increase in sample volume due to uptake of the swelling agent

Cellulose dissolution: transition from a two-phase system to a one-phase system (clear solution), in which the original supramolecular structure of cellulose is destroyed

However, there is often no clear-cut borderline between a swelling process and a dissolution process

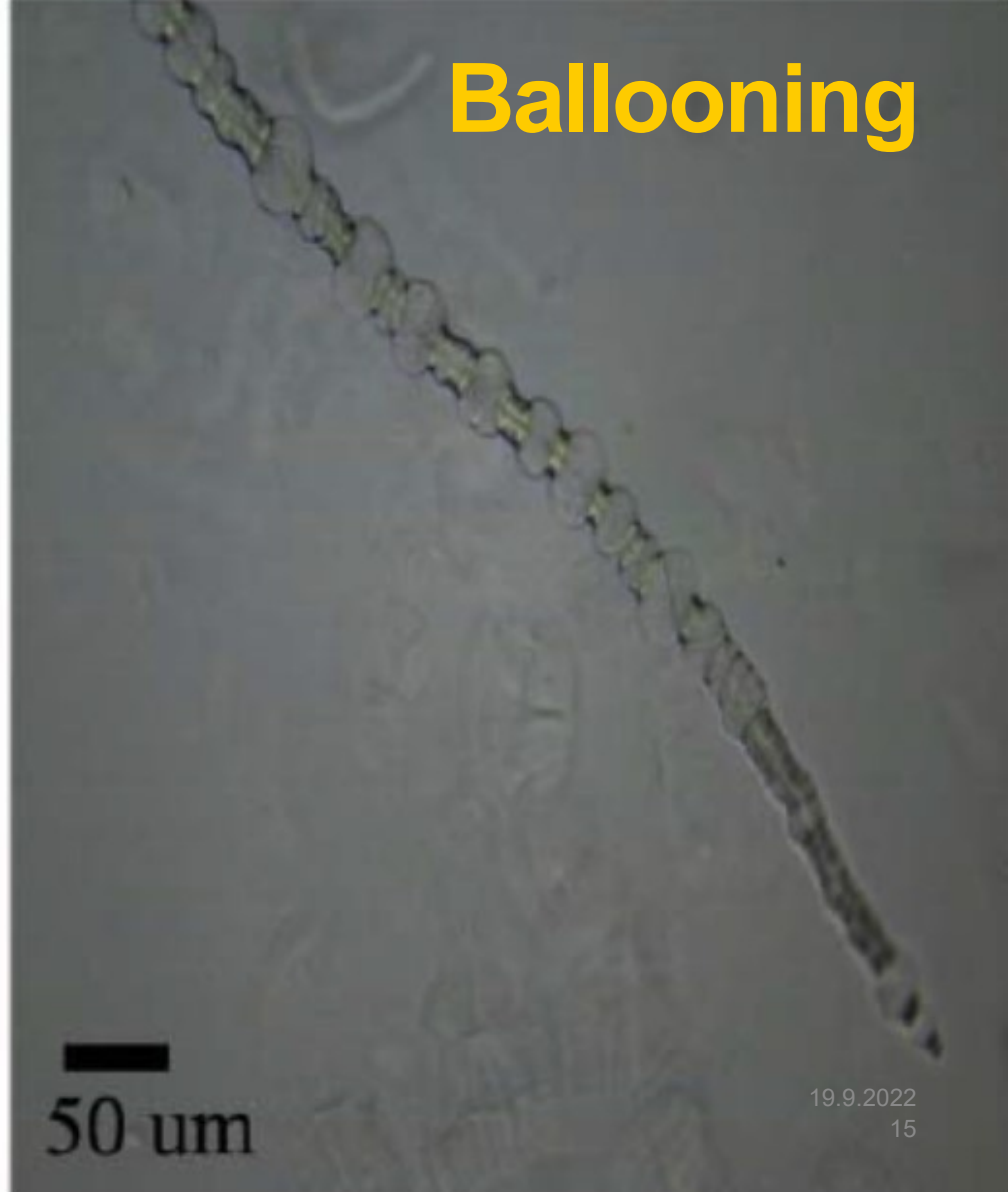
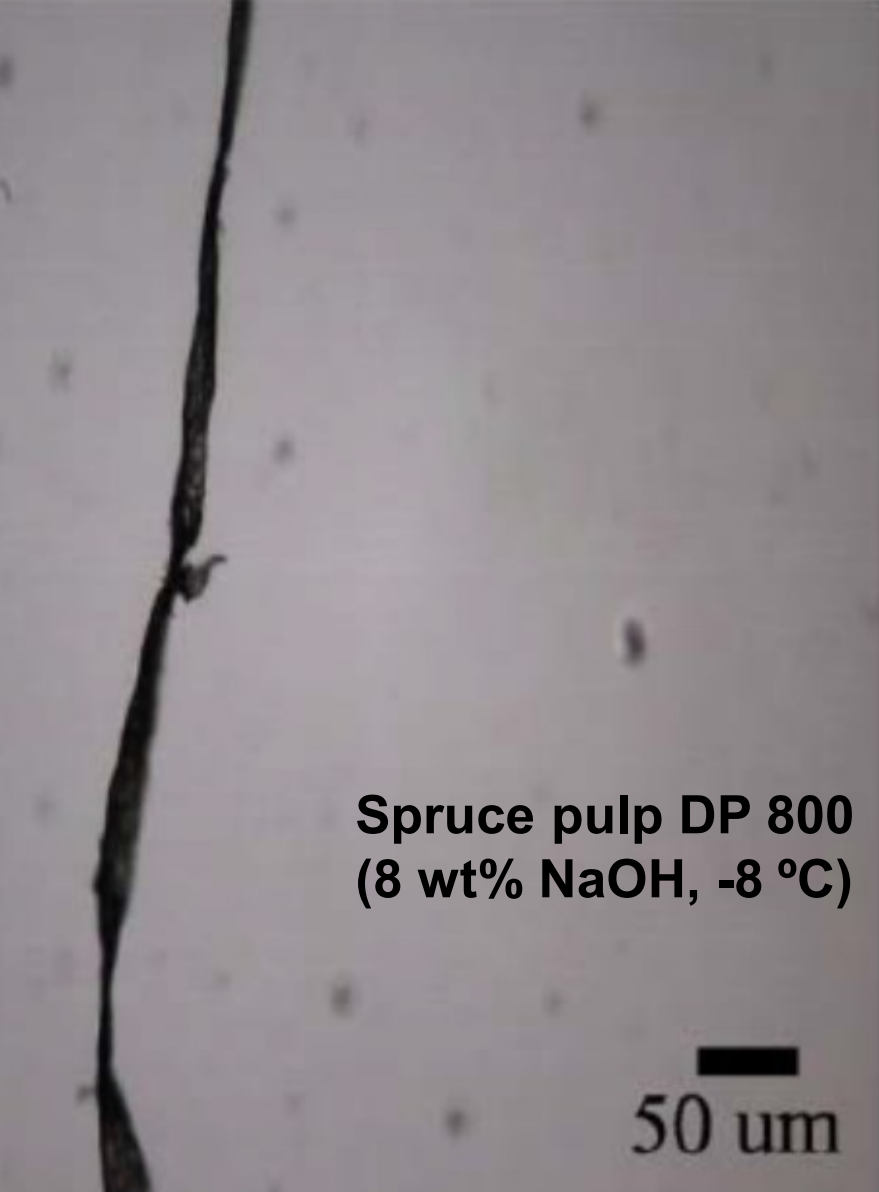
Ballooning

Cotton DP 1400
(8 wt% NaOH, -8 °C)

