PROCESS TECHNOLOGY OF PAPERMAKING

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Process Technology of Papermaking

Date	Time	Hour	Content
30 Sep	09:00-1200	3	History of papermaking
	13:00-15:00	2	Pulps – Beating and fiber properties
1 Oct	09:00-1200	3	Pulps – Additives and functions
2 Oct	09:00-1200	3	Papermaking processes & interfiber bonding
	13:00-16:00	3	Paper– Structural and absorption properties
3 Oct	09:00-1200	3	Paper– Mechanical properties
4 Oct	09:00-1200	3	Paper– Optical properties
	13:00-16:00	3	Recent trend of paper science and technol.

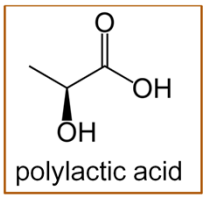
Lecture information and contact

- Homepage of “Process Technology of Papermaking (T. Enomae)”
- http://www.enomae.com/
  → Handouts in lecture(講義資料)
- E-mail address
  → t@enomae.com
  for any questions and comments

Biomaterial and Paper

- What biomaterial is

Materials constituting components and the structure of organisms processed to provide properties required for the use such as:
Wood, paper, cellophane, rubber, leather, polylactic acid



polylactic acid

Theory and method for providing high performance to biomaterials is called biomaterial science. Paper science is one of the most important biomaterial sciences.

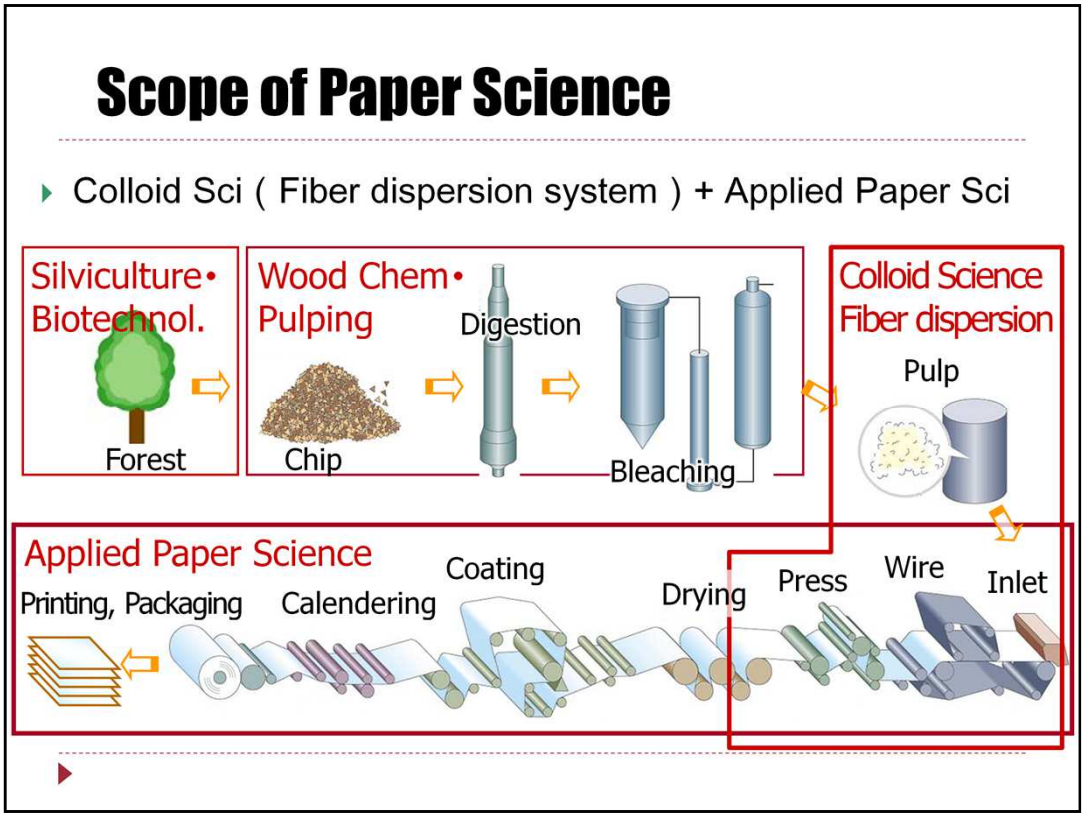
生物材料
生物体を構成する成分や構造体に、利用に必要な加工を施した材料
木材、紙、セロハン、ゴム、皮革、ポリ乳酸など

Biomaterial Scienceとは
生物材料を高機能化するための分析、製造、加工などの科学と技術

"Paper" —Definition

- "A thin, flat material obtained by sheet-forming and drying fibers especially of plants"
- "A thin, flat material made from crushed wood or cloth used especially for writing and printing on and in packaging" - Cambridge Dict.
- Plant fibers, especially wood-sourced, as a raw material of paper are called "a pulp"

Cambridge Dictでは、British Dictでは　in packaging　が抜けている。



Silviculture=造林学

Who has affected you most?

- “Who has affected you most in your life so far?” was voted in an internet site.
- Jesus Christ received the second largest numbers of votes
- (A) received the largest.
- Without paper, printing technology would not have developed, nor would wealthy life today be guaranteed.

Cai Lun（蔡倫）

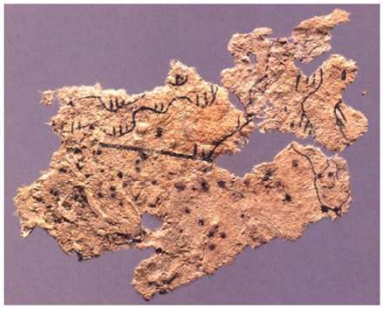
Origin of paper

- Ts'ai Lun is traditionally regarded as the inventor of paper. Exactly, however, he invented the composition for paper along with the papermaking in A.D. 105.
- The fibrous materials used in those day were bark, hemp, silk, and fishing net.

蔡倫

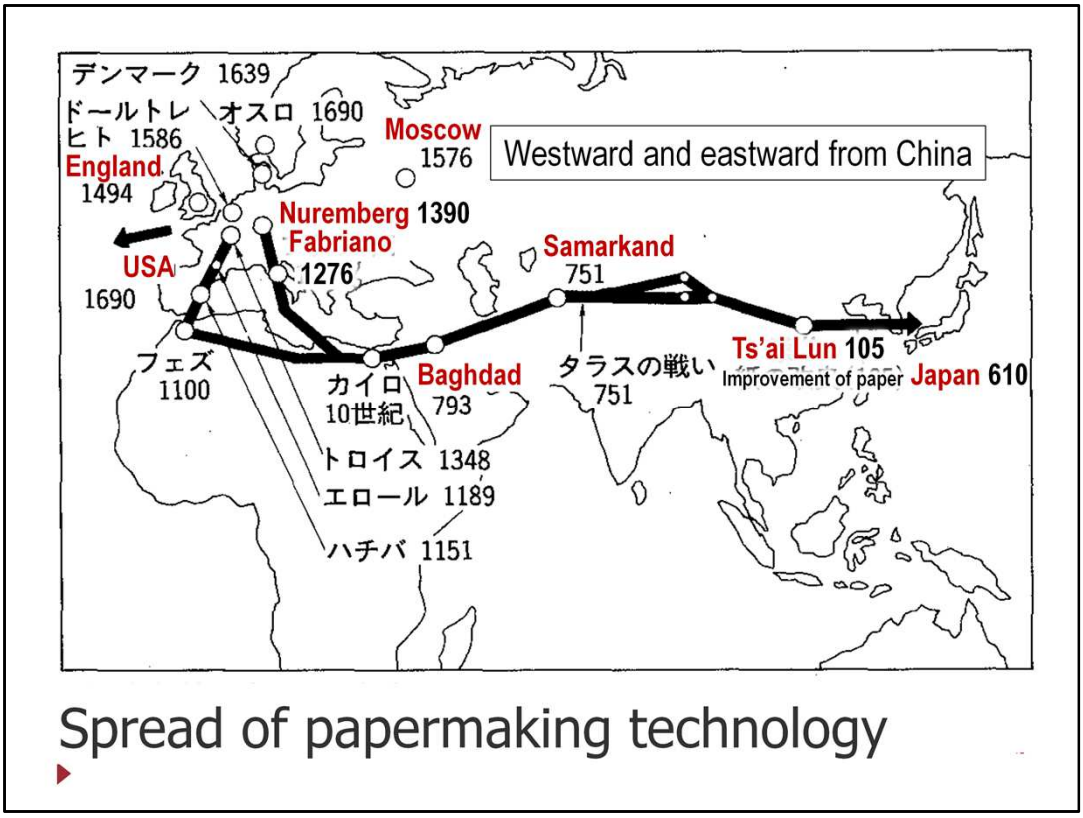
Origin of paper

- The world oldest paper discovered in an ancient tomb was estimated to be made between 179 and 142 BC (early Western Han 漢朝).
- It was used as a map, where mountains, waterways and roads are drawn.



Fangmatan (放馬灘) paper

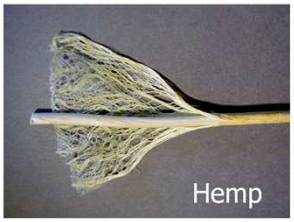
early Western Han 前漢



Nuremberg=Nürnberg=ニュルンベルグ

History of papermaking tech. -Materials

- **Hemp** (Cannabis大麻・ Linen亜麻)
  - → Cannabis has been used for cloth and fishing net in China and Japan. Linen in Europe.

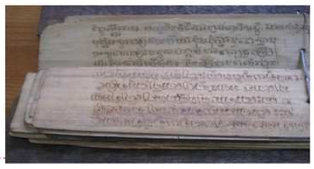


- **Rags**
  - → Recycling of cloth woven originally from hemp. Cotton from the age of Industrial Revolution
- **Bast (skin) fibers**, such as Paper Mulberry etc. for Japanese paper

History of papermaking tech. -Materials

- **Leaves**, of Treang tree to make "Sastra"
- **Wood**, capable of producing on a large scale
- **Kenaf**
  - → A kind of hemp promoted for forestry preservation, but not accepted any more.
- **Plastics**, synthesized paper from polypropylene called "Yupo"

Treang tree



Sastra

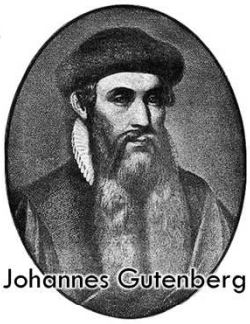
Origin of Printing technology

Gutenberg (1395? –1468)
invented a printing press in around 1445.

The invention consisted of

- mass-producing movable type;
- oil-based ink from linseed oil; and
- a wooden printing press similar to the agricultural screw presses

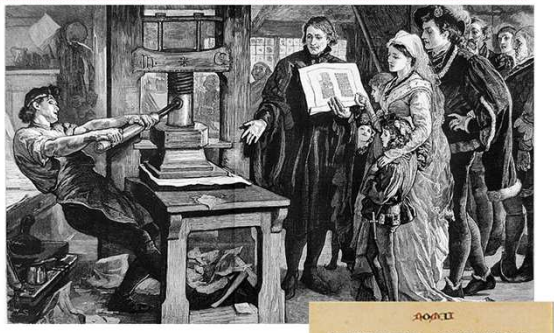
and allowed the mass production of printed books and was economically viable for printers and readers alike.


Johannes Gutenberg


Movable type

42-line Bible (42B)

- Gutenberg printed and published 180 copies of 42-line Bible.
  - → The start of the age of the printed book in the West



- Relationship with paper
  - → Increased paper demand
  - → Development of mass production of paper
  - → Use of wood as a papermaking material
  - → Invention of paper machine to produce "continuous paper".

The Greatest Inventions of the Past 2000 Years

Edited by John Brockman and published on Jan 12, 2000

- John Brockman, a novelist of USA, asked "What is the most important invention in the past two thousand years? and Why?" to famous.
- "Reading glasses" and "eraser" were unexpectedly proposed.
- Many people including Dr. Philip Anderson, a Nobel prize winner, chose "**printing technology**" because it promoted knowledge occupied by privileged people to the public.
- Another physical scientist chose "watch" for quantification of time passage that was dependent on one's sense so far.
- "Heliocentric theory", "mathematics", "differential and integral calculus", "democracy", and "religion" were also supported.

- See http://www.edge.org/documents/Invention.html

2000年間で最大の発明は何か [単行本]
ジョン ブロックマン (著),
heliocentric theory=地動説 Copernican system

History of papermaking tech. – Machine

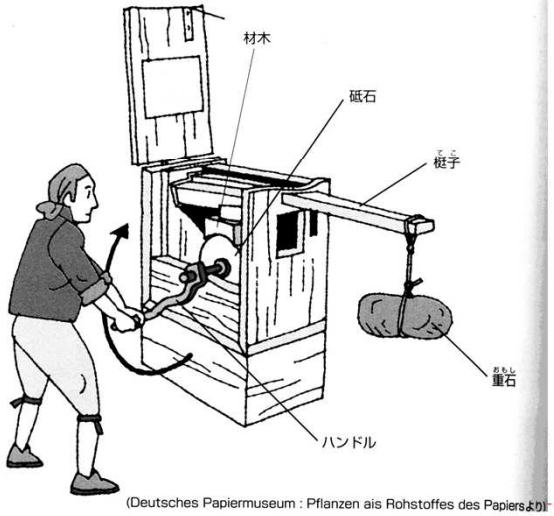
1670	Hollander beater invented [Holland]
1719	Reaumur submitted his invention - paper can be made from wasp hives- to the Academy [France]
1798	Louis-Nicolas Robert invented manufacture of continuous paper [France]
1844	Keller invented ground wood pulp [Germany]
1851	Burgess [USA] and Watts [England]invented soda pulping to make wood pulp.
1856	Healey received a patent of corrugated [England]
1856	Tilghman invented the sulfite pulping [USA]
1879	Dahl invented Kraft pulping [Germany]
1950	Hardwood pulping initiated[Japan]
1968	Thermo-Mechanical Pulping (TMP) Developed[Sweden]
1977	Quinone-added pulping invented [Japan]

1977 キノン添加パルプ蒸解法の発明〔日本〕
1968 サーモメカニカルパルプ(TMP)を開発〔スウェーデン〕
1950 広葉樹材のパルプ化始まる〔日本〕
1879 ダールがクラフトパルプを発明〔ドイツ〕
1856 ティルマンが亜硫酸パルプ(Ca法)を発明〔アメリカ〕
1856 ヒーレイは初めて段ボールの特許を取得〔イギリス〕
1852 フェルターが砕木機を実用化〔ドイツ〕
1851 ワットとバルガスは木材を原料としたソーダパルプを発明
1844 ケラーが砕木パルプを発明〔ドイツ〕
1798 ルイ・ロベールが長網抄紙機を発明〔フランス〕
レオミュールはスズメバチの巣を見て木材から紙ができる
はずと学会に提案〔フランス〕
1719
1670

Mechanical pulping – Groundwood pulp

- GP or SGW ([Stone] Groundwood Pulp)

Keller invented ground wood pulp in 1844



(Deutsches Papiermuseum : Pflanzen ais Rohstoffes des Papiersより)

Old printed material in Japan

In 764, Emperor Koken had holy texts (無垢浄光陀羅尼経) printed on paper one million copies for peace of Japan, contained in one million wooden miniatures of a three story tower, and laid out in the ten great temples like Horyu-temple and Todai-temple.