50 um



50 um

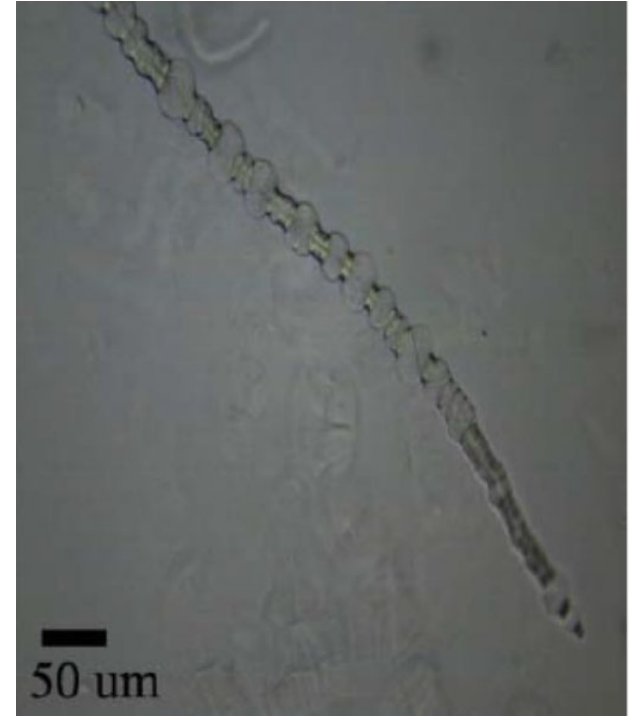


Swelling and dissolution

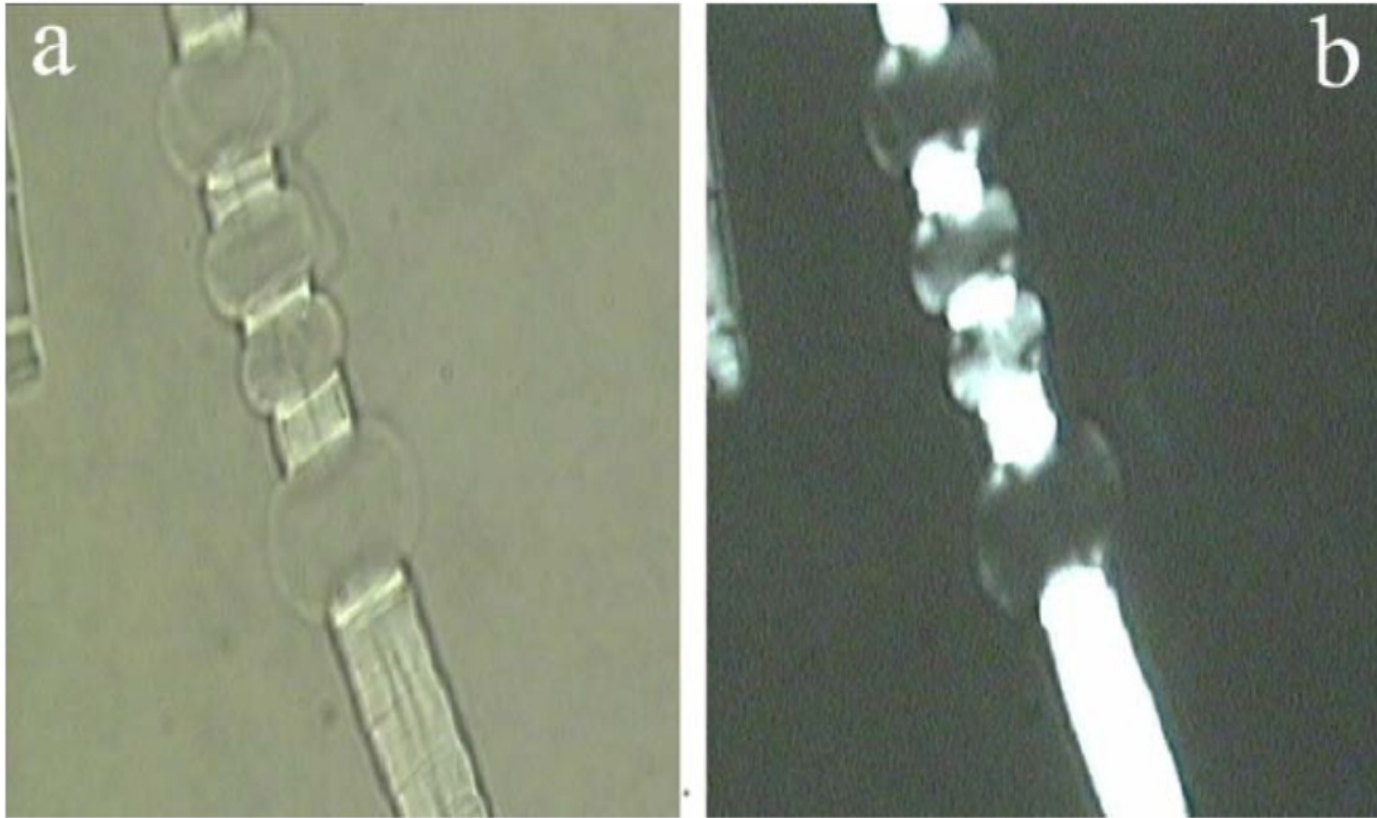
Solvent quality



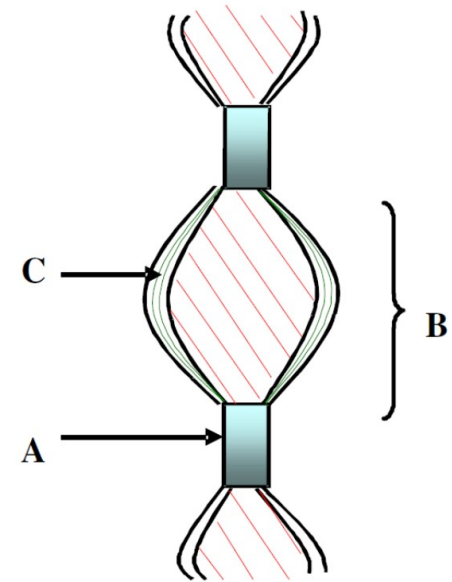
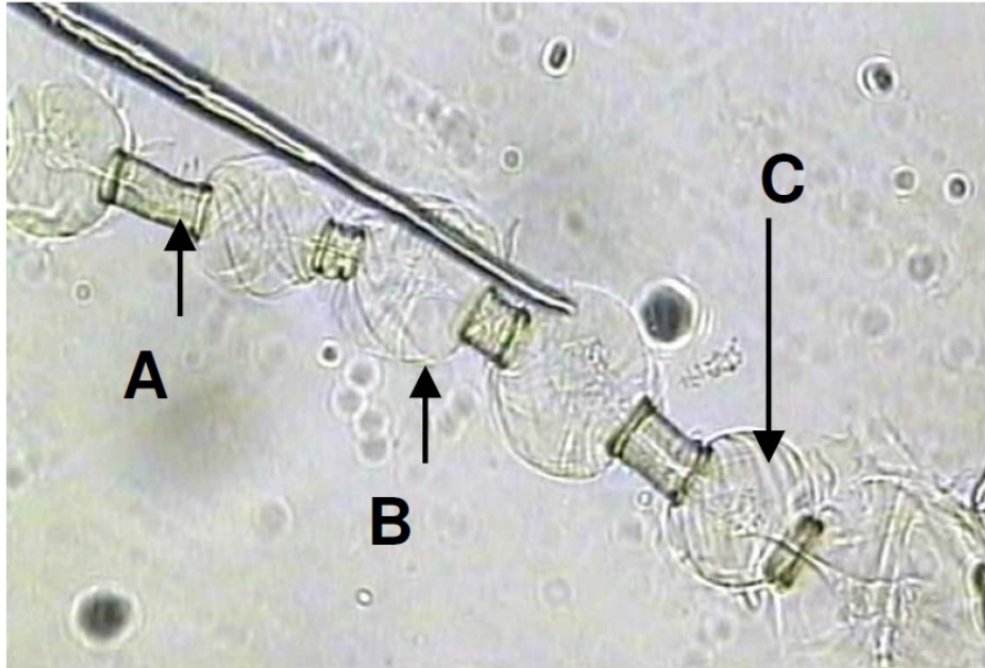
- **Mode 1:** Fast dissolution by disintegration into rod-like fragments
- **Mode 2:** Large swelling by ballooning and then dissolution of the whole fiber
- **Mode 3:** Large swelling by ballooning and partial dissolution of the fiber, still keeping its fiber shape
- **Mode 4:** Homogeneous swelling and no dissolution of any part of the fiber
- **Mode 5:** No swelling and no dissolution (non-solvent)



Mode 2: Balloning



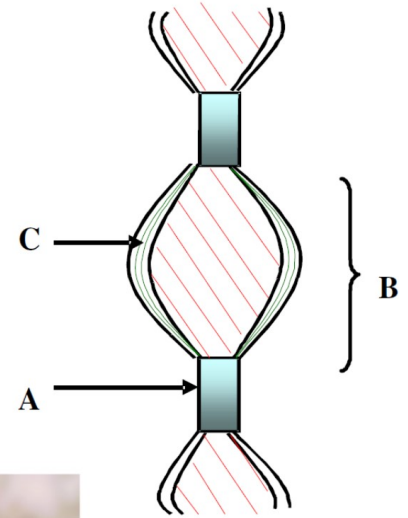
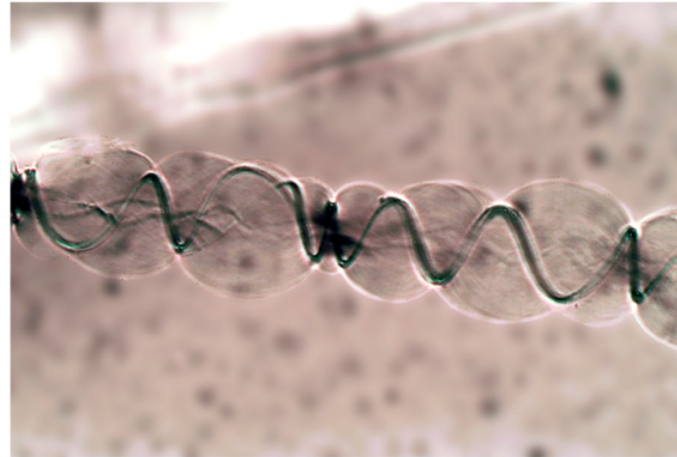
Mode 2: Balloning



A: unswollen fiber
B: dissolution and ballooning
C: undissolved P and S1 cell wall encapsulating dissolved cellulose

Mode 2: Balloning

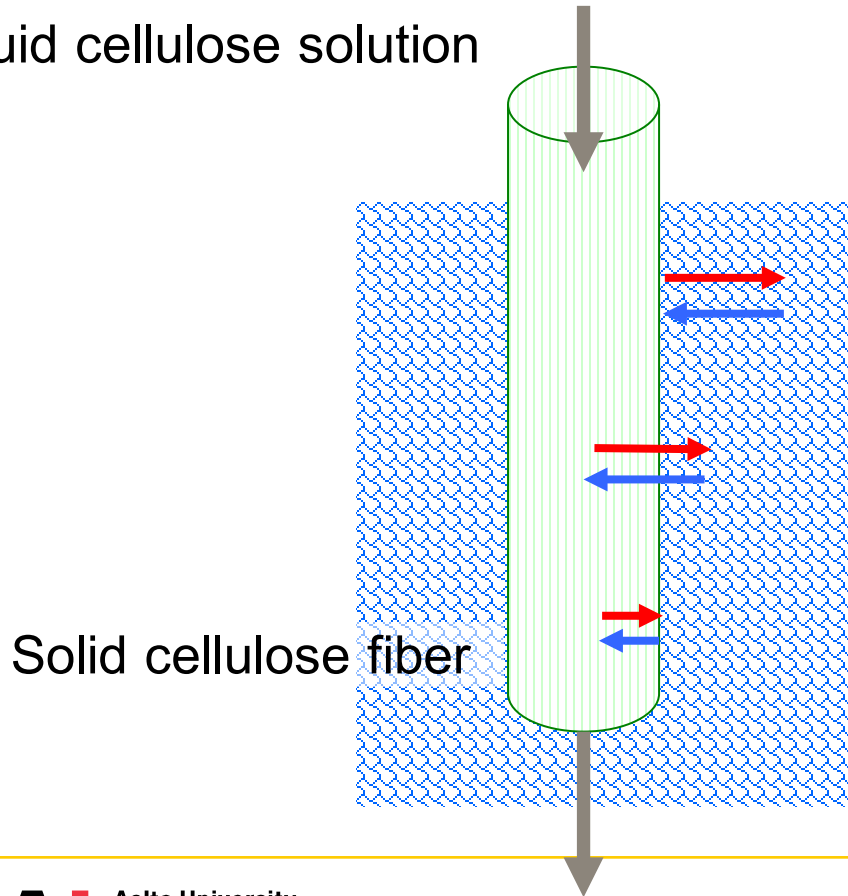
- Phase 1: balloon formation
- Phase 2: balloon bursting
- Phase 3: dissolution of the unswollen sections
- Phase 4: dissolution of the balloon membrane scraps



**Coagulation/regeneration
≠
inverse of dissolution**

Regeneration / coagulation

Liquid cellulose solution

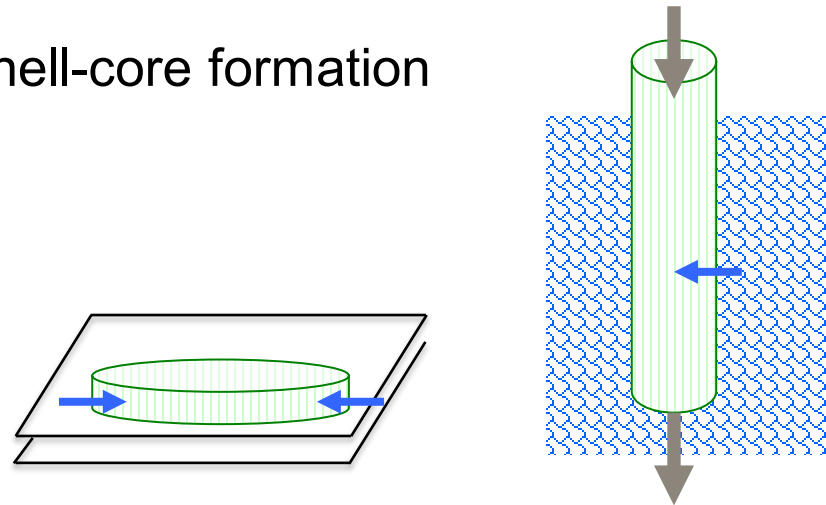
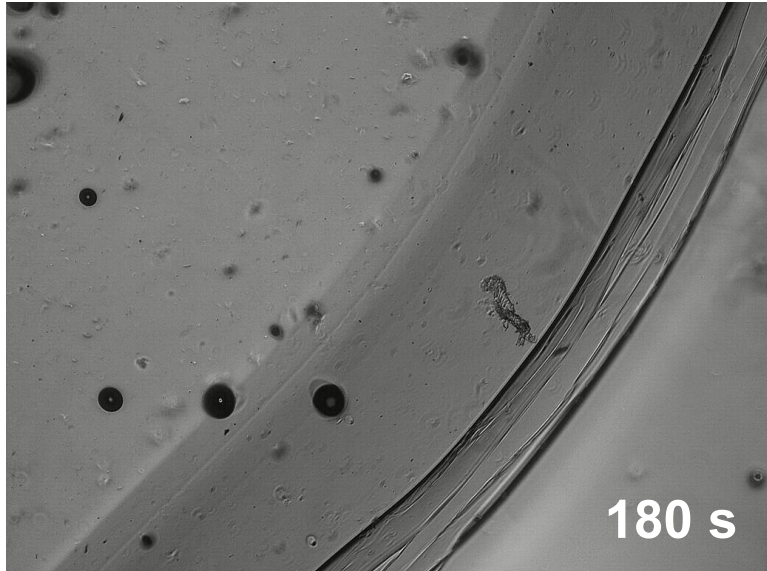