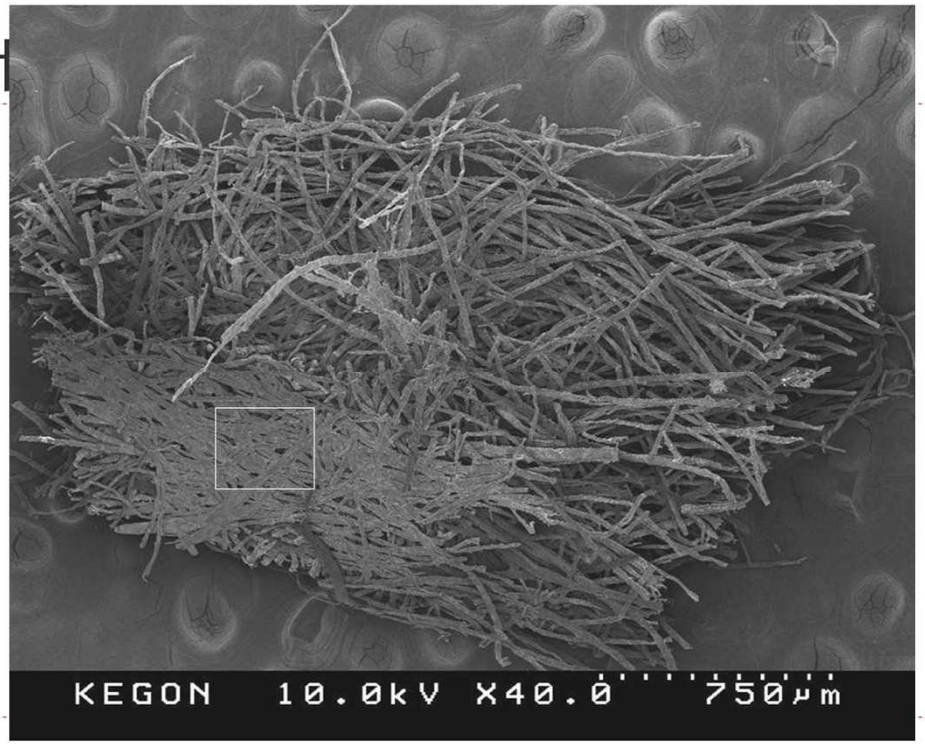
holy texts 経文（無垢浄光陀羅尼経）

The world oldest printed material

In 1966, printed holy texts was discovered in the Buddha tower of Bukkoku-temple (仏国寺) of Keishu, Shinra (新羅慶州), currelty Korea(韓国). This tower is known to have been built in 751.

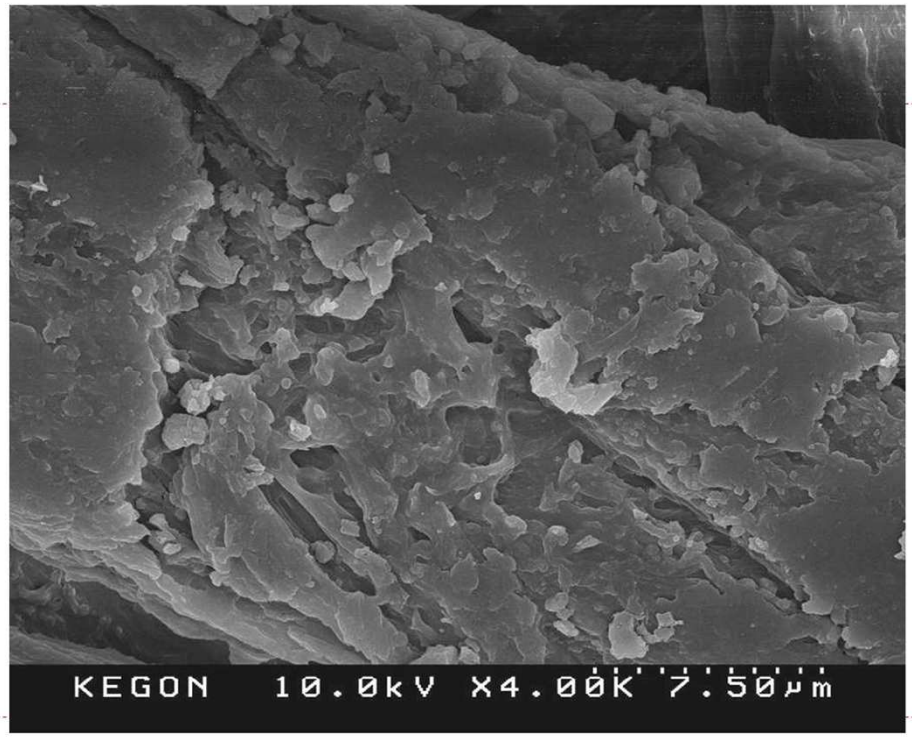
The world oldest printed material

Paper with holy texts (華厳経) written in 755, Silla era (新羅) was analyzed.

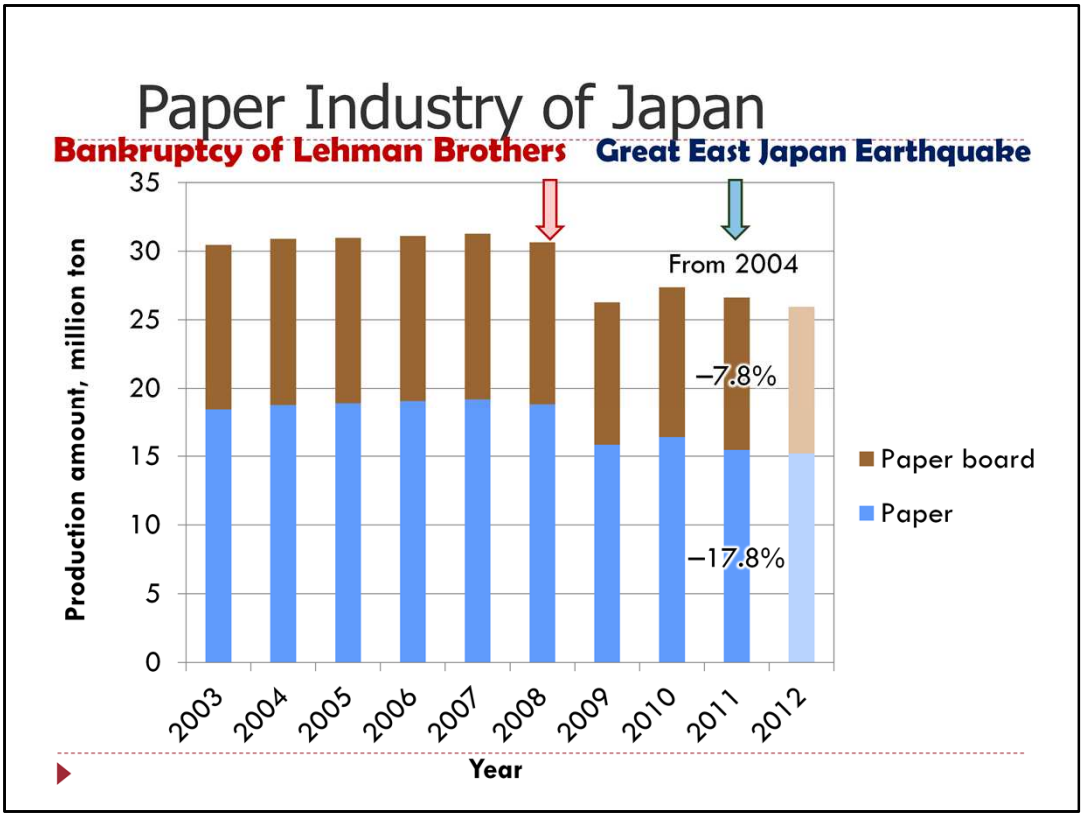


755年に新羅時代の華厳経が書かれた紙の走査電子顕微鏡写真

755年に新羅時代の華厳経が書かれた紙の走査電子顕微鏡写真

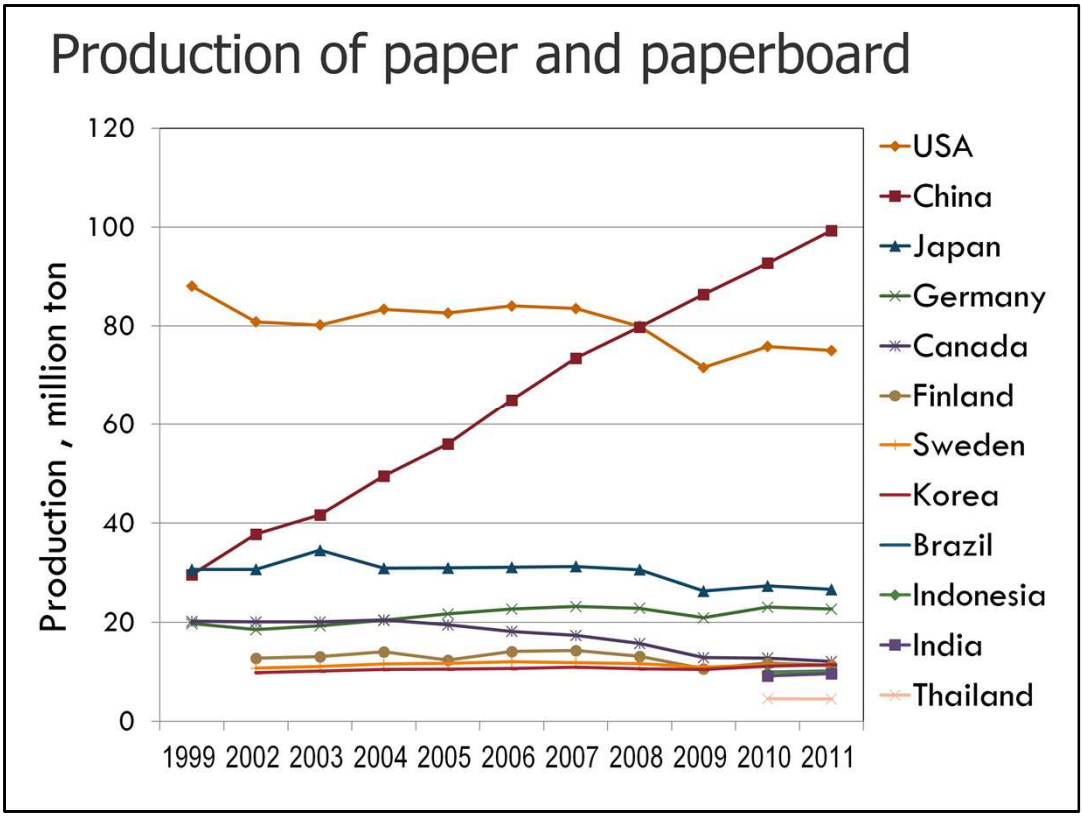


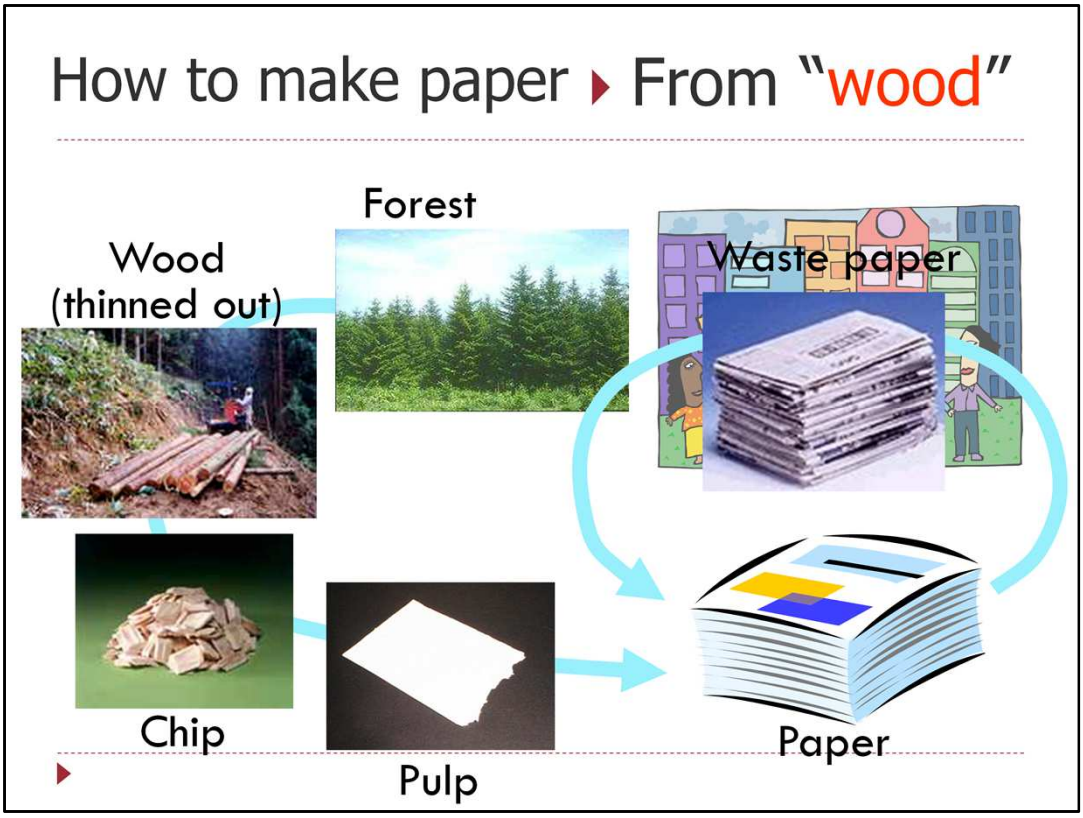
755年に新羅時代の華厳経が書かれた紙の走査電子顕微鏡写真



subprime mortgage (モーゲッジ) crisis, August 2007

Financial crisis of 2007–2008
2008-2012 global recession


Production of paper and paperboard
Production , million ton
120
100
80
60
40
20
0
1999 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011
USA
China
Japan
Germany
Canada
Finland
Sweden
Korea
Brazil
Indonesia
India
Thailand


How to make paper ▸ From "wood"
Forest
Wood
(thinned out)
Waste paper
Chip
Pulp
Paper

Wood tissue－cells of beech tree

Component of hardwood tissue	
Vessel	20%
Wood fiber	60%
Axial parenchyma cell	10%
Radial parenchyma cell	10%

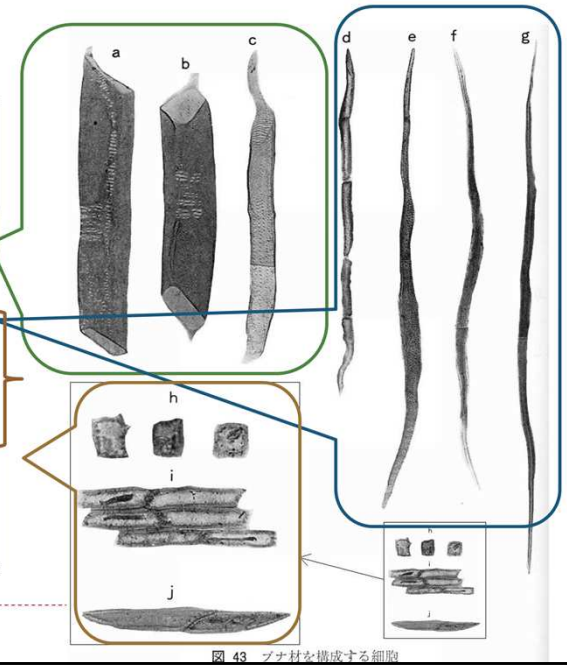
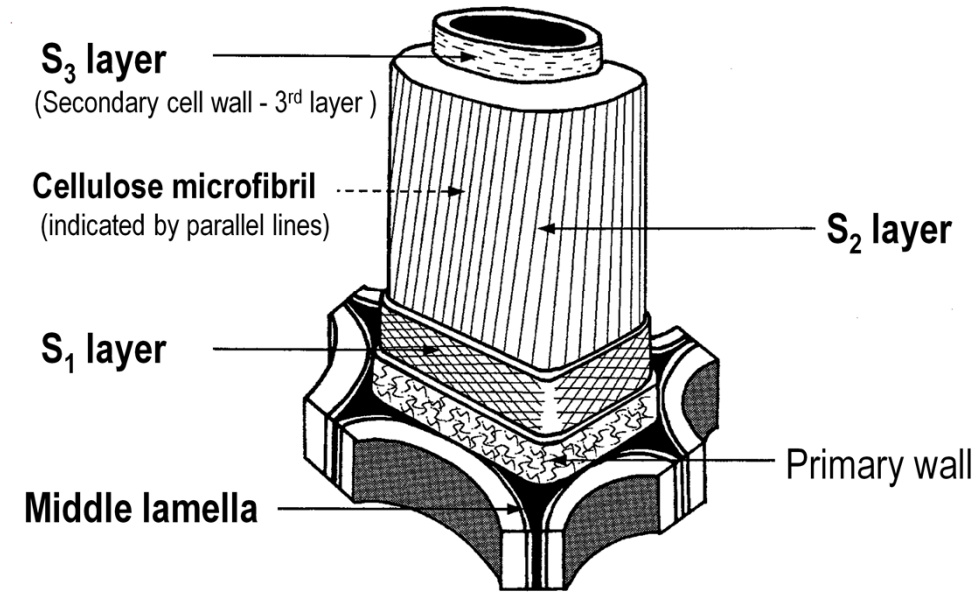


図 43 ブナ材を構成する細胞

アカマツは針葉樹か広葉樹か？
どこが繊維か？
繊維の太さなどが突然変化しているところは？
早材と晩材
年輪界

Tissue = 組織

Wood tissue – structure of cell wall

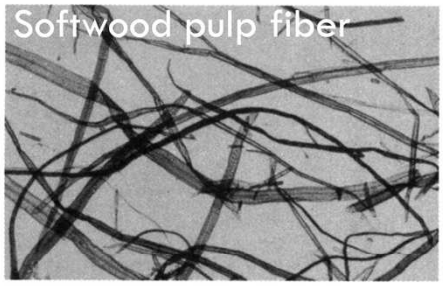


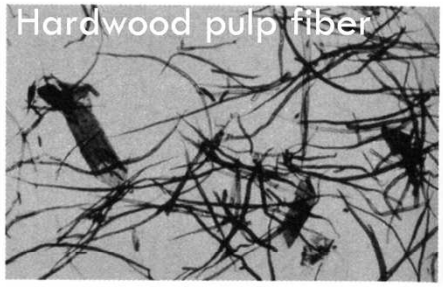
Structure of plant cell wall and axial direction of cellulose microfibrils

Kind of pulp

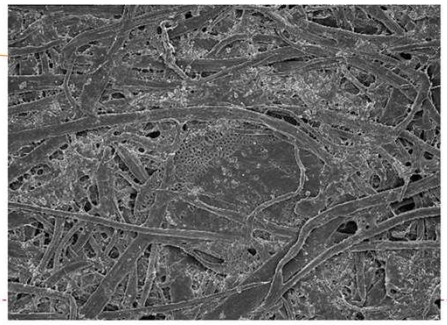
- **Pulp**
  - **Fibers mainly consisting of cellulose extracted from plant such as wood by mechanical or chemical treatment**
- Mechanical pulp [MP]
  - Fibers extracted from wood by crushing
- Chemical pulp [CP]
  - Fibers extracted from wood by dissolving lignin
- Deinked pulp [DIP] (recycled pulp)
  - Fibers extracted from waste paper by removing ink

Chemical pulp – Fiber geometry



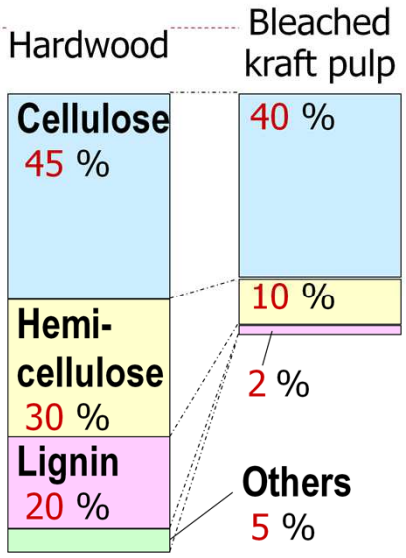


- Copy paper consists of (B) wood pulp fibers
- Observe pulps



Wood composition – Major 3 components

Chemical component	Approx. ratio (%)	
	Softwood	Hardwood
Cellulose	45	45
Hemicellulose	25	30
Lignin	25	20
Others Terpenoid Resin acid Fatty acid etc.	2 - 8	



Change of Composition by kraft pulping

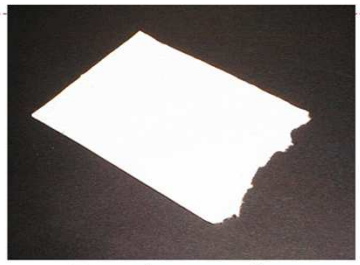
Laboratory tour- what kind of apparatus

What apparatus do you explain to me?

- Choose one apparatus.

1. What is measured or treated?
2. How does it works?
3. How is this measurement or operation important?

Form of pulp



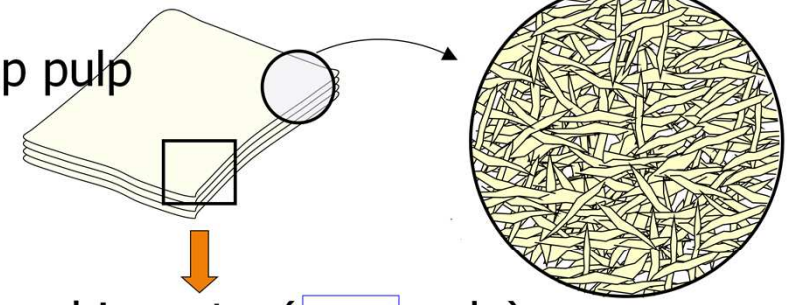
Dry lap pulp

- **Slush pulp**
  Pulp suspension with concentrations of approx. 1-4%
- **Lap pulp**
  Pulp Formed and folded by wet machine. Called "**Dry lap**" when dried
- **Bale pulp**
  A bunch of pulp sheets compressed and bound with a wire

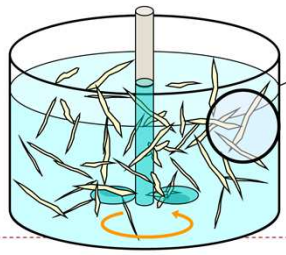
- Transporting (C) pulp

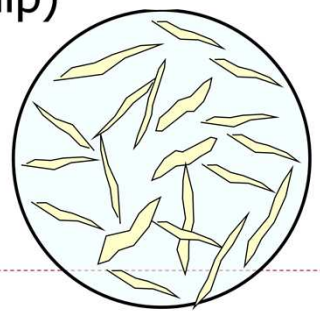
Disintegration - Separation into individual fibers

Dry lap pulp



Dispersed in water ((D) pulp)





Standard disintegrator (defibrator)

- Pulp is put in water in steel container with ca. 3.4 L capacity
- Stirred with a propeller mixer at 3000 min^{-1} (rpm)
- Latency of MP should be removed at high temperature (Latent=hidden)

Pulp	Dry mass	Water volume	Revol-utions
Chemical	30 g	2.0 L	30,000
Mechanical	60 g	2.7 L	60,000

レーテンシィ（紙パルプ事典のカタカナ訳）
例えば乾燥処理したRGPを、単純にパルパーなどでスラッシュ状に戻しても、元の特性（例えば強度）には戻らない。高濃度でのリファイニング（叩解）、乾燥などの処理により生じたひずみが、繊維の曲がり、フリーネスの見かけ上の上昇などとしてパルプ中に残存していること。熱水を用いて離解すると、潜在化している部分（レーテンシィ）もかなり顕在化できる。
Latent=hidden
30,000回転は何分間離解すればよいか？
A. 30000/3000=10（分）

Beating (refining)

- Post-disintegration process
- Process where shear stress is applied to water-containing fibers resulting in **fibrillation** (formation of small filaments or fibers) on the surface and **concentrically loose structure**

叩解とは、水を含む繊維に機械的剪断力を与え、毛羽立たせたり、同心円状の緩みを与えることにより繊維を柔軟にし、乾燥時に生じる繊維間結合を強くする工程。
この処理により紙の強度が増す。

Beating (refining)

- Beating achieves large bonded area between fibers and thus higher paper strength.

- Q. Why can this breaking process increase paper strength?

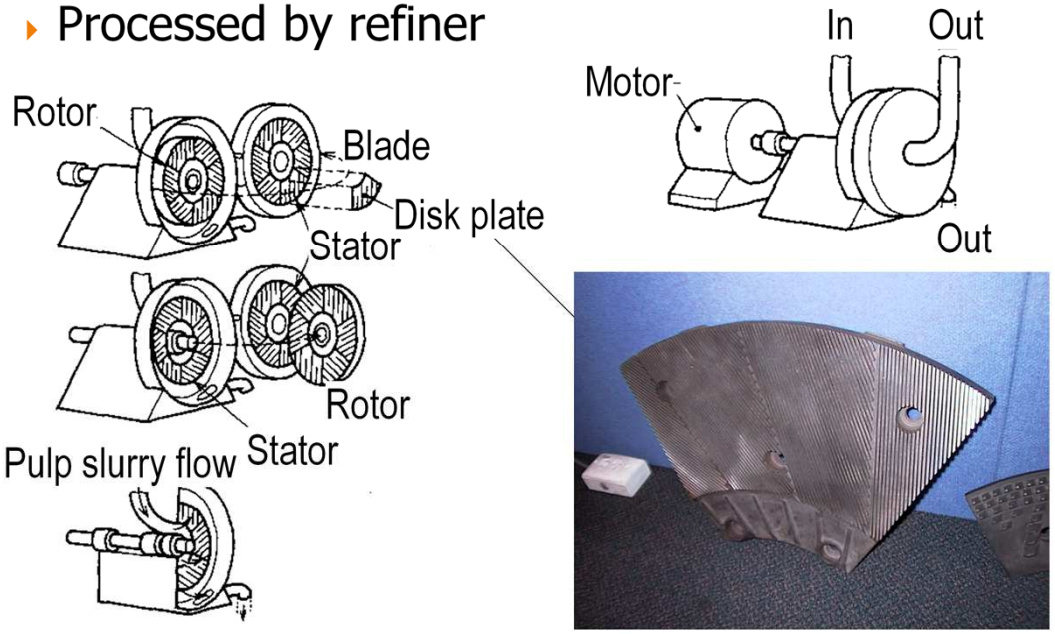
叩解とは、水を含む繊維に機械的剪断力を与え、毛羽立たせたり、同心円状の緩みを与えることにより繊維を柔軟にし、乾燥時に生じる繊維間結合を強くする工程。
この処理により紙の強度が増す。

Difference between disintegration and beating

- **Disintegration** is a process to separate fibers bonded or entangled, keeping fiber characteristics
- **Beating** is a process to treat mechanically individual fibers, changing fiber characteristics

Beater – Refiner(refining)

- Processed by refiner

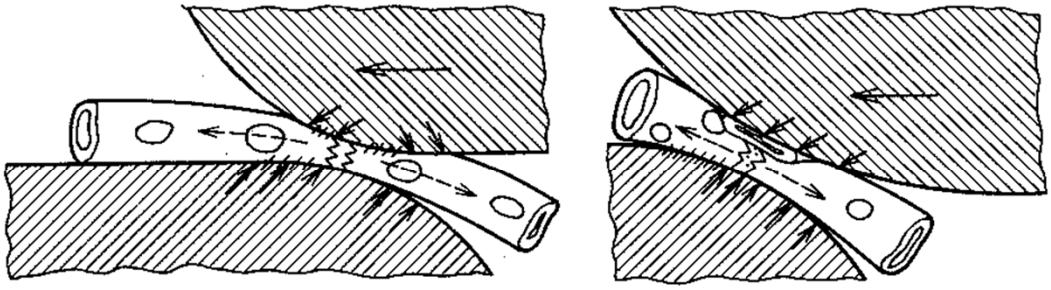


Refining by disc refiner
Pulp concentration is 2-5%

ディスクリファイナ　　-パルプ濃度2-5%
リファイナー機械パルプ

Beater – PFI mill (beating)

Beating – mechanism



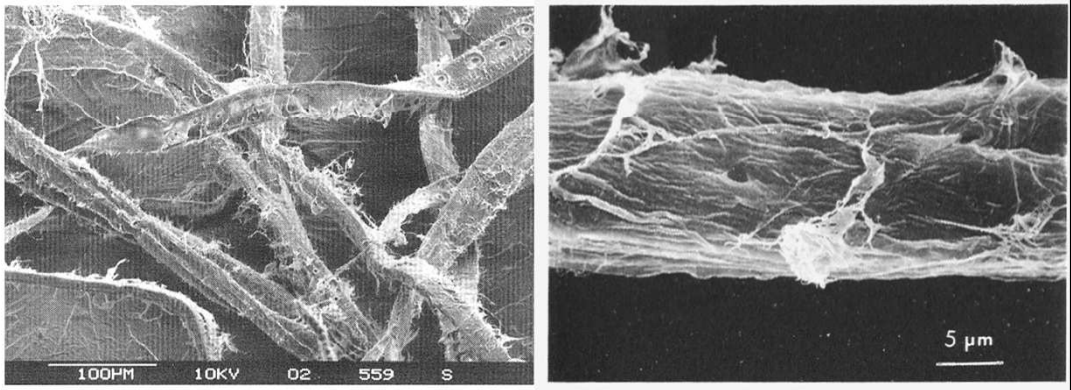
Effect of blades on pulp fibers during beating

Refining – movie – refiner

Three kinds of force apply to fibers.
3種類の力が作用している
- Compression(圧縮)
- Shear stress (せん断力)
- Tension (張力)

Beating－change of fibers－**external** fibrillation

- External fibrillation
- Internal fibrillation



Scanning Electron Micrographs of freeze-dried softwood pulp fibers after beating

Fibrils are different from microfibrils that are crystal units of cellulose.
A fibril has a thickness of 0.5 to a few micrometers while a microfibril 3 to 20 nanometers.