- Cellulose solution immerses into coagulation bath
- Solvent and anti-solvent diffusion
 - filament-water interface
 - in coagulation bath
 - in fiber body
- Structure formation; fiber morphology

Regeneration / coagulation

Regeneration / coagulation proceeds from the surfaces towards the center of the solution

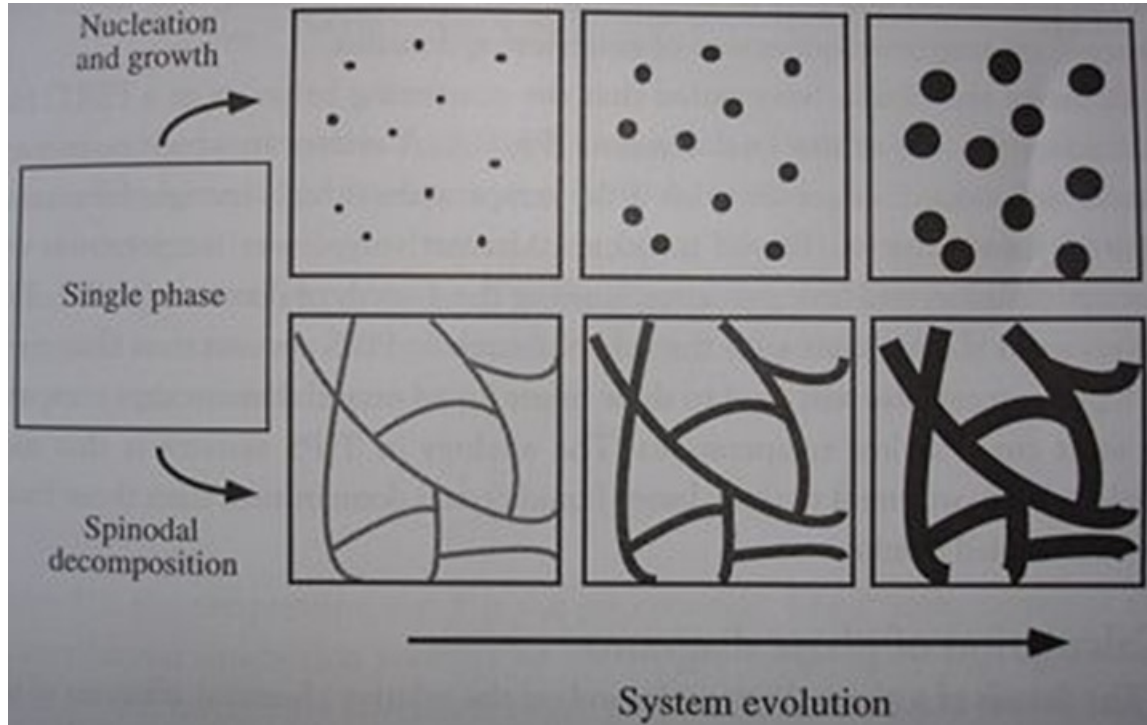
Shell-core formation



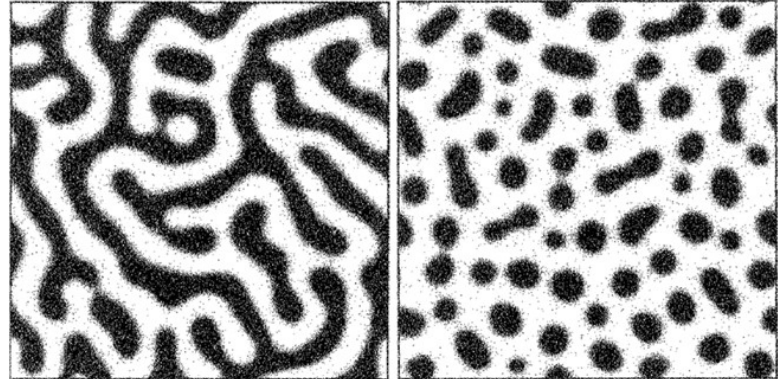
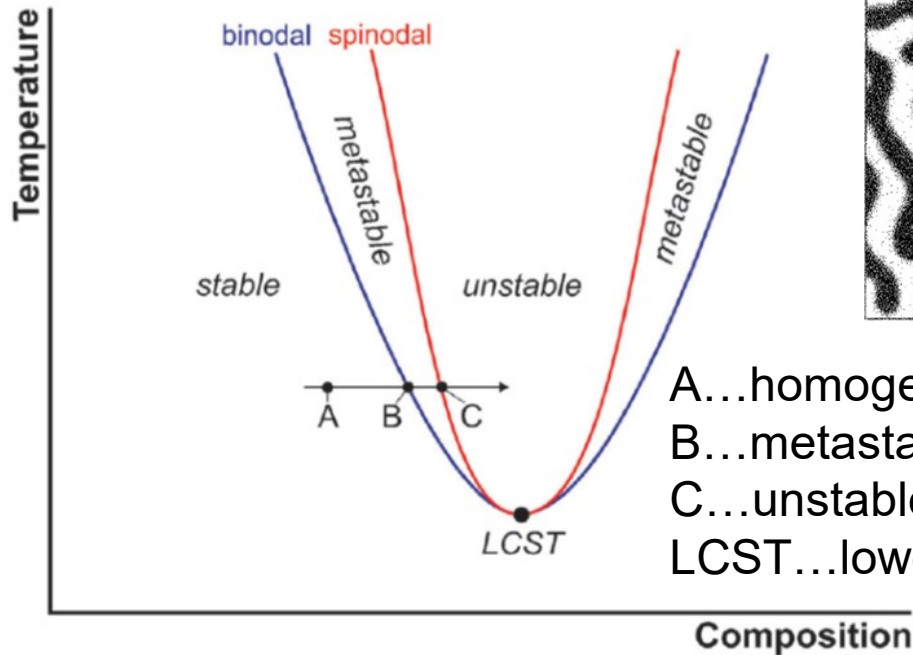
Spinodal decomposition vs. Nucleation & growth

How does matter solidify from a melt/solution?

Spinodal decomposition vs. Nucleation & growth



Spinodal decomposition vs. Nucleation & growth



A...homogeneous region, stable solution
B...metastable solution; binodal demixing = nucleation
C...unstable solution, phase separation inevitable
LCST...lower critical solution temperature

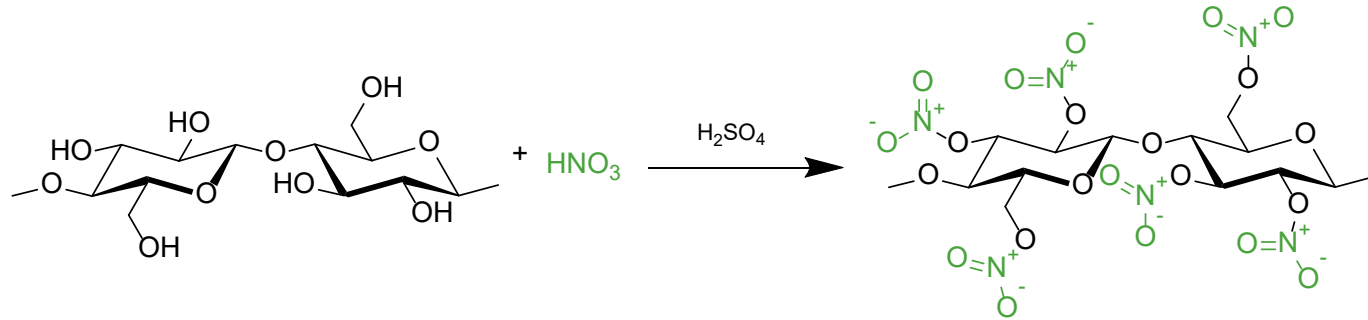
Summary questions

- **Why cellulose dissolution?**
- **What is the difference between spinodal decomposition and nucleation & growth?**

Regeneration

Intermediate Derivatization

Cellulose nitrate



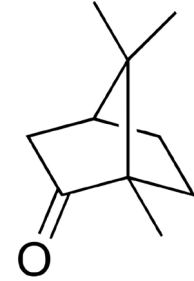
- Alternatively in DMF/ N_2O_4
- Cellulose nitrate soluble in ether/ethanol/acetone
- Solution spun through nozzles into regeneration bath containing $(\text{NH}_4)(\text{HSO}_4)$
- Flammable ("mother-in-law silk")

Cellulose nitrate - Celluloid

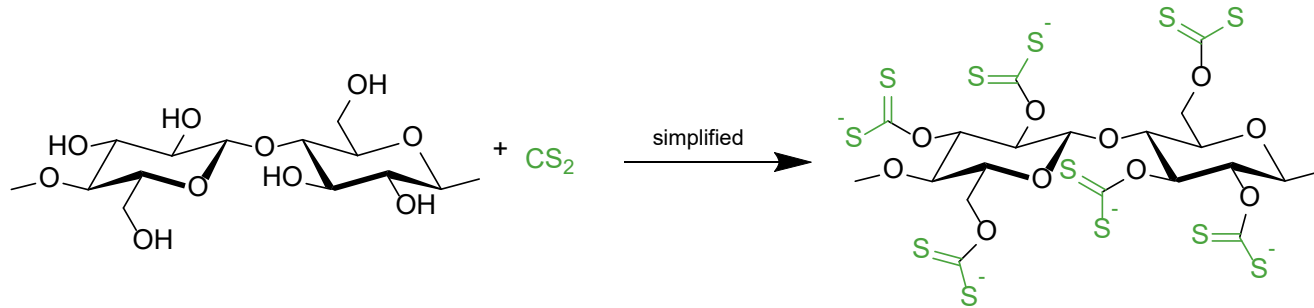
Celluloid = thermoplast containing cellulose nitrate and camphor