外部フィブリル化のフィブリル＝繊維表面の毛羽立ち
フィブリル＝fibrils＝繊維が枝状化した状態及びその枝（毛羽）でミクロフィブリルが集まったもの。太さは光学顕微鏡でも観察可能な0.5μm(500nm）～数μm程度。

（セルロース）ミクロフィブリル＝(cellulose) microfibril＝セルロース分子の集合単位。幅は3～20nm程度で長さは不定。

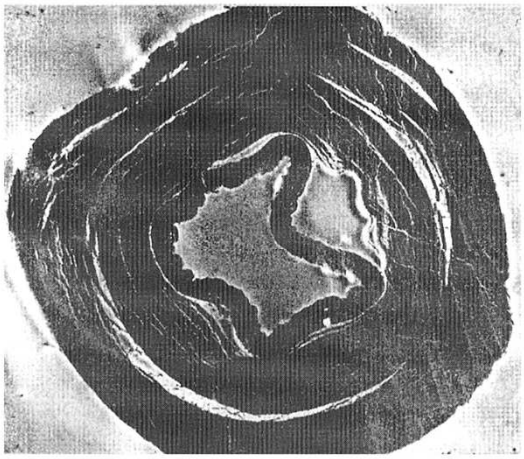
内部フィブリル化＝同心円状の緩み（層状の剥離）
リグニンの溶出した小さな空隙の連結など

Beating－change of fibers－**internal** fibrillation

External fibrillation
Internal fibrillation

＝Concentric loosening
(Lamellar separation)

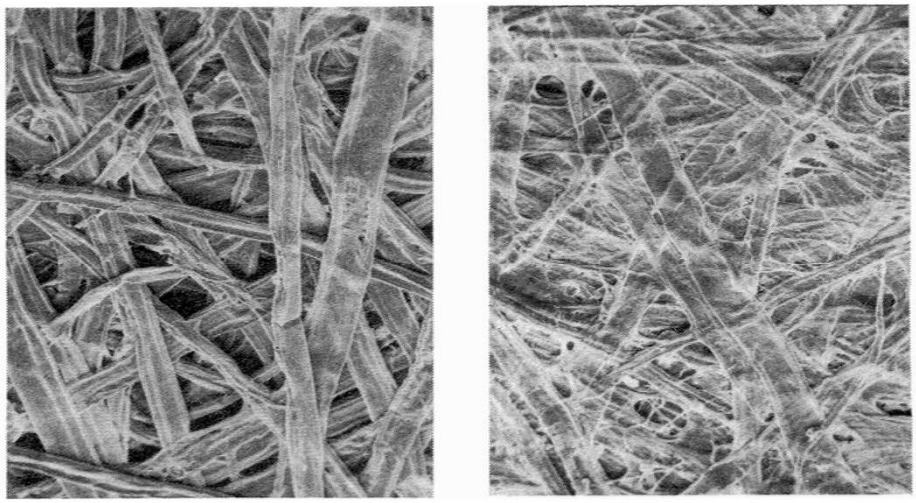
Connection of small pores formed by lignin removal



Lamellar separation of fiber cell wall by beating

外部フィブリル化のフィブリル＝繊維表面の毛羽立ち
内部フィブリル化＝同心円状の緩み（層状の剥離）
リグニンの溶出した小さな空隙の連結など

Beating – change of paper structure



Unbeaten (left) and beaten (right) softwood pulp sheets

Q. How did fibers and sheets change by beating?

- 繊維の扁平化（叩解しなくてもある程度　扁平になる）
- 繊維間の密着
- 空隙減少と密度増加、

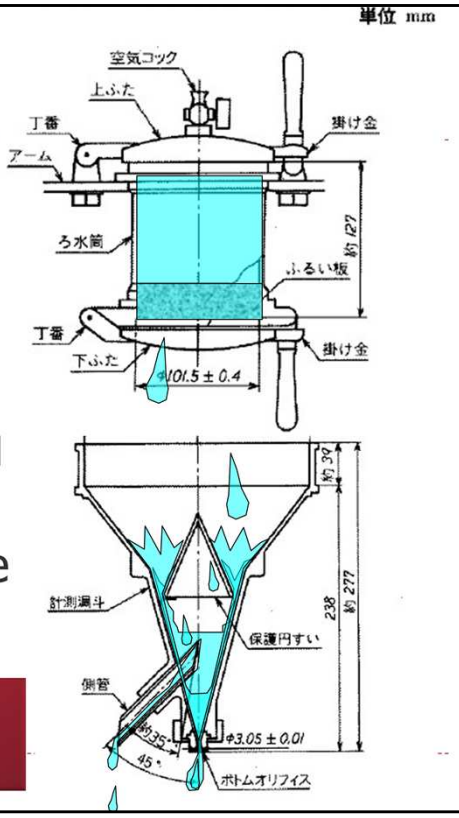
Evaluation of fiber properties

- Freeness (Drainability)
- Specific surface area
- Fiber length distribution
- Distinguishment by staining
- Fiber coarseness
- Curl index

Evaluation of Freeness

- Canadian standard freeness (mLCSF)
  - One L of pulp suspension at 0.3% and 20 °C is pored and the volume (mL) of water drained from the side pipe is measured.

Q. Does CSF increase or decrease by beating?



Canadian Standard Freeness (CSF)

Evaluation of Freeness

- Canadian standard freeness
  - Unbeaten pulp ca. 650 mL CSF
  - Beaten pulp ca. 400 mL CSF
  - Reasons why freeness (E) by beating are
    - More fines (small pieces of fibers)
    - Fibrillation

    make water paths between fibers in a pulp mat thin, winding, and long.

(E) decreases

Water Retention Value (WRV)

- M_w : Mass of pulp after centrifugation
  M_d : Mass of the pulp after oven drying

$$WRV(\%) = 100 \times (M_w - M_d)/M_d$$

Q. Calculate WRVs to two significant figures in %.

Pulp	After cent.(g)	Oven dried(g)
SBKP beaten	**0.61**	**0.23**
SBKP unbeaten	**0.59**	**0.28**
HBKP beaten	**0.54**	**0.22**
HBKP unbeaten	**0.45**	**0.24**

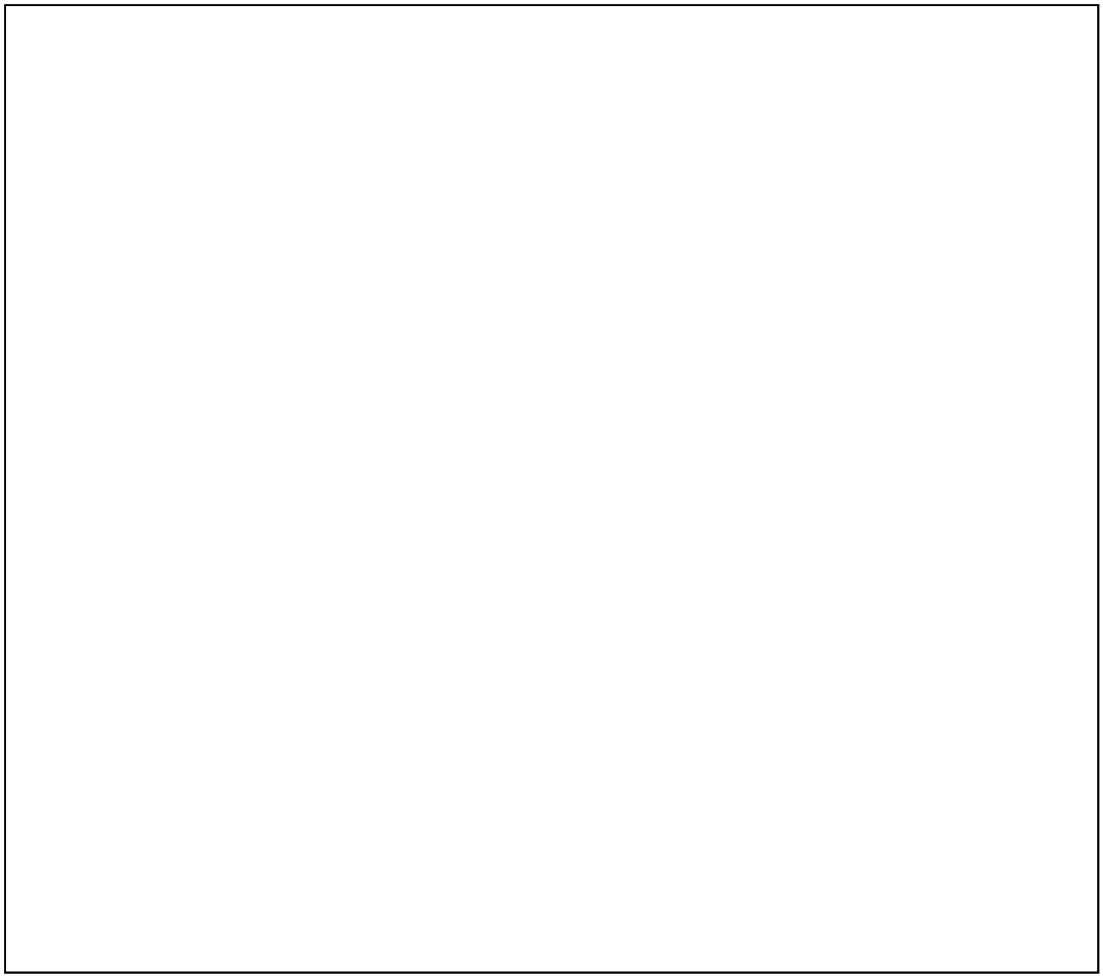
Q. Calculate WRVs to two significant figures in %. (The expression modified a little.)

A.

Pulp	After cent.(g)	Oven dried(g)	WRV(%)
SBKP beaten	**0.61**	**0.23**	**170**
SBKP unbeaten	**0.59**	**0.28**	**110**
HBKP beaten	**0.54**	**0.22**	**150**
HBKP unbeaten	**0.45**	**0.24**	**88**

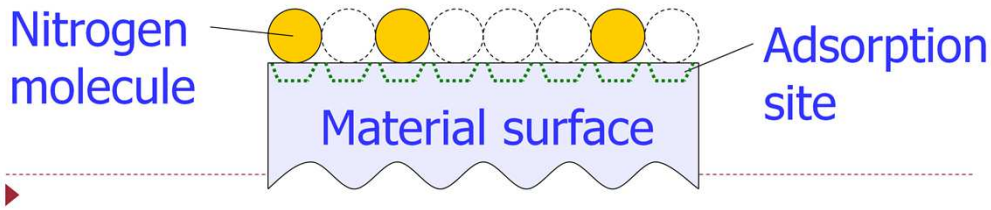
Nitrogen adsorption method

- Langmuir model
  - All the adsorption sites are equivalent and the surface is homogenous.
  - Monolayer coverage
  - No interactions between adsorbate molecules on adjacent sites



Nitrogen adsorption method

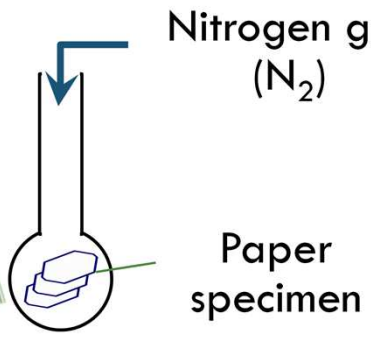
- Langmuir model (cont'd)
  - The fractional coverage of the surface θ changes at the adsorption rate proportional to gas pressure p and the number of empty sites $N(1-\theta)$.
  - The desorption rate proportional to $N\theta$.



Adsorption rate is expressed as $d\theta_a/dt = k_a p N(1-\theta)$
Desorption rate is expressed as $d\vartheta_d/dt = k_d N\theta$
At equilibrium, the two rates are equal. Therefore, it is assumed that $d\theta_a/dt = d\theta_d/dt$
Then, $k_a p (1-\theta) - k_d \theta = 0$
Αφτερ ρεπλαχεμεντ $K=k_a/k_d$,
$Kp(1-\theta) - \theta = 0$,
$Kp = \theta + Kp\theta$
are obtained.

$d\theta_a/dt = k_a p N(1-\theta)$
$d\theta_d/dt = k_d N\theta$
平衡状態では吸脱着の速度が等しいので、$d\theta_a/dt = d\theta_d/dt$ とすると、
$k_a p (1-\theta) - k_d \theta = 0$
$K=k_a/k_d$とおくと、$Kp(1-\theta) - \theta = 0$、$Kp = \theta + Kp\theta$

Nitrogen adsorption method



Nitrogen adsorption method

- Langmuir theory
  - Langmuir adsorption equation is obtained.

$$\theta = \frac{Kp}{1+Kp} \quad Kp\theta + \theta = Kp \quad \text{where, } K = \frac{k_a}{k_d}$$

  - Given that the volume of adsorbing gas is V (volume of adsorbed state is slight, but as a gas at 1 atm) and the volume at full absorption is V_∞, then $q = V/V_\infty$ and rewritten as:

$$\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{KV_\infty}$$

Plots of p/V vs. p give a linear relationship with a slope of $1/V_\infty$ and an intercept of $1/KV_\infty$.

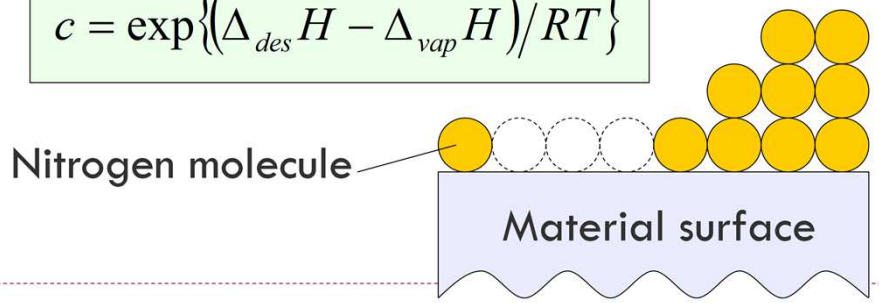
Kp =θ+Kpθに$\theta = V/V_\infty$を代入し、
$Kp = V/V_\infty + Kp\ V/V_\infty$
$p/V = 1/KV_\infty + p/V_\infty$となる。
等温式とは一定温度での気体の分圧に対する吸着量を示す式

pとVは実測できる。 V_∞ が知りたい値。

Nitrogen adsorption method

- BET theory (applied to practically)
  - Multilayer adsorption is possible.
  - Desorption heat $\Delta_{des}H$ of adsorbate molecule on monomolecular layer and vaporization heat $\Delta_{vap}H$ of liquid adsobate molecule on the 2nd or higher layers are different.

$$c = \exp\left\{\left(\Delta_{des}H - \Delta_{vap}H\right)/RT\right\}$$



Nitrogen adsorption method

- BET theory (cont'd)
  - BET equation is obtained

$$\frac{V}{V_{mon}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \quad \text{where,} \quad z = \frac{p}{p_0}$$

  - Given p_0 is saturation gas pressure above the layer of adsorbates like a bulk liquid with a thickness of one or more molecules and V_{mon} is the volume of monomolecular layer, then,

$$\frac{z}{(1-z)V} = \frac{1}{cV_{mon}} + \frac{(c-1)z}{cV_{mon}}$$

V_{mon}が知りたい値で、Vと zは実測可能。

Nitrogen adsorption method

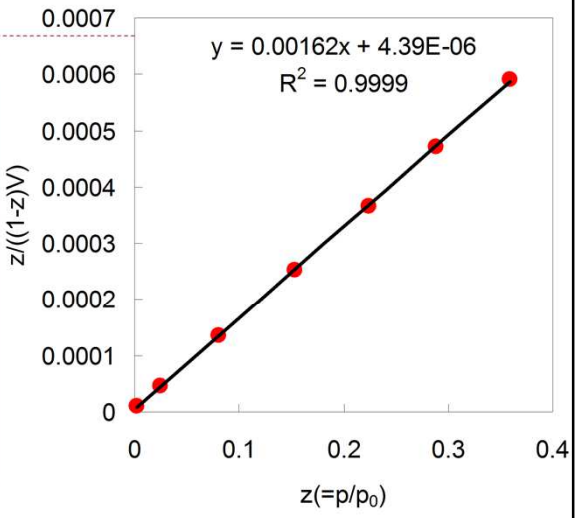
- BET theory (cont'd)
  - $\frac{z}{(1-z)V}$ plotted vs. z *will give a linear relationship with a slope of* $\frac{(c-1)}{cV_{mon}}$ and a intercept of $\frac{1}{cV_{mon}}$.
  - V_{mon} and equation of state give the number of nitrogen molecules n $(= p_0 V_{mon}/RT)$. n multiplied by the adsorption area of one nitrogen molecule A_m $(\approx 0.162\ \mathrm{nm}^2)$ gives surface area S_a, where NA *is Avogadro number* that is 6.022×10^{23}.

$$S_a = n \times NA \times A_m$$

Nitrogen adsorption method

- Use BET equation.

Q. In nitrogen adsorption on given material at 75 K (P_0=570 Torr), nitrogen partial pressure p in gas phase and the volume V of adsorbing nitrogen (1 atm at 273 K) is tabulated. Calculate V_{mon} and c.



p, Torr	1.2	14	45.8	87.5	127.7	164.4	204.7
V, cm^3	235	559	649	719	790	860	950

A.
From the graph you will know
1/(cVmon) 4.39E-06
(c-1)/(cVmon) 0.00162
Then, you can calculate and obtain
c 370
Vmon, cm^3 615

In equation of state of ideal gas, PV=nRT, where, P(Pa), V(m^3), n(mol),
R(J/K/mol =Pa m^3 K^{-1} mol^{-1})=8.314
n=PV/RT is a value you need and can be calculated as
n=101325×615×$(10^{-2})^3$/(8.314×273)=0.027454849 (mol)
The surface area of this piece of material is
0.027454849 (mol)x6.022x10^{23} x 0.162 nm^2＝2678 m^2

1/(cVmon) 4.39E-06
(c-1)/(cVmon) 0.00162
c 370
Vmon, cm^3 615
理想気体の状態方程式は、PV=nRTで、P(Pa), V(m^3), n(mol), T(K)で、
R(J/K/mol =Pa m^3 K^{-1} mol^{-1})=8.314となる。n=PV/RTを計算すると、
n=101325×615×$(10^{-2})^3$/(8.314×273)=0.027454849 (mol)
よって、この試料の表面積は、0.027454849 (mol)x6.022x10^{23} x 0.162 nm^2＝

2678 m^2となる。

Nitrogen adsorption method

- BET equation – more questions

Q. Usually, c>>0. Given c=∞, then simplify BET equation.

Q. If simplified, specific surface area can be calculated from only one partial pressure p measured for saving time. Usually one value around z=0.3 are used. Apply this tequnique to the previous question.

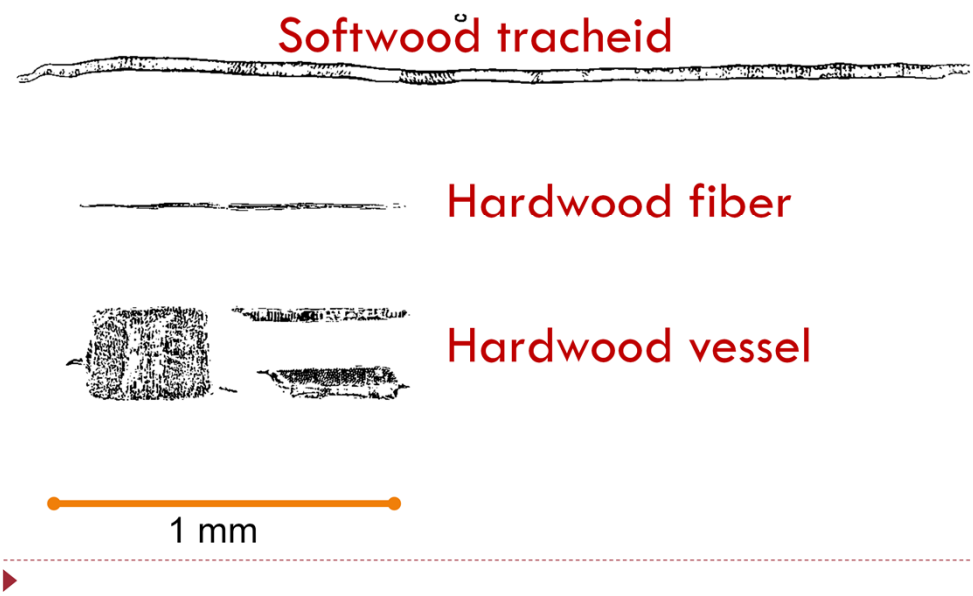
A.
Substitute c=∞ into BET equation: z/{(1-z)V}=1/cVmon+(c-1)z/cVmon
Then, you will obtain
Vmon=(1-z)xV
The data set 164.4(Torr) and 860(cm3) should be used because
z=p/p0=164.4/570=0.288 is nearest to 0.3.
Then,
Vmon =(1-0.288)x860= 612 (cm3)
This value is close to real BET value 615.

Specific surface area (SSA)

Drying method	Sample	BET SSA, m^2/g
Solvent exchange	Unbleached Spruce KP	230
	Bleached Spruce KP	185
	Spruce α-cellulose	185
	Spruce GP	25
	Birch KP	129
Evaporation at 105 °C	Unbonded pulp fibers	1.2
	Paper	0.5 – 1.0

KP=kraft pulp, GP=ground wood pulp

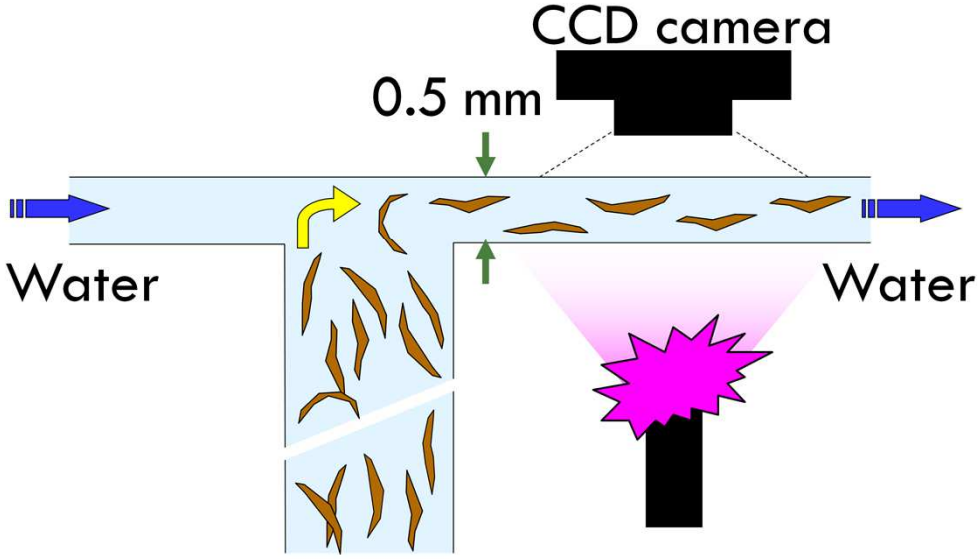
Length and width of fibers



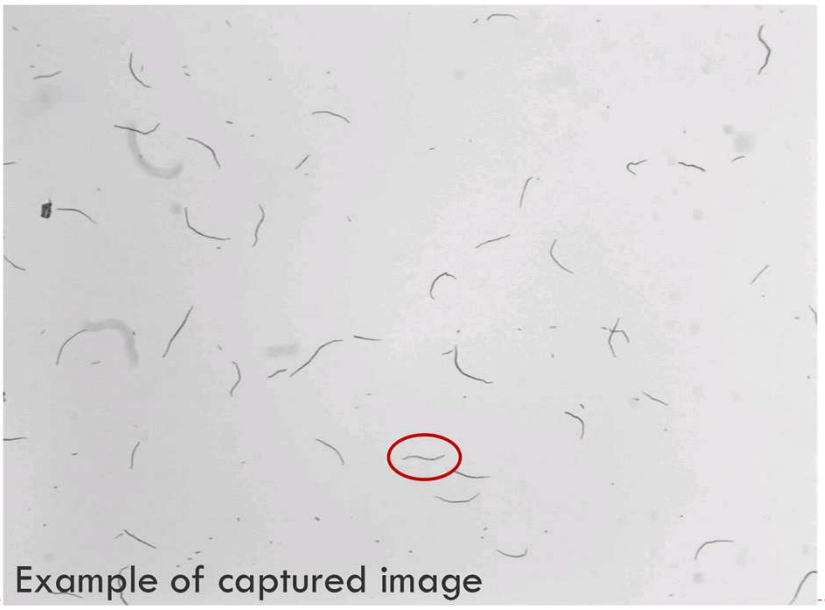
Fiber length and width distribution

Fiber tester, ABB(L&W), Sweden

Fiber length and width distribution

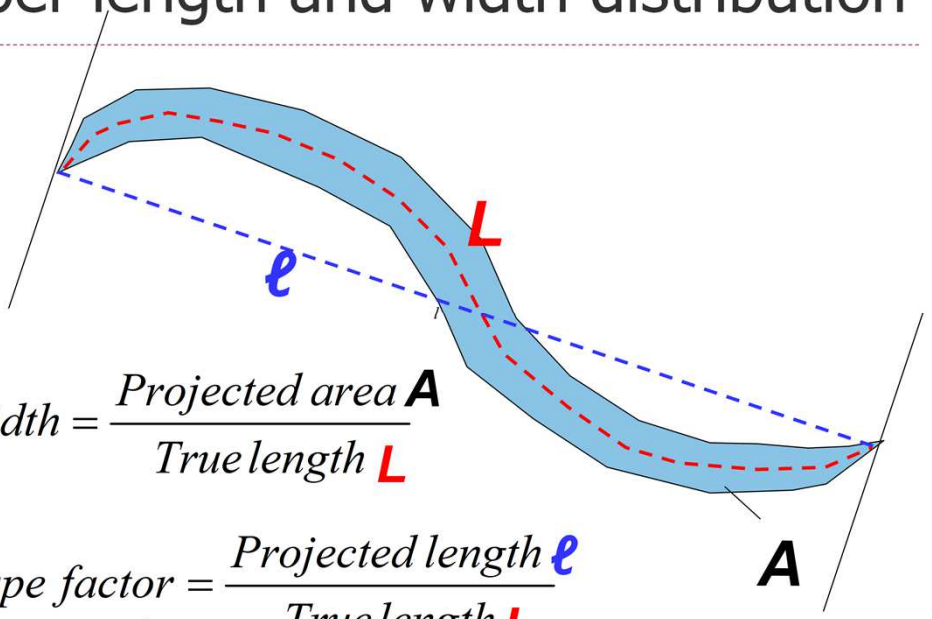


Fiber length and width distribution



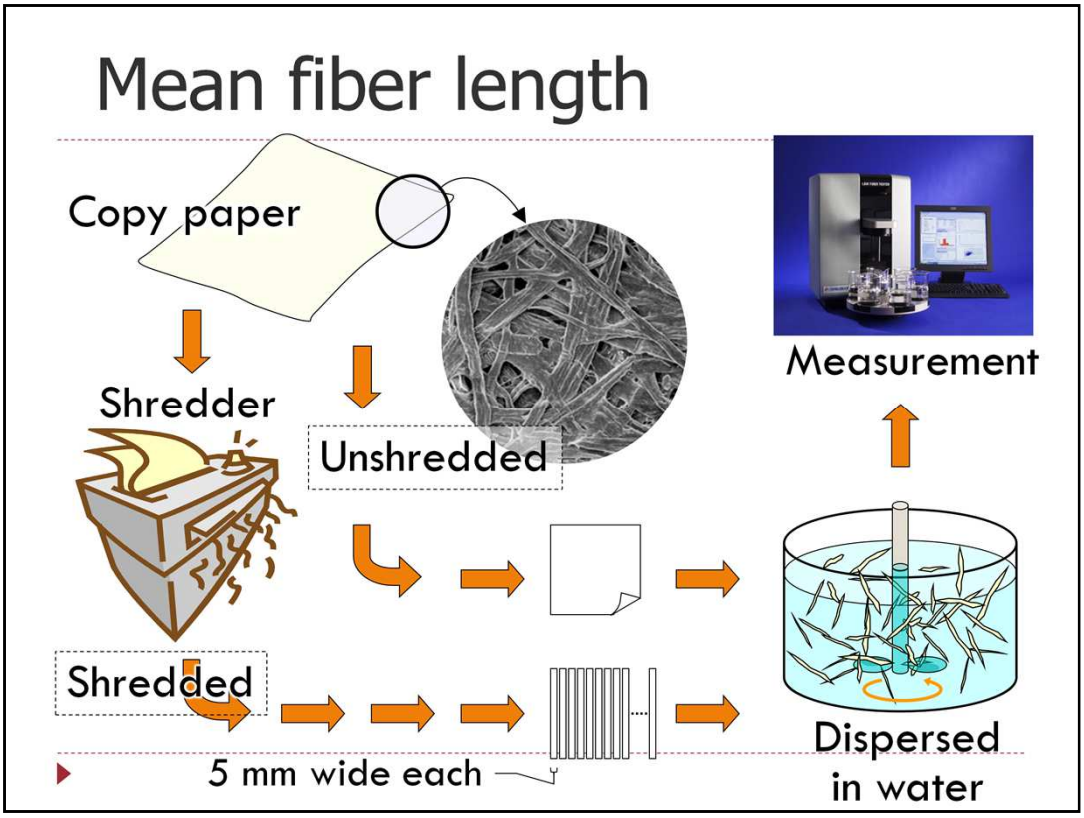
Example of captured image

Fiber length and width distribution



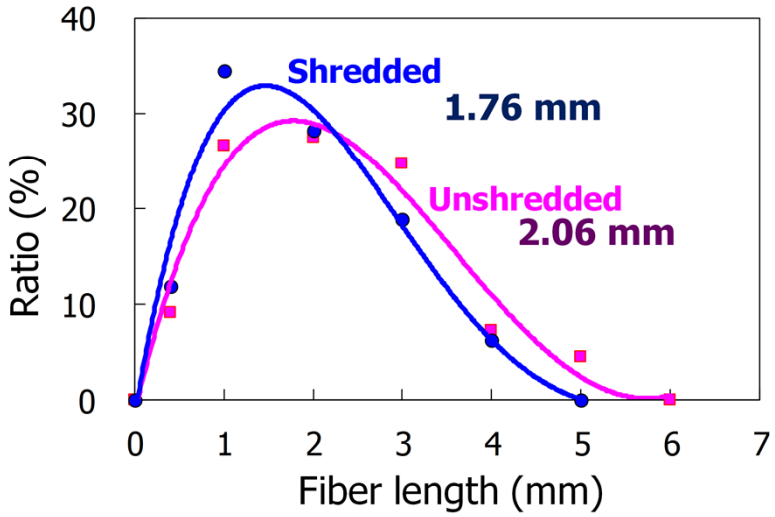
$$Width = \frac{Projected\ area\ A}{True\ length\ L}$$

$$Shape\ factor\ (Linearity) = \frac{Projected\ length\ \ell}{True\ length\ L}$$


Mean fiber length
Copy paper
Shredder
Unshredded
Measurement
Shredded
5 mm wide each
Dispersed
in water