1856 first created by Alexander Parkes; called it Parkesine

1870 John Wesley Hyatt patents it as „Celluloid“ to be sold through the Celluloid Manufacturing Company



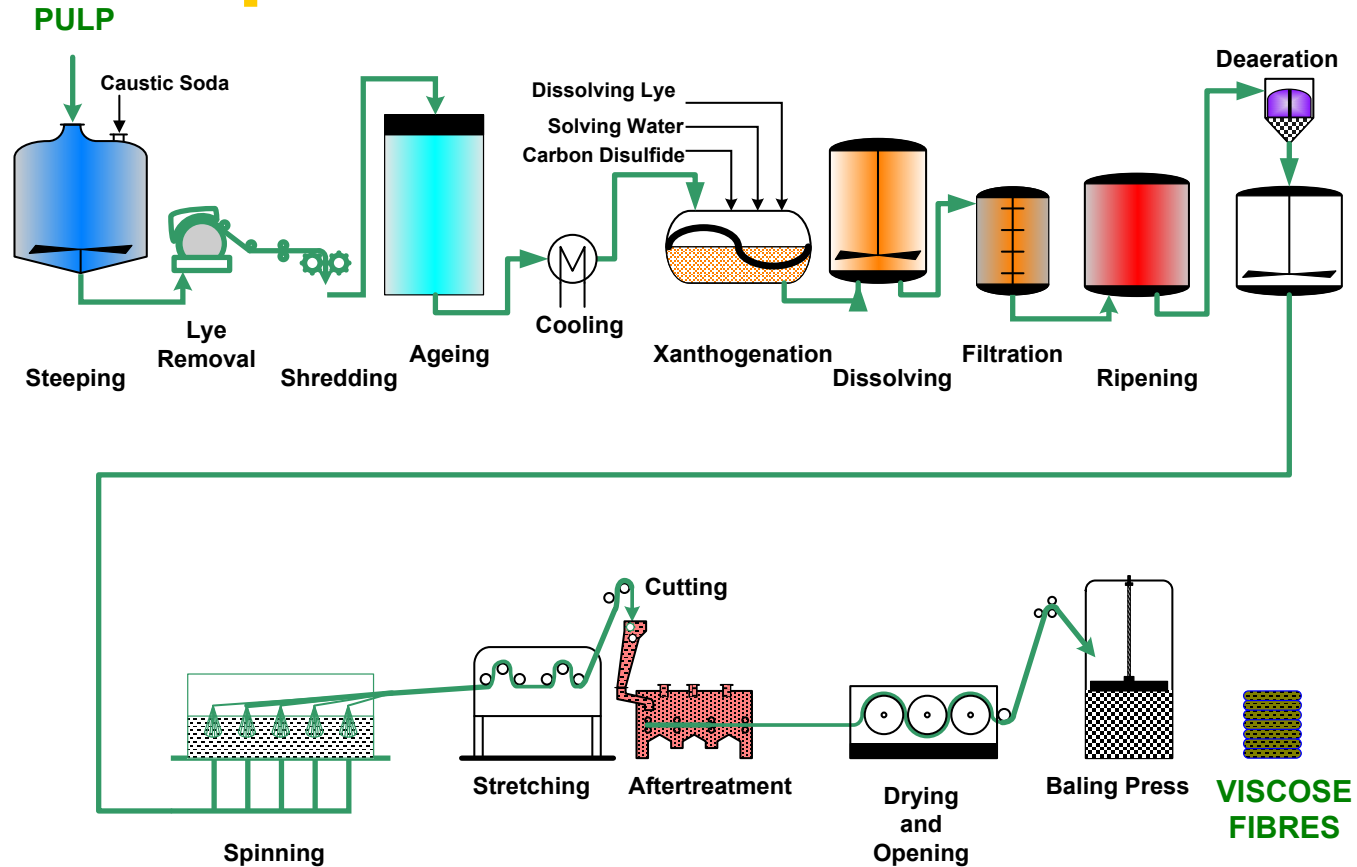
Xanthate (viscose)



- Cellulose xanthate soluble in caustic solution
- Solution spun through nozzles into regeneration bath containing H_2SO_4 / Na_2SO_4 and additives

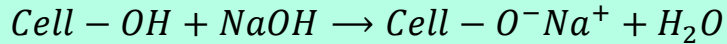
YouTube: The production of viscose fibres at Kelheim Fibres GmbH
<https://www.youtube.com/watch?v=zcxcPVX5ejY>

Viscose process

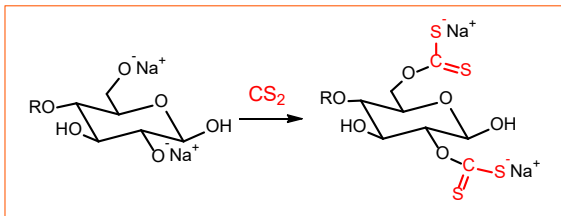
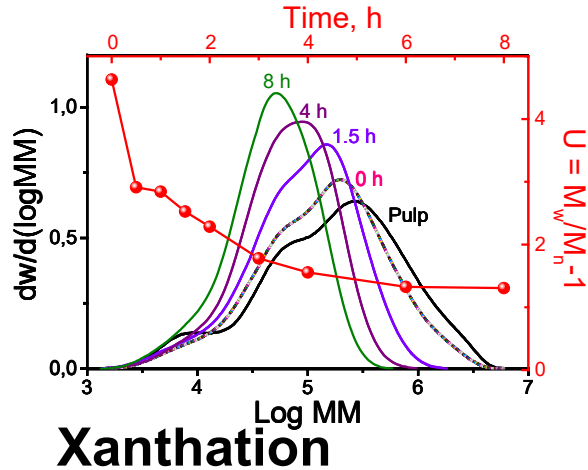


Viscose process

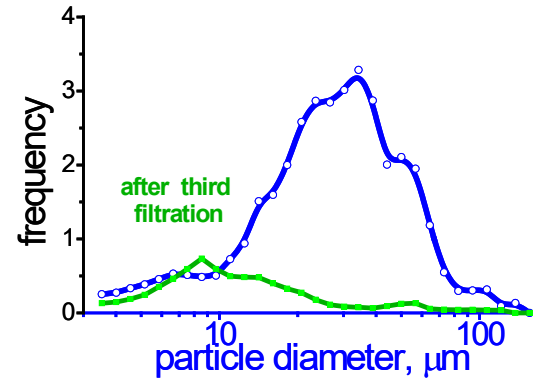
Steeping (alkalization):
conversion to cellulose-II lattice



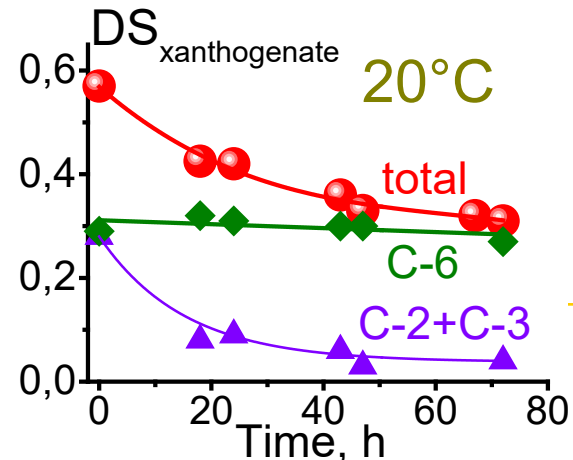
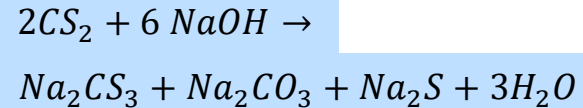
Ageing (DP adjustment)



Viscose Filtration



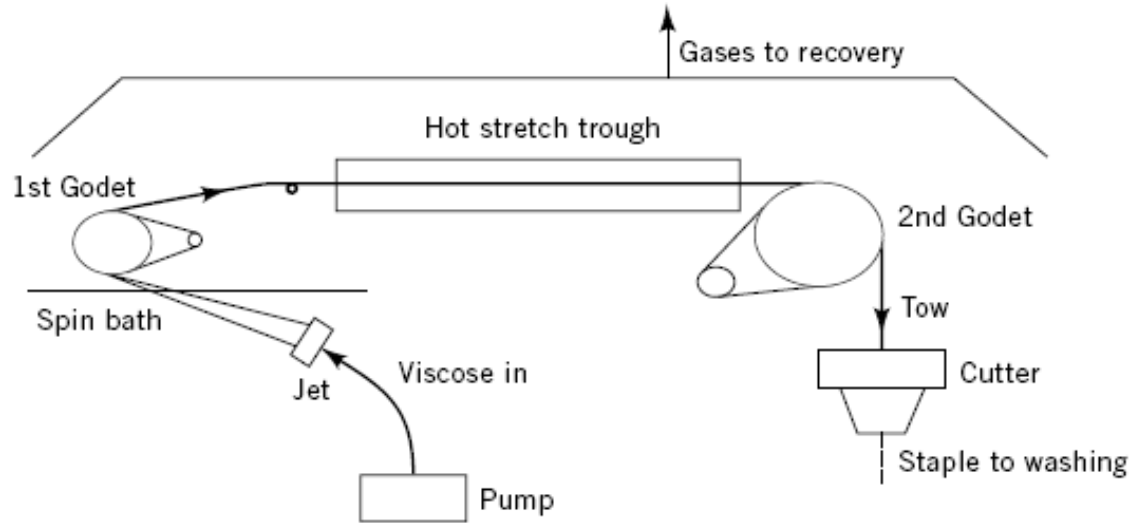
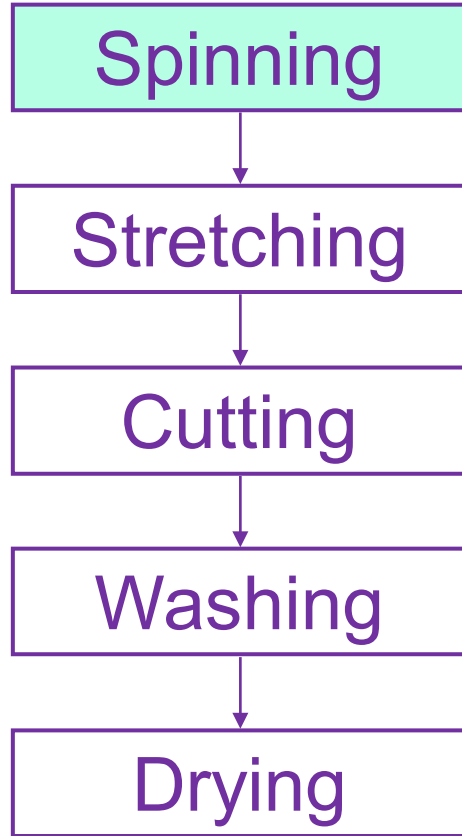
Ripening



19.9.2022

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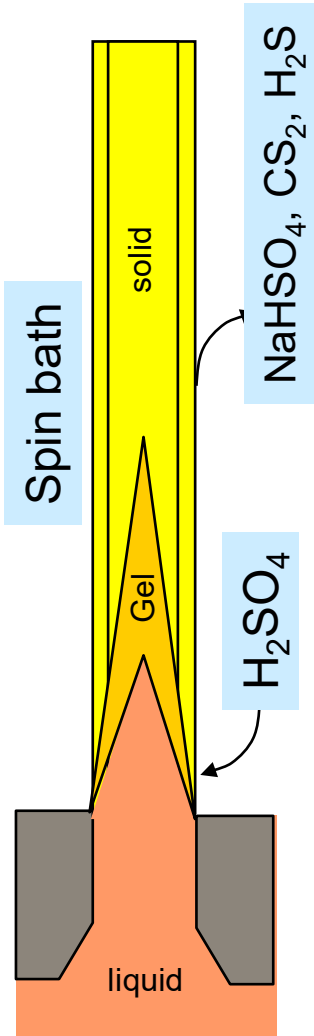
Viscose process



Viscose process

- Each spinning position has up to **200.000 holes** for staple fibres.
- The diameter of the typically round shaped holes is between 40 and 90 mm.
- Spinning velocity is slow in wet spinning, only **12 to 20 m/min.**
- The viscose is pumped through the spinnerets into the spinbath where it coagulates.