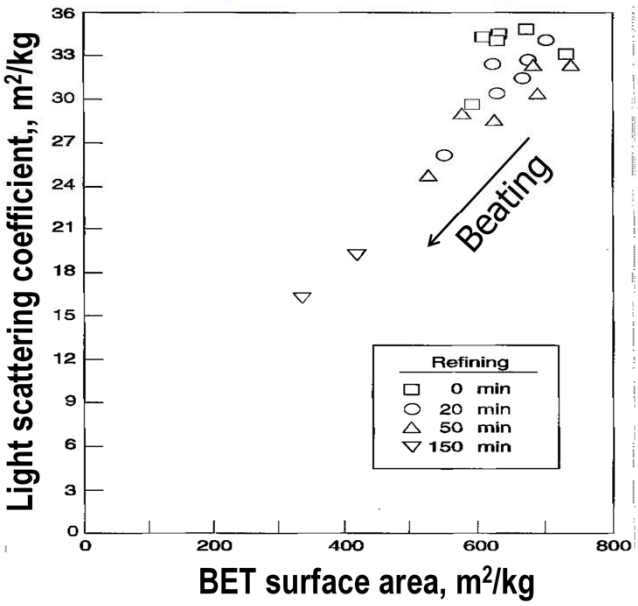
Mean fiber length

- Comparison in fiber length between shredded and unshuredded copy papers



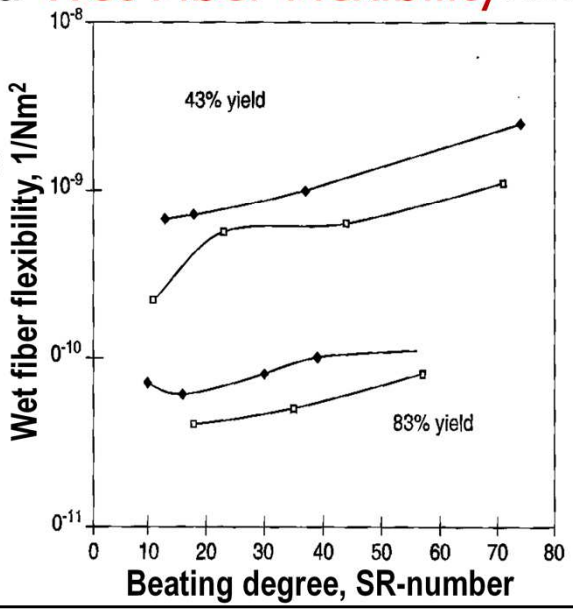
Effect of beating on paper properties

- **S**pecific **S**urface **A**rea on **L**ight **S**cattering **C**oefficient
  - LSC decreases as fiber bonding area increases by beating.
  - Interfiber bonding area can be evaluated by SSA.
- Beating increased interfiber bonding area.



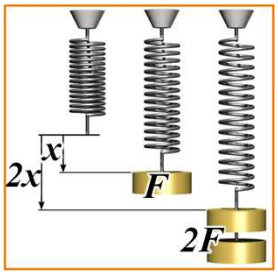
Effect of beating on paper properties

- Beating increased Wet Fiber Flexibility (WFF)
  - Bending strength of single wet fibers was measured for determination of WFF.
  - SR = Schopper-Riegler method for determination of drainability



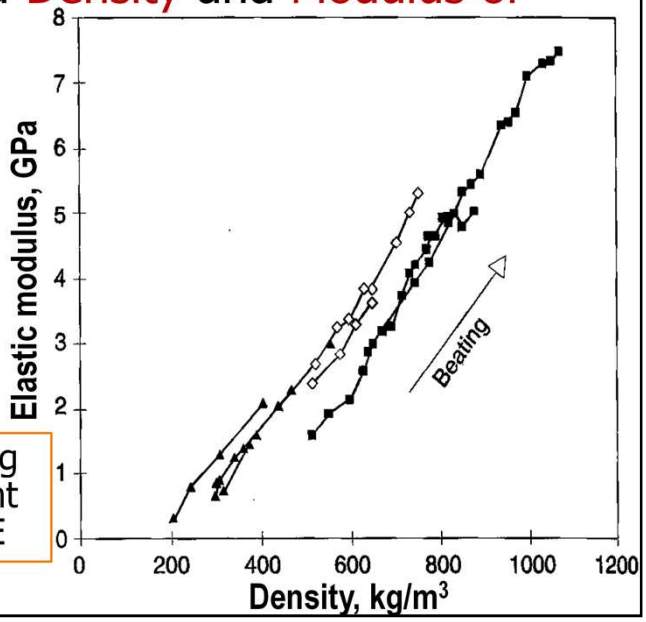
Effect of beating on paper properties

- Beating increased Density and Modulus of Elasticity (MOE)
  - Linear relationship between density and MOE regardless of kind of fibrous material



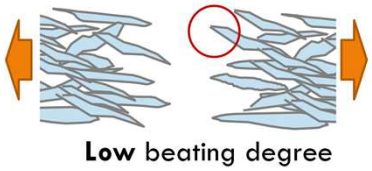
$F=kx$

k; spring constant = MOE

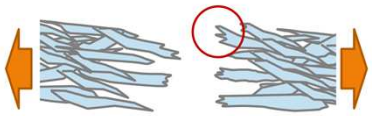


Effect of beating on paper properties

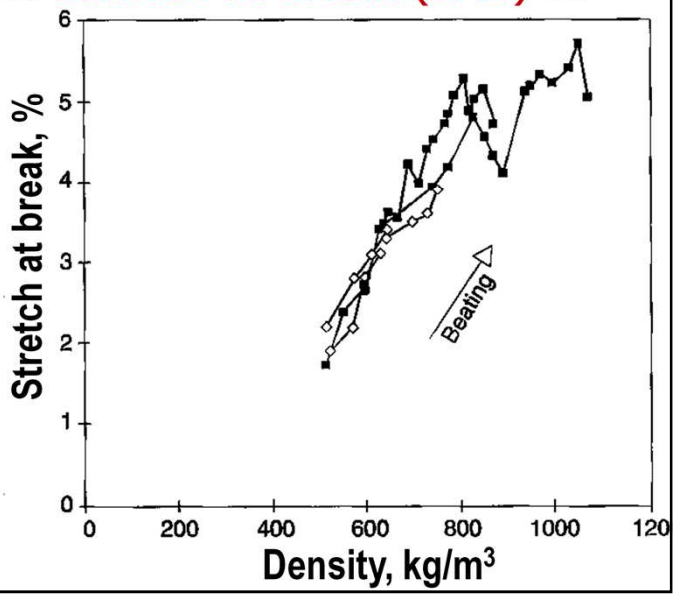
- Beating increased Stretch at Break (SAB) to certain degree
  - However, increase in SAB levels off.



Low beating degree



High beating degree



Stock preparation – additives

- **Paper quality** control
  - **Size (sizing agent)** - water repellency
  - **Filler** - brightness and opacity
  - **Strength agent** – dry or wet strength
  - **Dye** – optical brightening agent (OBA)
- **Paper manufacturing** control
  - **Retention aid** – ex. *aluminum sulfate* – fines, fillers, and size retained more
  - **Aintiseptic** (preservative)

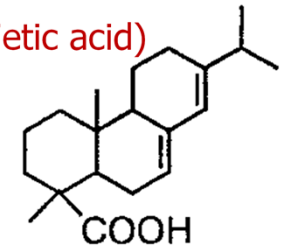
Additives – size and filler

	Acidic paper	Non-acidic paper
Size (sizing agent)	Rosin (Abietic acid)	Alkyl ketene dimer (AKD), Alkenyl succinic anhydride (ASA)
Retention aid	Aluminum sulfate (alum), deteriorates paper	Cationic polymer such as Polyamine-amide epichlorohydrin (PAE)
Filler	Clay, Titan dioxide, Talc	Calcium carbonate, Titan dioxide
pH at papermaking	4.5～5.5	7.5～8.5 (7 or slightly greater)

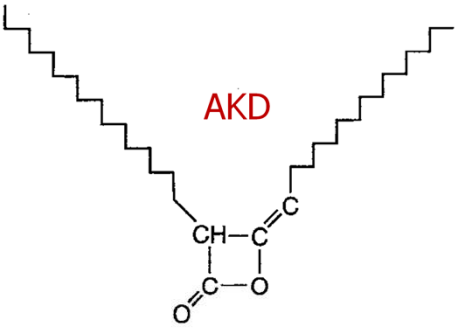
Q. Why is calcium carbonate not used for acidic paper?

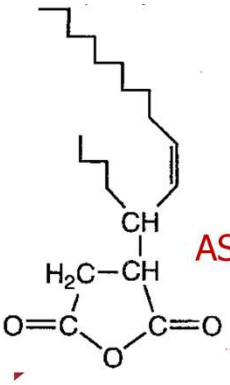
Additives – size and filler

Rosin (abietic acid)

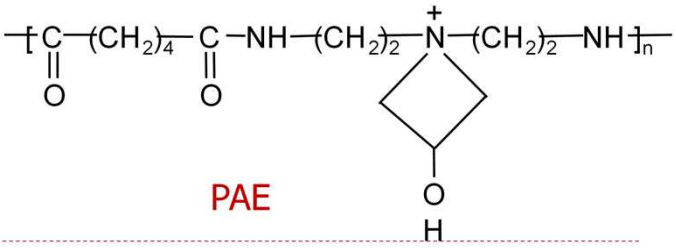


AKD





ASA



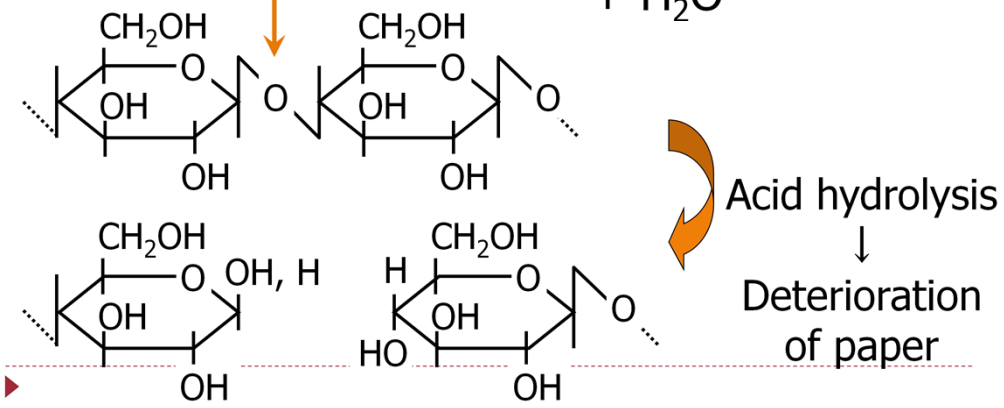
PAE

Additives – deterioration of acidic paper

Aluminum sulfate deteriorates paper.

$$Al_2(SO_4)_3 + 2H_2O \rightarrow 2Al(OH)^{2+} + 2H^+ + 3SO_4^{2-}$$

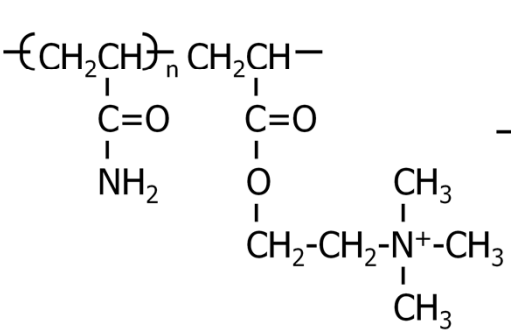
$$+ H_2O$$



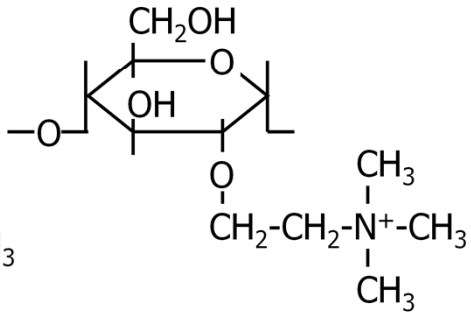
β(1→4)-glycosidic bonds

Additives – size and filler (2)

	Acidic paper	Non-acidic paper
Strength resin	Cationic polyacrylamide (C-PAM)	Cationic starch