Viscose regeneration

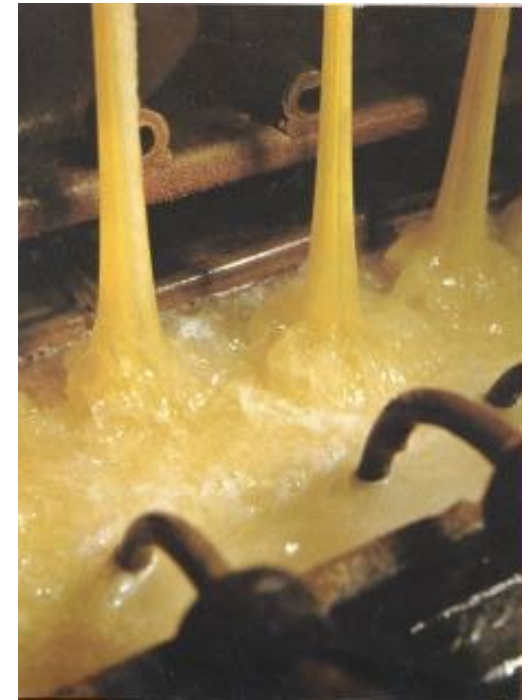


Prim. Structure Formation

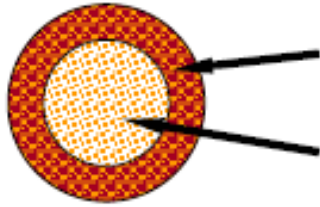
- Coagulation

Second. Structure Formation

- Dehydration, densification
- Regeneration
- Orientation, crystallization



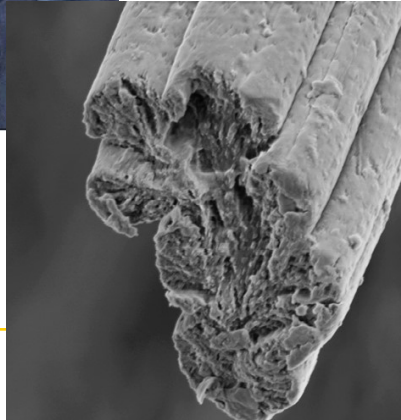
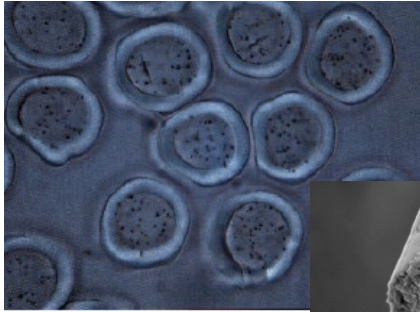
Viscose regeneration: Skin core structure



Skin plastic

Core not yet coagulated

- Skin show higher orientation; smaller sized crystallites
- Core less oriented
- Skin thickness can be increased by additives which retard coagulation



Viscose – High tenacity variations through delayed regeneration

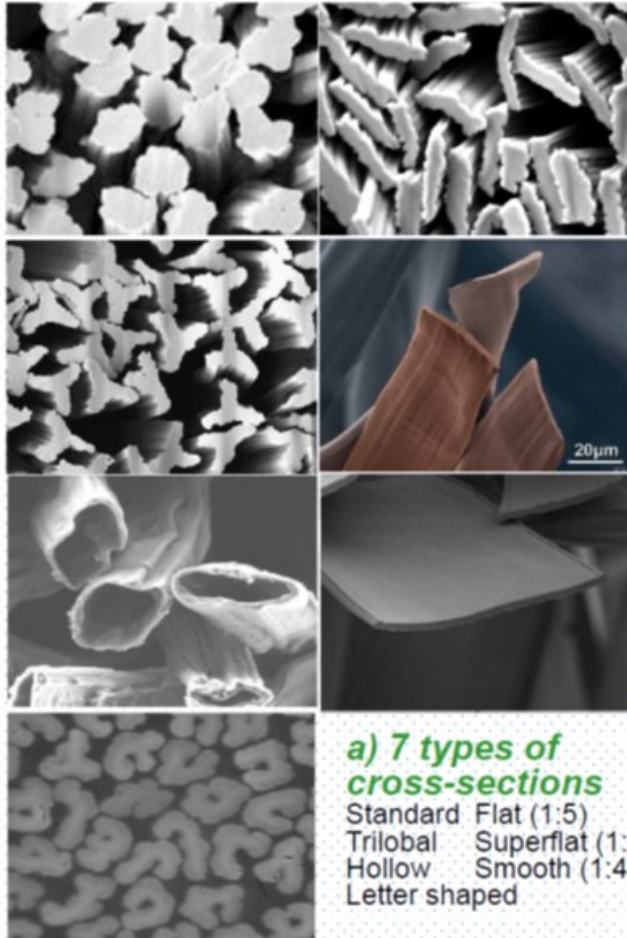
Modifiers in viscose to delay regeneration

- Zn salts
- Organic modifiers
- Mixed modifiers
- Formaldehyde

Plasticizing coagulation bath

- Hot water or steam
- Hot, diluted sulfuric acid solution

Viscose variations



a) 7 types of cross-sections

Standard Flat (1:5)
 Trilobal Superflat (1:20)
 Hollow Smooth (1:40)
 Letter shaped

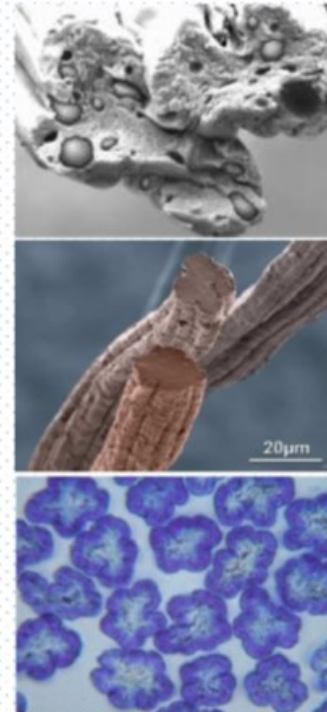


b) Titer (diameter):

0,5dtex–28dtex,
 (7–48µm)

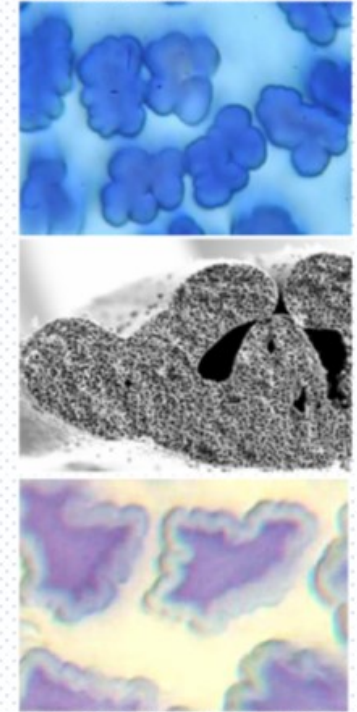
c) Fibre length:

3–120mm;
 endless tow



d) Incorporation of particles/ chemicals

Pigments,
 Microcapsules,
 Ion exchange additives,
 ...



e) Polymer blends

f) Coating, impregnation

Inorganic polymers
 Biopolymers
 Modified biopolymers
 Synthetic polymers

Viscose variations

Viscose Fibres for diversified end uses

- **Textiles, Apparel**

- Active wear, Shirts, Denim, Knits, Work wear
- Home and interior textiles
- Technical- and automotive applications,

- **Nonwovens**

- Technical nonwovens,
- Household articles
- Medical- and Hygiene-products

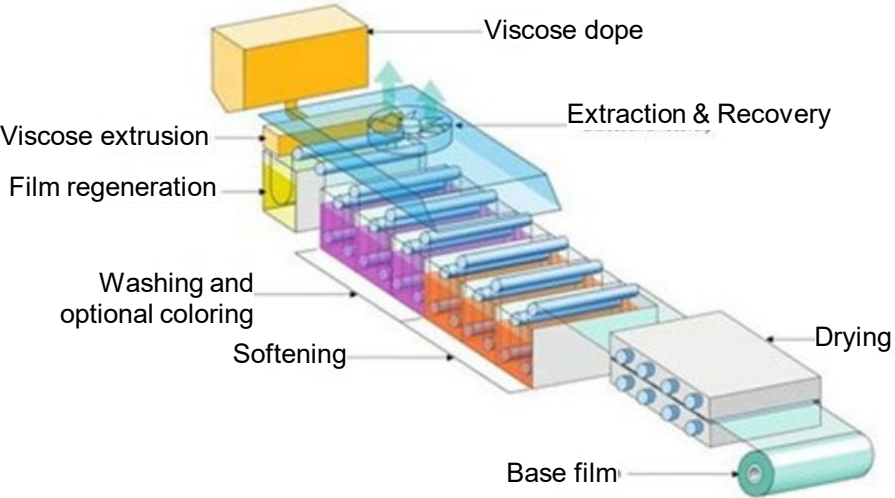
- **Specialty papers (shortcut)**

- Filter papers (Food, automotive, ...), Cigarette papers
- Security papers, Banknote papers, Wall coverings
- Battery separators

- **Flock, Carbon precursor, Composite materials**



Viscose – Cellophane



Good barrier properties regarding air and grease
 Coating needed to decrease water permeability



Viscose – Cellophane

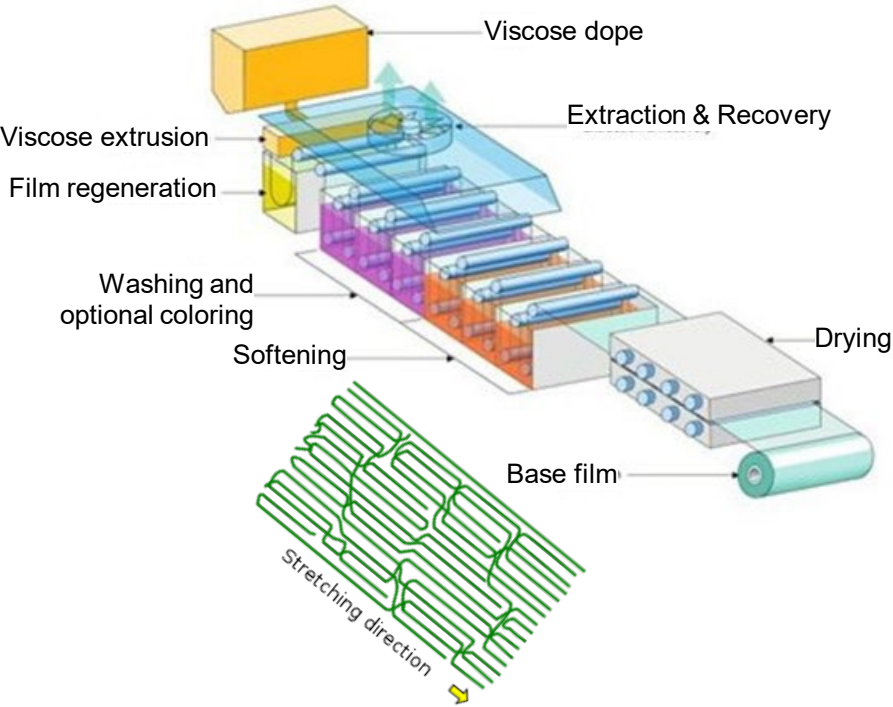


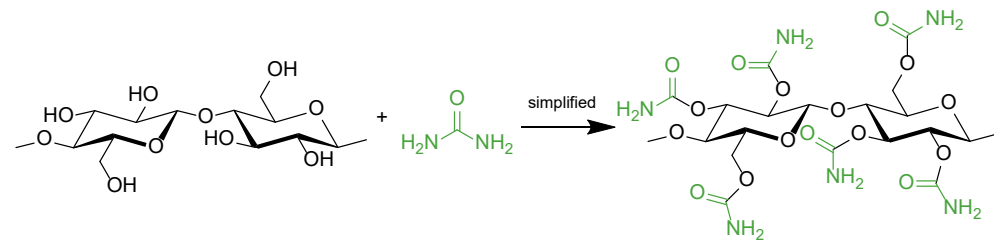
TABLE II
Mechanical Anisotropy of Test Specimens

Specimen	Tensile dynamic modulus $E_t \times 10^3, \text{ kg/mm}^2$ ^a						
	$\delta = 0^\circ$ ^b	$\delta = 10^\circ$	$\delta = 20^\circ$	$\delta = 30^\circ$	$\delta = 45^\circ$	$\delta = 60^\circ$	$\delta = 90^\circ$ ^b
C-1-D _{ex}	7.7	7.6	7.3	6.8	6.0	5.6	5.4
C-1-D _{e1}	6.2	6.2	6.1	5.6	5.3	4.7	4.7
C-1-D _{st}	5.4	5.3	5.2	4.5	4.4	4.0	3.7
C-1-W	0.21	0.20	0.18	0.14	0.11	0.09	0.08
C-2-D _{ex}	7.7	7.2	7.0	6.8	6.3	5.9	5.5
C-2-D _{e1}	6.8	6.4	6.4	5.6	5.2	4.7	4.5
C-2-D _{st}	5.6	5.4	5.0	4.6	4.3	3.9	3.9
C-2-W	0.20	0.20	0.17	0.15	0.11	0.09	0.08
C-3-D _{ex}	6.7	6.6	6.5	6.1	5.5	5.5	5.4
C-3-D _{e1}	6.0	5.7	5.6	5.4	4.7	4.5	4.6
C-3-D _{st}	5.0	4.9	4.7	4.5	4.1	4.0	3.8
C-3-W	0.16	0.16	0.14	0.12	0.10	0.09	0.08

^a Measured by the Viscoelastic spectrometer at 20°C. The modulus is the real part of the tensile complex dynamic modulus at 11.0 cps.

^b The angle 0° corresponds to the x_1 axis (the machine direction); and 90° corresponds to the x_2 axis (the transverse direction) within the film plane; δ is the angle between the direction of tensile deformation and the machine direction.

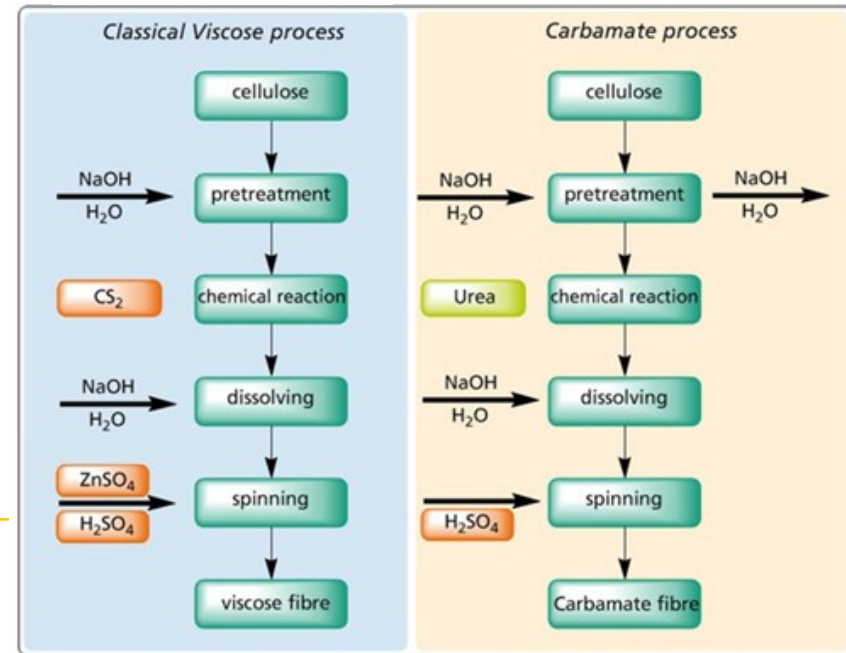
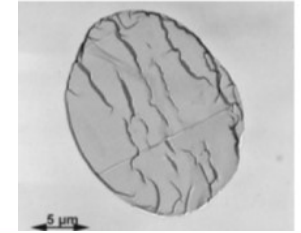
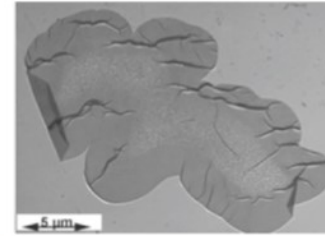
Carbamate



Initial development by Neste Oy (Ekman et al. Lenz. Ber. 1984 57, 38-40.

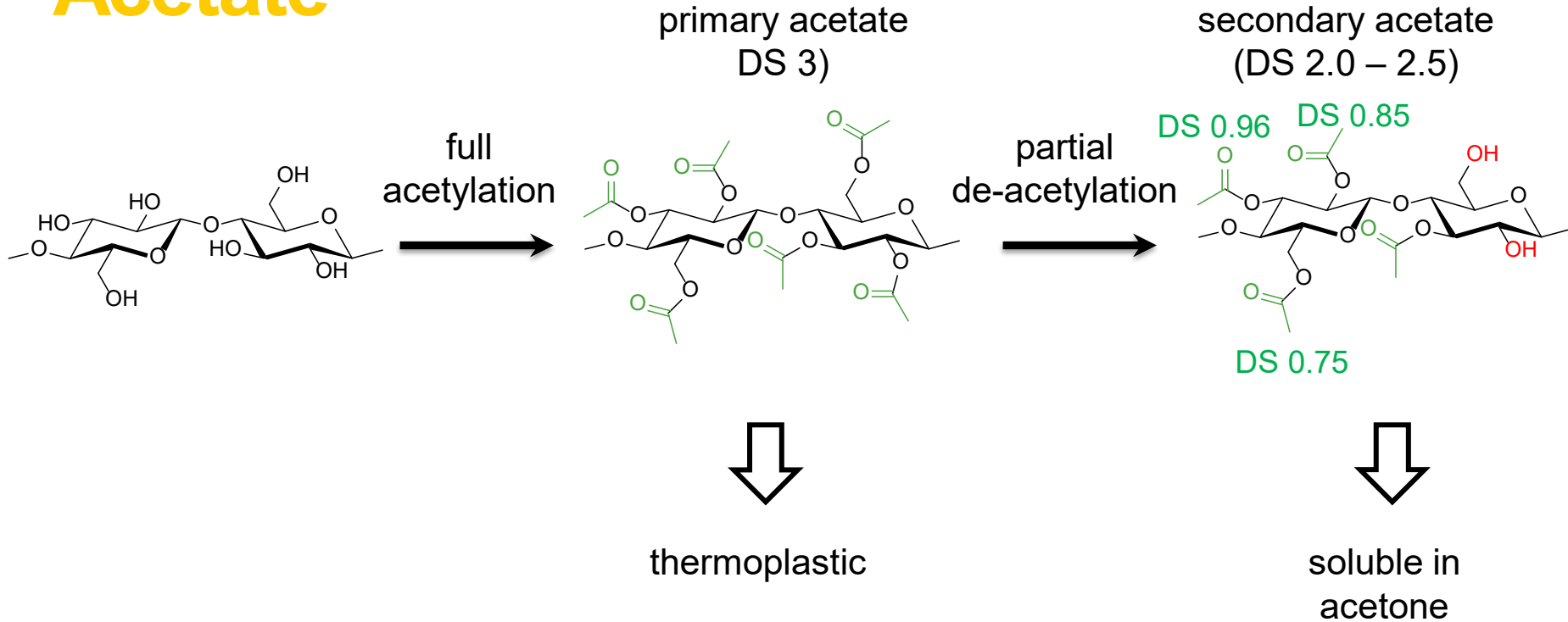
Regeneration in acidic spin bath.

Conditioned fiber strength comparable to viscose; extremely low wet strength



Stable derivatives

Acetate



Acetate



Melt processed:

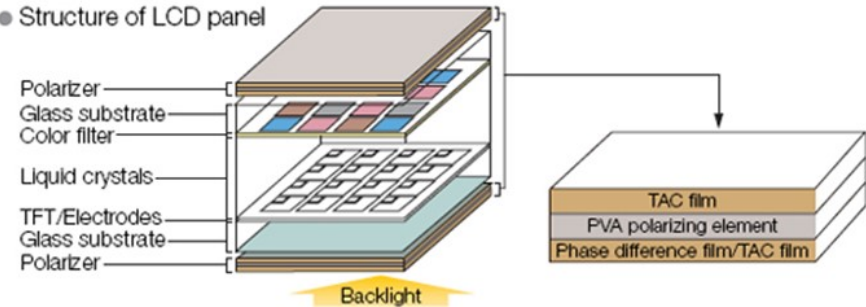
- Frames for glasses
- First Lego bricks (today acrylonitrile butadiene styrene)
- TAC films for LCD



Solution spun:

- Fiber tows for cigarette filters
- Fortisan fibers: spun as secondary acetate and subsequently saponified; high orientation of cellulose molecules enables high mechanical properties

● Structure of LCD panel



Fortisan: regenerated CA



Fortisan^{*}
A CELANESE SYNTHETIC YARN

FOR LIGHTNESS
FOR STRENGTH

The World's Strongest Yarn

Just to make a simple test of the strength of Fortisan is an astonishing experience. You hold in your hands a sheer, lustrous square of cloth woven of Fortisan, such as is used for U. S. flare parachutes. It's so light it wafts gently down in the air.

Now try to tear it! Try with all your strength to break a single tiny thread! It's almost uncanny!

This development of Celanese research—a yarn stronger than any in existence, either natural or synthetic, yet amazingly light and beautiful—has unlimited fields for peacetime employment. Think of what you could do—what you could make—with Fortisan! Celanese Corporation of America, 180 Madison Avenue, New York 17, N. Y.

Fortisan, the world's strongest yarn, developed from the laboratories of Celanese Corporation of America when the nation needed material for flare parachutes—in great quantities of proofing, light, strong fabric and cord, and so on, all proved Fortisan production has been absorbed by this and other wartime applications.

CELANESE CORPORATION OF AMERICA... Textiles... Plastics... Chemicals

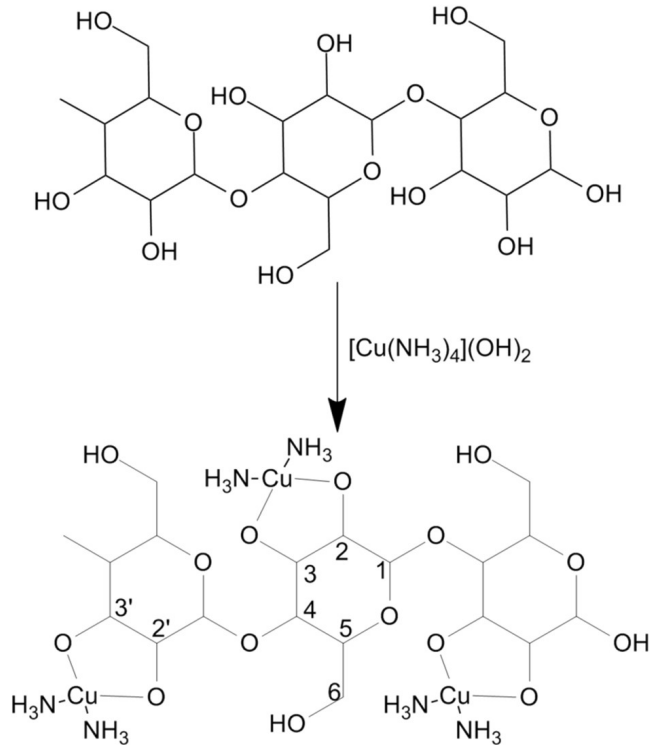
CA fiber is spun and then stretched under steam, resulting in high molecular orientation

The fiber is then saponified (de-acetylated = regenerated) to yield pure cellulose with high strength (cf. next lecture)