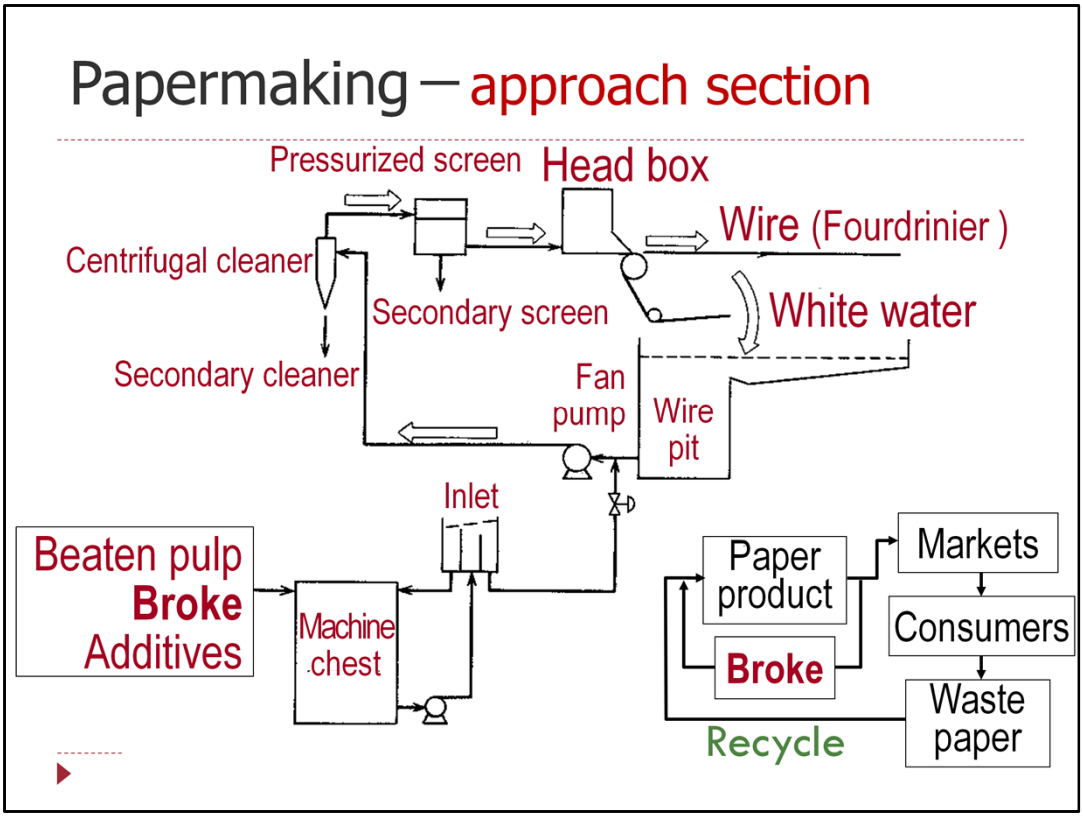


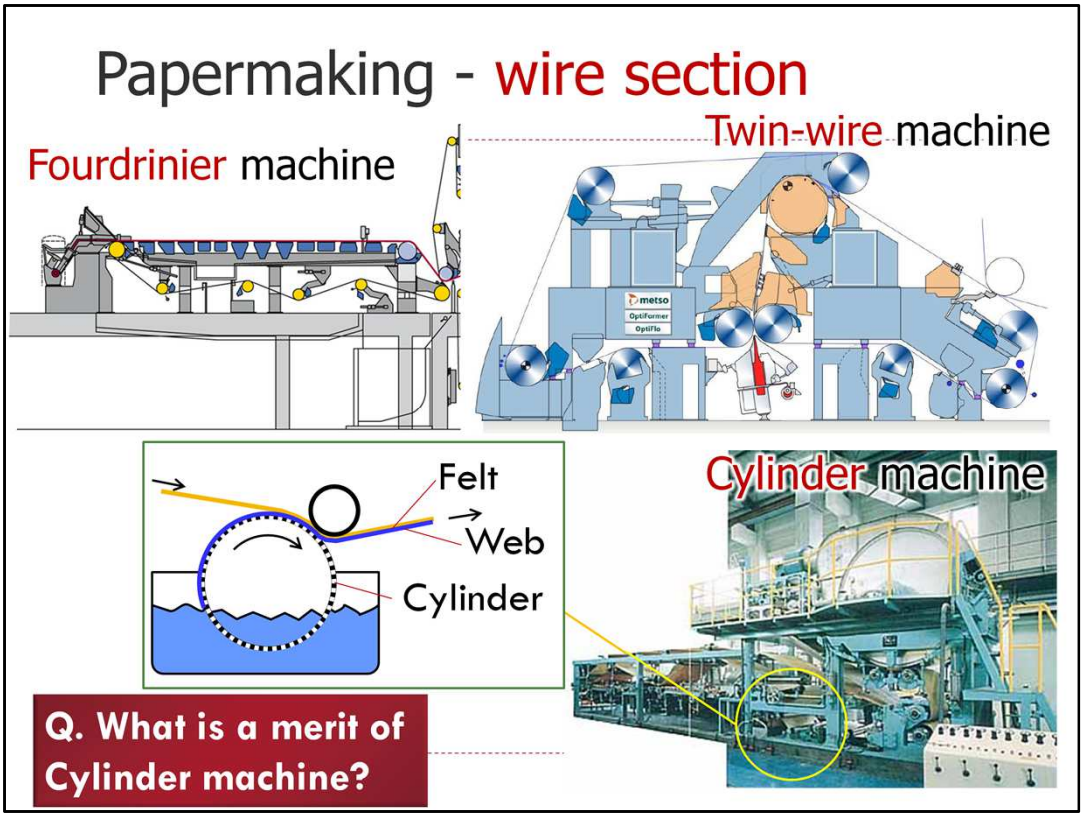
Cationic polyacrylamide



Cationic starch

Papermaking – Additives - movie

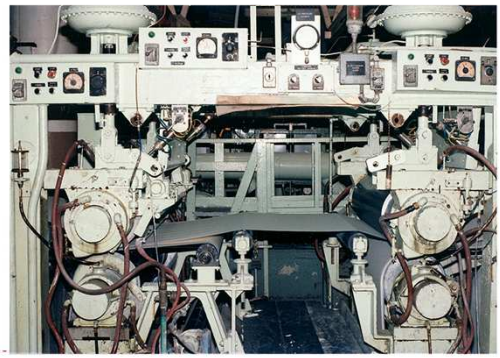

Papermaking – approach section
Pressurized screen
Head box
Wire (Fourdrinier)
Centrifugal cleaner
Secondary screen
White water
Secondary cleaner
Fan pump
Wire pit
Inlet
Beaten pulp
Broke
Additives
Machine chest
Paper product
Markets
Consumers
Broke
Waste paper
Recycle



These pictures are cited from
日本フェルトHPから図を引用
梅原製作所【製紙機械】
http://www.umebara.co.jp/syoshibumon.html

Papermaking – (wet) press section

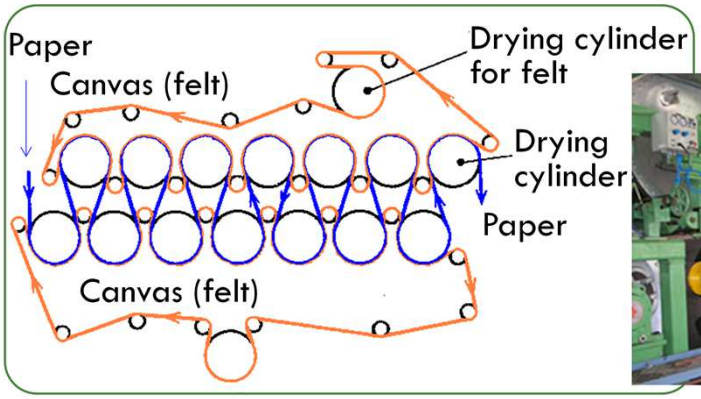
- A wet web is pressed at high pressure between large rolls to squeeze out excess water.
- Water transfers to felts that sandwich the wet web.
- Pressing increases density and wet web strength.
- The common number of nips is 3 or 4.



Kodak Historical Collection #003 (1986)

Papermaking – dryer section

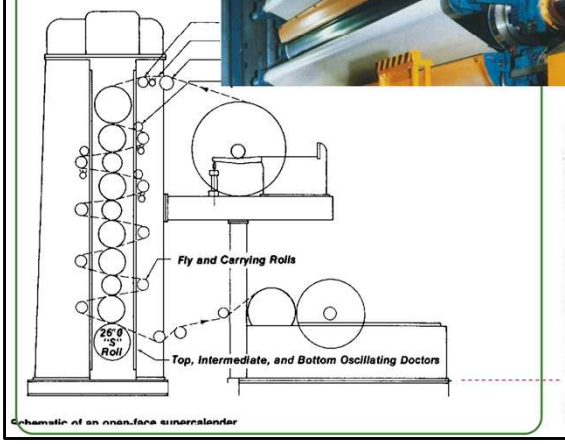
- Steam-heated cylinders dry a paper web with canvases.
- Free water evaporates, between fibers first , inside fibers second, and between fibrils last.



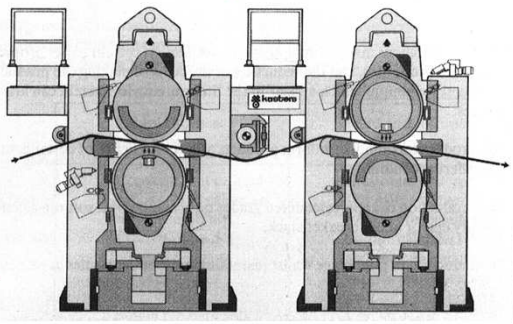
Papermaking – calender section

- A number of rolls press the passing paper.
- They make the paper surface extra smooth and glossy with friction, and provide a higher density and more uniform thickness

Supercalender

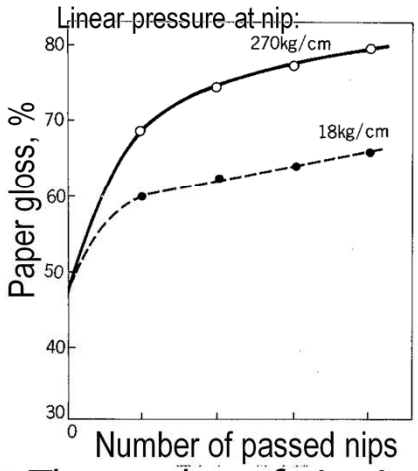


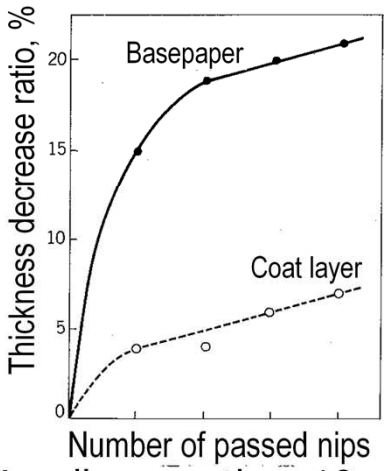
Soft nip calender



Papermaking – calendering effect

- Gloss improvement and compression of paper





- The number of nips is occasionally more than 10.

Q. Why is it as many as 10 although only 3 or 4 for wet press?

Types of chemical bond

- Ionic bond = a chemical bond in which two ions are joined together because one has a positive charge and the other a negative charge
- Covalent bond = a chemical bond in which two atoms share one or more pairs of electrons that hold them together (ca. 500 kJ/mol)
- Hydrogen bond = a weak connection that is formed between an atom of hydrogen (= a gas) and an atom of another substance such as oxygen or nitrogen (= a gas) (10～40 kJ/mol)
- Van der Waals forces = the relatively weak attractive forces that act on neutral atoms and molecules and that arise because of the electric polarization induced in each of the particles by the presence of other particles
- Dipolar bond (coordinate bond)
- Metallic bond

From Wikipedia
Ionic bond: electrostatic interaction between atoms which have a large electronegativity difference
Covalent bond: a common type of bonding, in which the electronegativity difference between the bonded atoms is small or nonexistent
Hydrogen bond:An example of intermolecular hydrogen bonding in a self-assembled dimer complex reported by Meijer and coworkers.[1] The hydrogen bonds are the dotted lines.

Van der Waals interaction: the van der Waals force (or van der Waals interaction), named after Dutch scientist Johannes Diderik van der Waals, is the sum of the attractive or repulsive forces between molecules (or between parts of the same molecule) other than those due to covalent bonds, the hydrogen bonds, or the electrostatic interaction of ions with one another or with neutral molecules or charged molecules

Intramolecular hydrogen bonding in acetylacetone helps stabilize the enol tautomer.
A hydrogen bond is the electromagnetic attractive interaction between polar molecules in which hydrogen (H) is bound to a highly electronegative atom, such as nitrogen (N), oxygen (O) or fluorine (F).

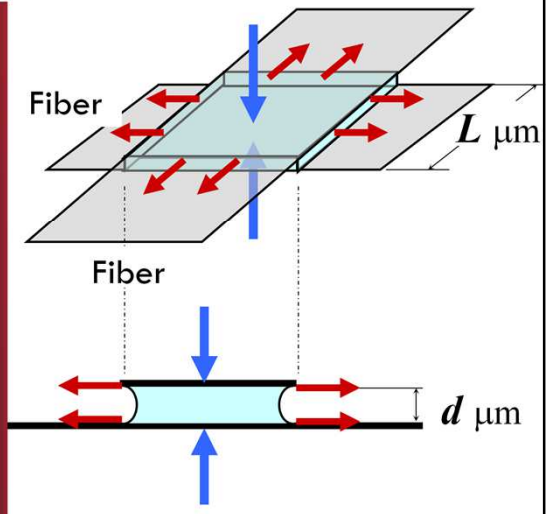
セルロース分子内の結合　共有結合
セルロース分子間の結合　水素結合

繊維間の結合　　水素結合

Inter-fiber bond

- Effect of water on interfiber bond formation

Q. Suppose two crossing flat fibers with the square , length L on a side at the crossing point. As they dry and the interfiber distance d comes to 1 μm, How much contraction stress develops between the two fibers?



- The attractive force is called Campbell force.

The water between fibers is pulled by its surface tension horizontally. Consider one side of the four sides (Calculated pressure is the same however many sides are taken into account.)

•Pulling forceF＝2L(μm)xγ (mN/m)
•Pressure P＝F/area＝ 2Lγ/(d (μm)× L (μm)) ＝ 2γ/d(mN/(mxμm))
(Coefficient 2 means that the water has two contact lines with the upper and lower fibers respectively.)
•P is also a contraction stress. At d= 1 μm, P=2×72.8/1 ＝
145.6(10^{-3}N／(10^{-6})m^2)＝145.6×10^3(N/ m^2)＝145.6 kPa

This is equal to 1.5kgf per 1cm^2. If these two fibers approach to d=1nm, it becomes1.5ton per 1cm^2.