Coagulation

Non-derivatizing – aqueous

Metal complexes

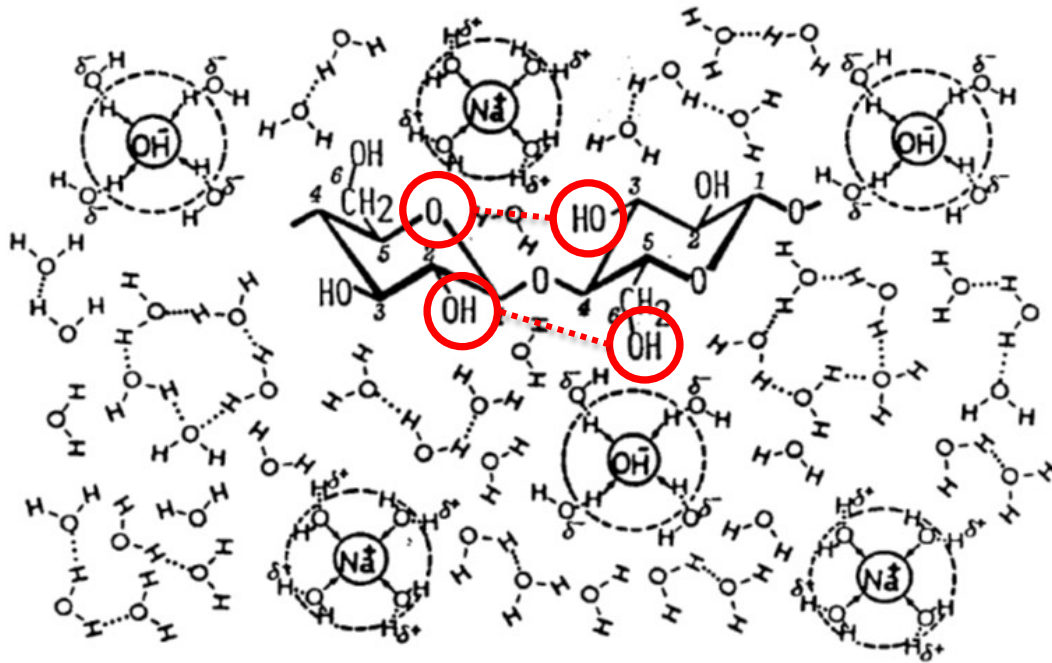


- Cuoxam: tetraammine diaqua copper hydroxide, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{OH})_2$
- Cuen: Copper(II) ethylenediamine hydroxide
- Nioxam ($[\text{Ni}(\text{NH}_3)_6][\text{OH}]_2$)
- Zincoxen ($[\text{Zn}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_3][\text{OH}]_2$)
- Cadoxen ($[\text{Cd}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_3][\text{OH}]_2$)
- Nitren ($[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2)_3\text{N}][\text{OH}]_2$)
- Pden ($[\text{Pd}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)][\text{OH}]_2$)
- Ferric sodium tartrate complex $\text{Na}_6[\text{Fe}(\text{III})(\text{C}_4\text{H}_3\text{O}_6)_3]$

Dissolution through complex formation; spun into acidic spin bath which causes de-complexation and regeneration of cellulose

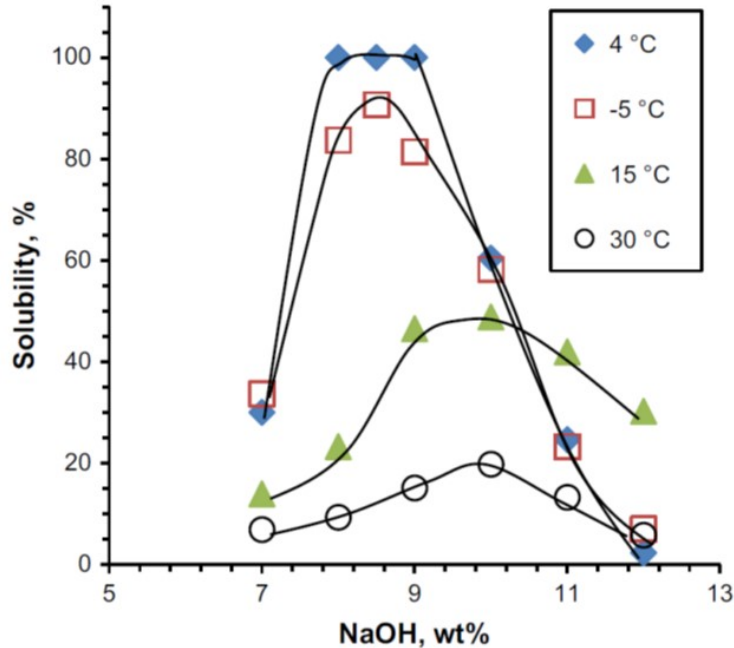
Commercial cupro fiber (Cuoxam, tradename Bemberg™ fiber) produced on a scale of ca. 25 000 t/a as specialty fiber

NaOH solutions

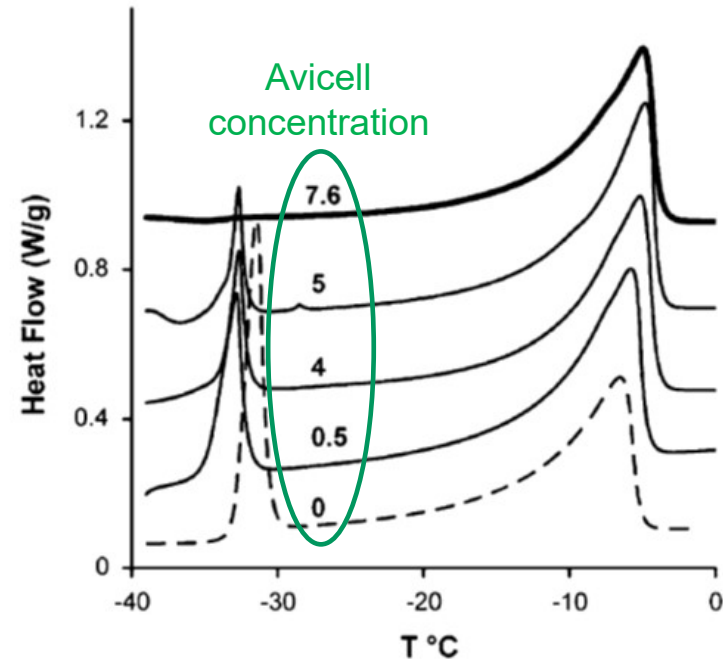


Deconstruction of intramolecular $O_3-H...O_5'$ and $O_2-H...O_6'$ H-bonds

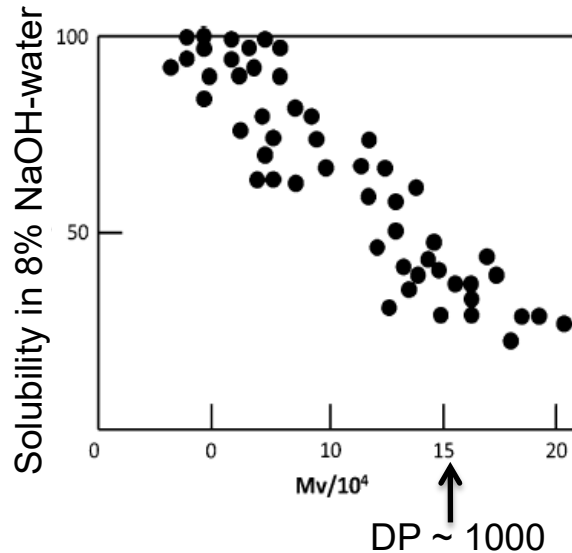
NaOH solutions



Best dissolution performance of pure NaOH solution at 7-8 wt% NaOH, corresponding to 4 NaOH units per AGU



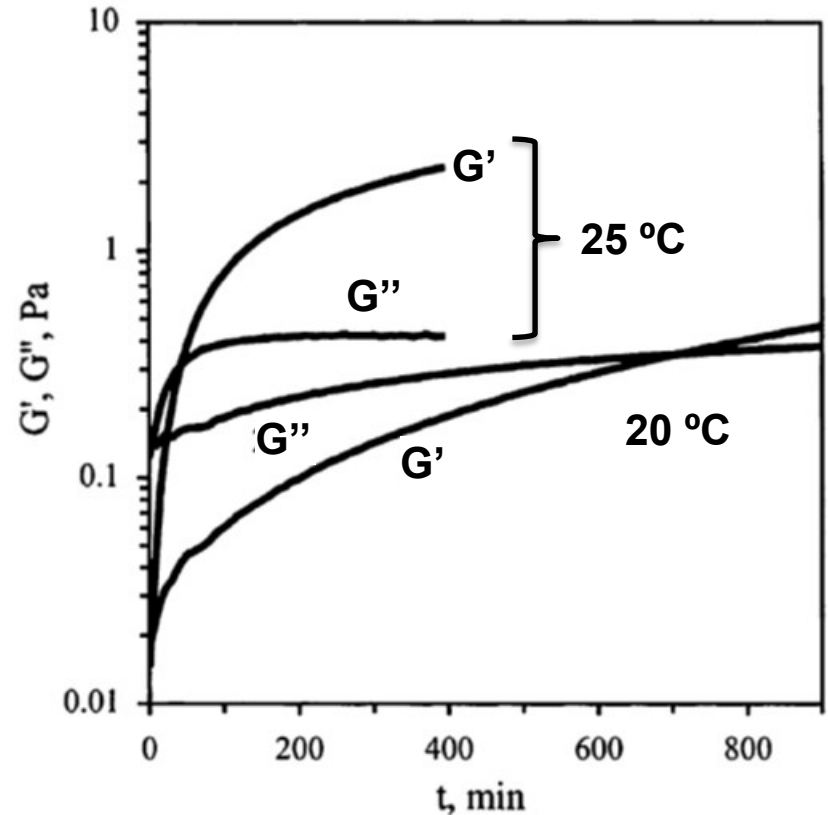
NaOH solutions



- Major limitation of NaOH as solvent: solubility of cellulose strongly dependent on DP
- Upper limit for relevant cellulose concentration;
- Limited mechanical properties of regenerated products

NaOH solutions

- second limitation of NaOH as solvent: tendency of solutions to gel irreversibly
- Gelling over time
- Pronounced gelling upon temperature increase

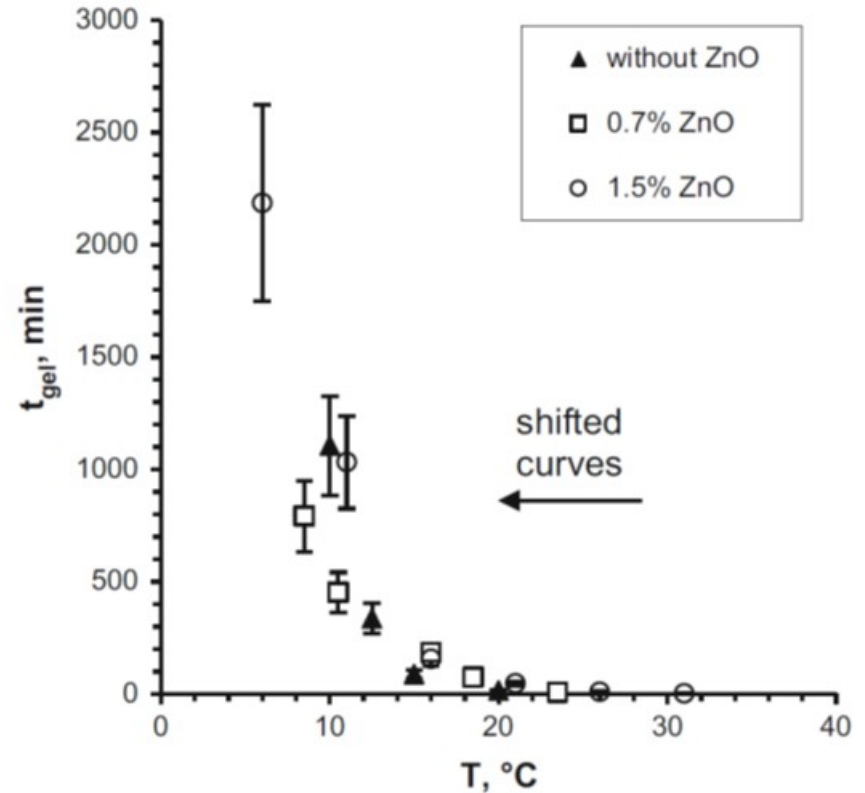


NaOH solutions – additives

Various additives tested:

- amongst longest know: ZnO
- also urea and thiourea

No confirmed effect on solubility maximum; but stabilization of solution state and hampering of gelation

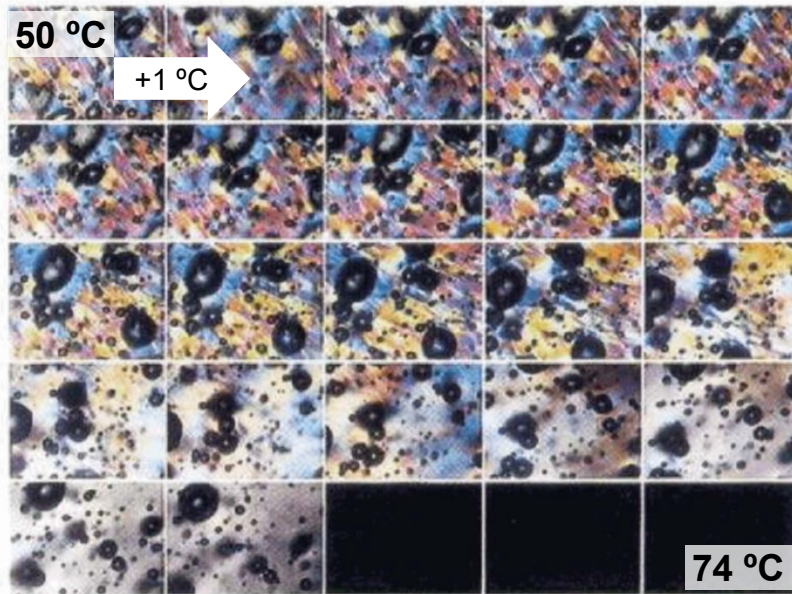


Non-derivatizing – non-aqueous

Superphosphoric acid

phosphoric acid: ca. 54–62% P_2O_5 (75–85% H_3PO_4)

superphosphoric acid: 70% P_2O_5 (almost 100% H_3PO_4)



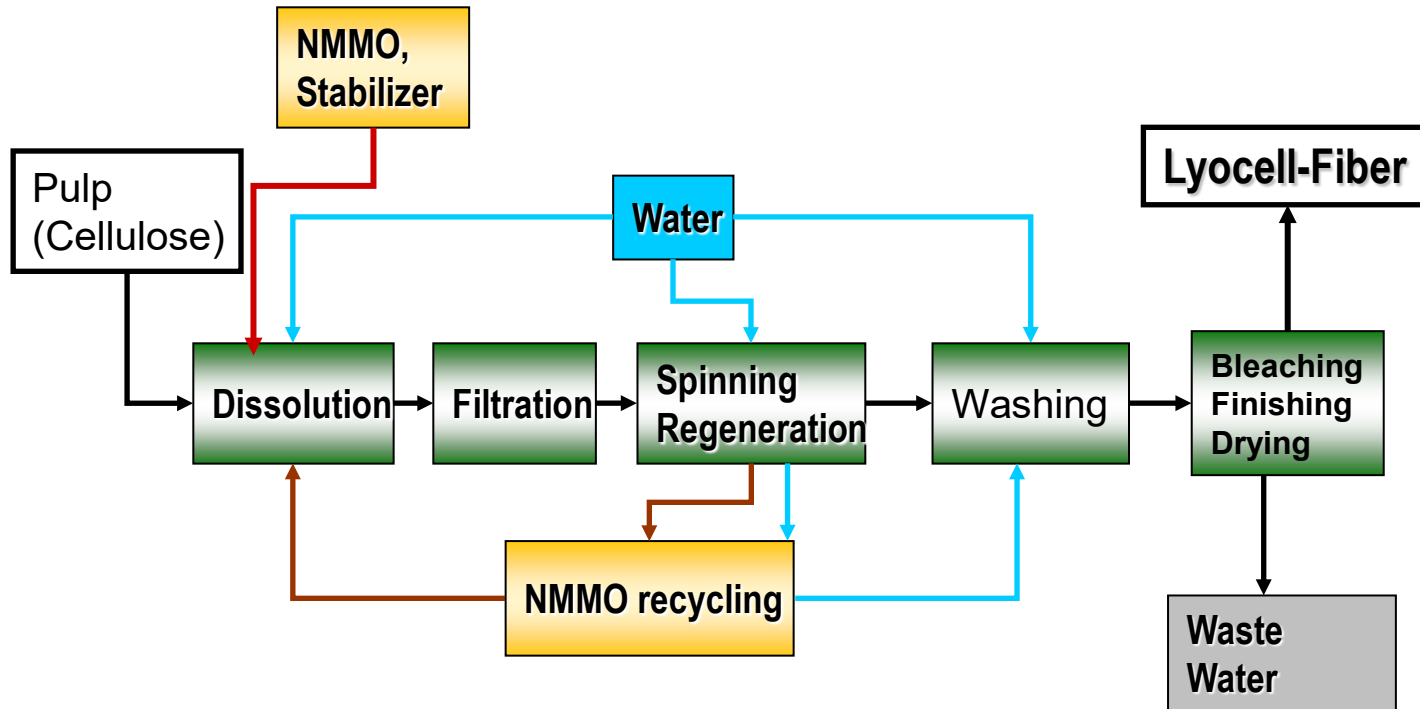
17.1 wt% cellulose in 74.4% P_2O_5

Cellulose dissolved in SPA forms anisotropic solutions (liquid crystalline-like) i.e. cellulose have structured; structure lost upon heating.

Clearing temperature depending on DP and concentration

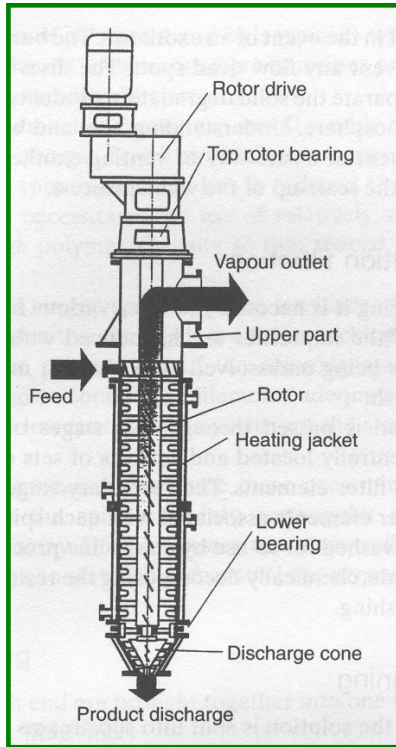
Pre-orientation can be used to prepare highly orientated cellulose products such as fibers = Fiber B (Bocell): 90 cN/tex

Lyocell Process



Video Lab Spinning

Lyocell Dope Preparation

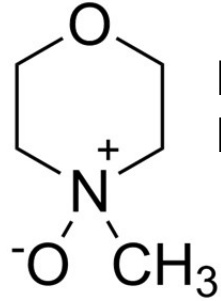


Buss Filmtruder

Long vertical vessel with steam heating in jackets around the vessel.

A shaft down the center of the vessel with blades attached to its circumference is rotated to smear the material around the heated surface to promote the evaporation process.

N-methylmorpholine N-oxide monohydrate



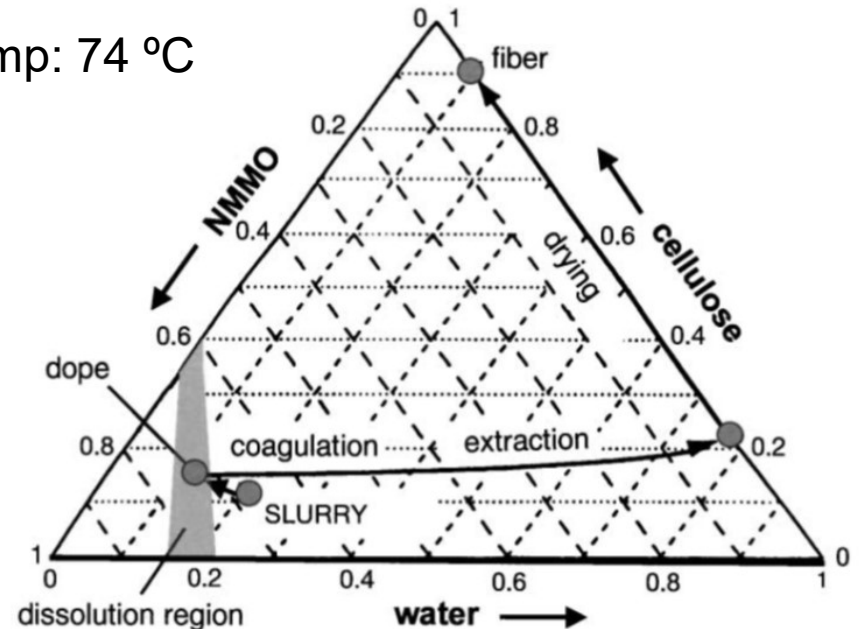
Neat NMMO: mp 170 °C

NMMO.H₂O (13.3 wt% H₂O): mp: 74 °C

Initial development started at the very end of the 1960s by American Enka/Akzona Inc.

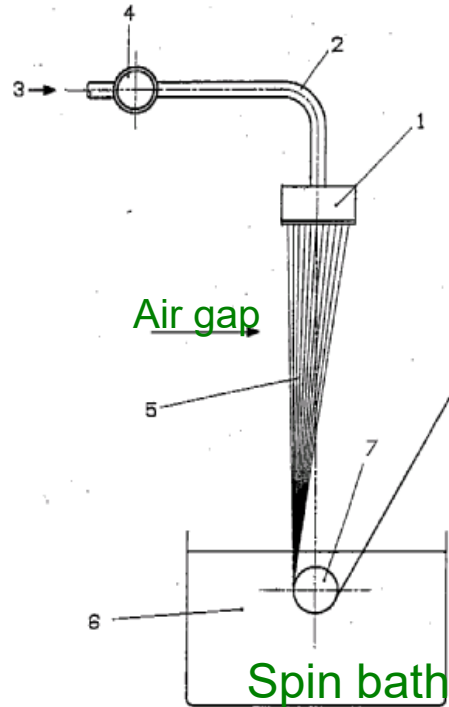
It took until 1992 when Courtauld started its first full-scale production plant in Mobile (USA), followed by Lenzing AG in Heiligenkreuz (Austria) in 1997.

Today, Lenzing owner of all spinning sites (Grimsby, UK)



Instability of NMMO

Dry-jet Wet Spinning (CLY)



- Extrusion of the hot solution via an air gap into an cold aqueous spin bath (20 – 30% solvent).
- The polymer chains are highly oriented through the ratio between take-up velocity and the extrusion velocity (draw ratio between 4 and 20).
- Coagulation takes place when the gel enters the spin bath. No further stretching is necessary.

Spinning, Precipitation

Spinneret, airgap:

chain orientation

Coagulation bath:

Spinodal decomposition, re-formation of hydrogen bonds -> **highly swollen gel in fibrillar form** -> **fibrillar cellulose II crystal structure**

Structure Formation:

Build-up of a fibrillar network.

Phase separation time < relaxation time

Summary questions

- **What is the difference between regeneration and coagulation?**
- **Which cellulose derivatives are (or have been) of importance?**
- **Advantages and drawbacks of the viscose process?**
- **Examples for non-derivatizing cellulose solvents?**
- **Advantages and limitations of aqueous NaOH solution as cellulose solvent?**
- **What is the Lyocell process**