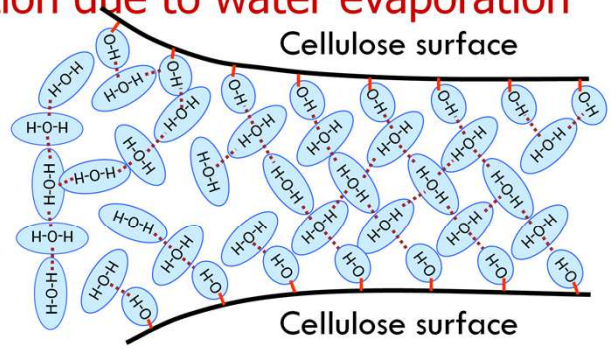
挟まれた水は表面張力により水平に引っ張られている。
4辺のうち1辺を考える(4辺全部考えても圧力は同じ)と、

•引張力F＝2L(⌈μ)×γ (mN/m)
•圧力P＝F/面積＝ 2Lγ／(d (⌈μ)× L (⌈μ)) ＝ 2γ/d(mN/(m･⌈μ))
•Pは収縮圧力でもある。d= 1 ⌈μとすると、Π=2×72.8 ／ 1 ＝
145.6(10^-3N／(10^-6)m^2)＝145.6×10^3(N/ m^2)＝145.6 kPa

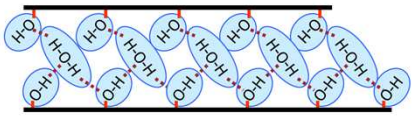
これは1cm^2で1.5kgfである。もしd=1nmまで接近したら1cm^2で1.5tである。

Inter-fiber bond

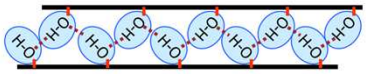
- Interfiber approach and hydrogen bond formation due to water evaporation



Loose hydrogen bond mediated by water



Firm hydrogen bond with a water monolayer



Direct hydrogen bond

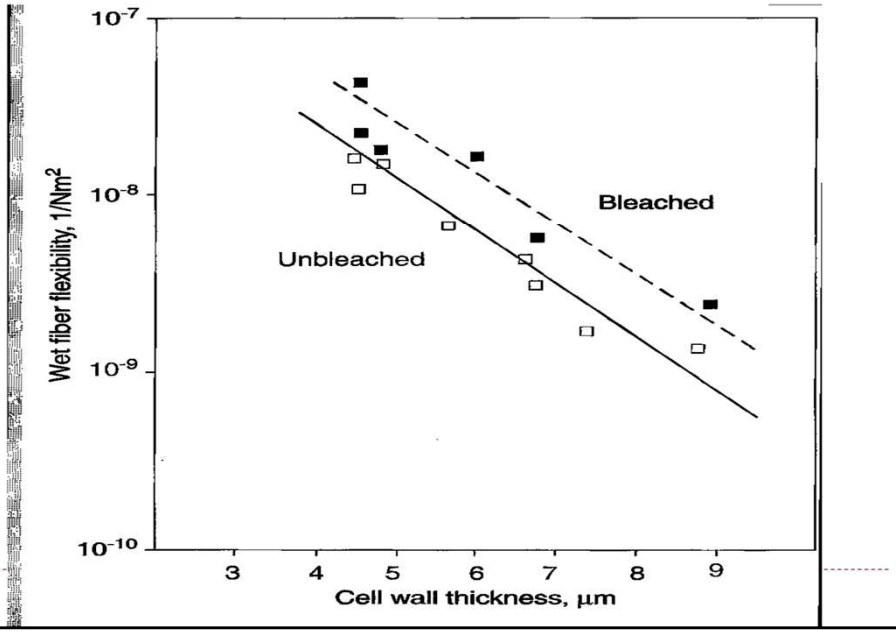
Inter-fiber bond

- Evidence of hydrogen bond
  - When paper mass was measured after allowing to stand in deuterium water (D_2O) vapor until saturation, 0.5 to 2.0 % of hydrogen of all the hydroxyl groups was not replaced with deuterium. This ratio corresponds to the percentage of hydrogen bonded hydroxyl groups.
  - Energy required for tensile breakage was calculated. 19 kJ/mol (equivalent to hydrogen bond energy)
  - Strength decreased with acetylation of carboxyl groups $\mathbf{Cell\text{-}OH \rightarrow Cell\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3}$

4.5kcal/mol紙の破壊強度から計算したものと思われる。
Casey → Corte, Schaschek and Broens, Tappi 40(6), 441(1957)

Inter-fiber bond

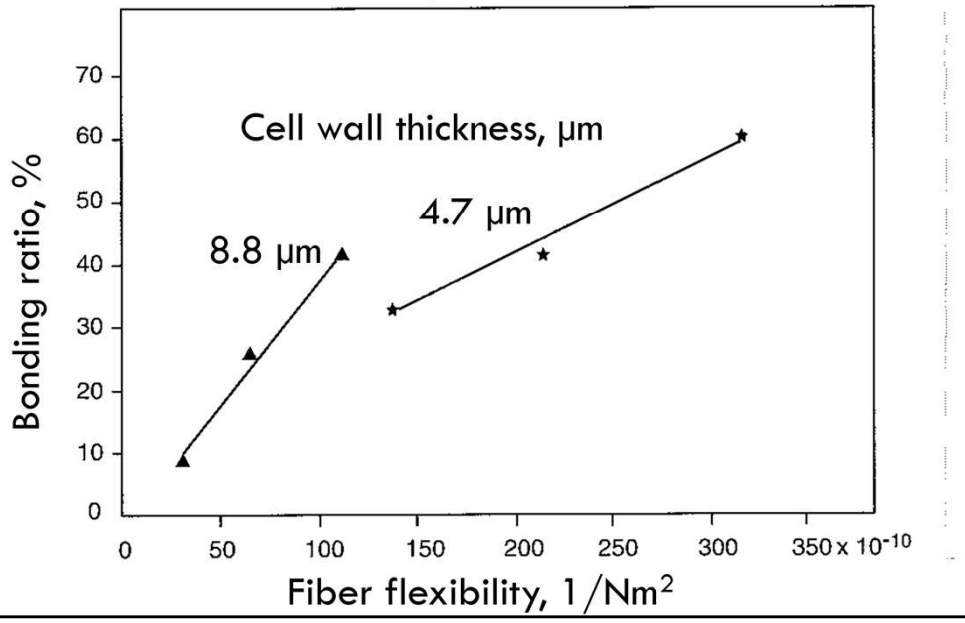
- Effect of **cell wall thickness** on **wet fiber flexibility**



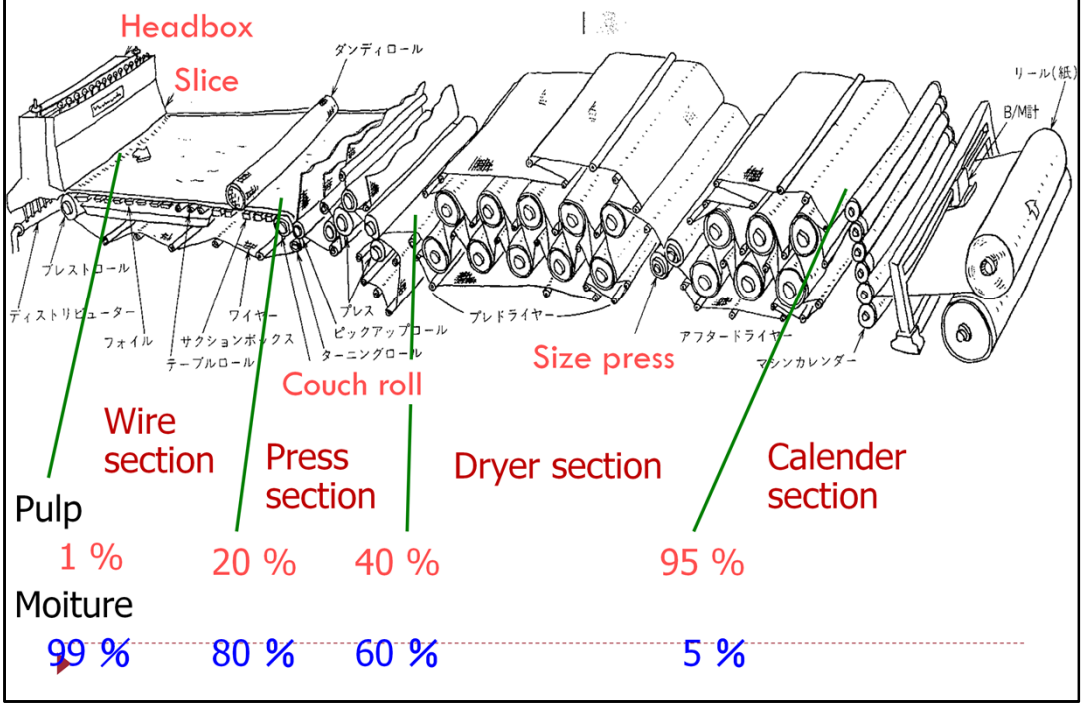
繊維間結合の生成は水の表面張力による圧力と繊維の柔軟性に依存することの説明

Inter-fiber bond

- Effect of fiber flexibility on Relative Bonded Area



Forming (Wire section) – Moisture content



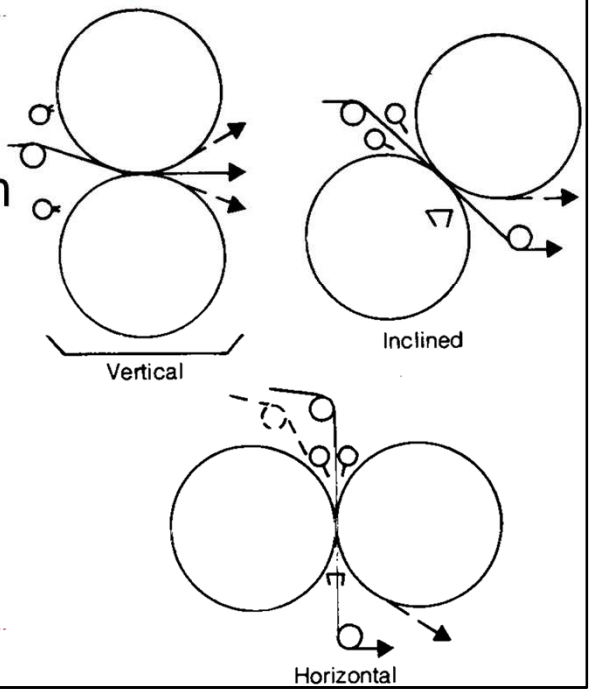
Post-forming – Size press

- Sizing
  - Internal sizing- addition to pulp slurry
  - External (surface) sizing – application to surface
- What is surface sizing (size press)?
  - The treatment for providing water-resistant property to paper by application of starch solution etc.
  - Other than starch, carboxymethyl cellulose, polyvinyl alcohol, polyacrylamide etc. are applied. Strong water-repellency is not required.
- Advantages over internal sizing
  - 100% retained. No deposit on walls of former or froth

サイズプレスの説明を簡潔にわかりやすく！

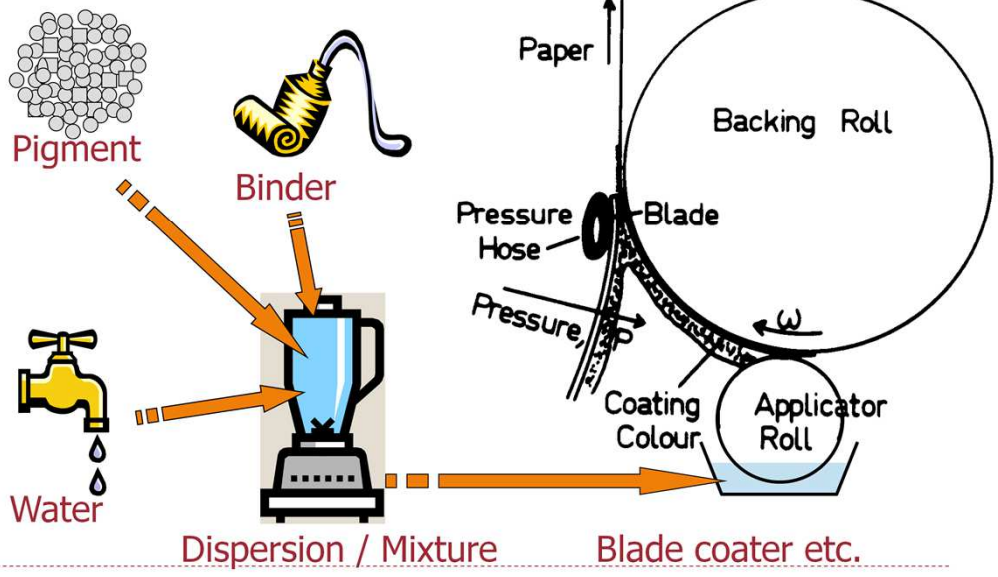
Post-forming – Size press

- Purpose and effect
  - Picking prevention in offset printing
  - Ink jet printability to prevent bleeding

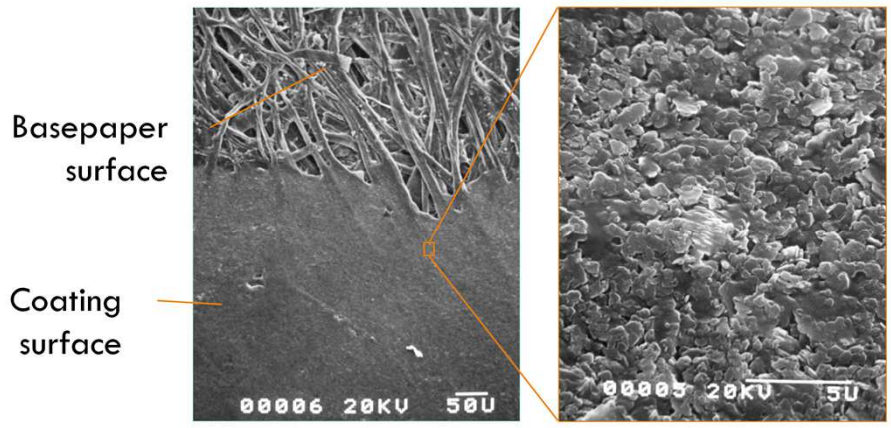


“デンプン塗工面のオフセット印刷時の湿し水による粘着性（ネッパリ）を改善する。”
何が言いたい？

Pigment coating



Coated paper surface -
Scanning Electron Micrograph



- To increase smoothness, brightness, opacity, and gloss, and control liquid penetration

Drying and processing – movie

Paper properties –
Fundamental and applied properties

- Conditioning
- Structure
- Surface chemistry
- Liquid absorption
- Mechanical properties
- Optical properties

Conditioning and test atmosphere

- 23 ºC 50% RH (Relative Humidity)
  - Paper properties depend on humidity, but less on temperature
  - although temperature difference by more than 10 ºC changes ex. tensile strength significantly.

Conditioning and test atmosphere

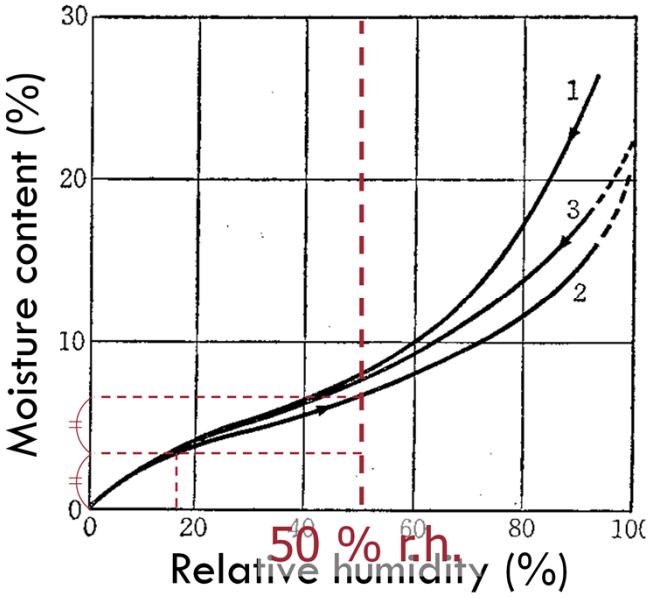
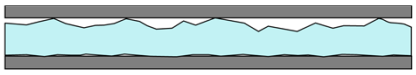


図 98 亜硫酸パルプシートの水分収着等温線
(Seborg, C. O. et al., 1938)

- Hysteresis
- Dry paper to half the equilibrium moisture content and back to 50% RH for testing
- Moisture content is affected by crystallinity

Paper structure – basic properties

- Grammage (g/m^2)
  - Mass (g) per square meter at 23 ºC and 50%RH
  - ⇔ **Grammage (oven-dry basis)** is based on the constant mass attained when kept at 105 ºC
- Thickness (mm)



  - **Single sheet thickness**, distance between two parallel planes holding a sheet at 100 kPa
  - **Bulking thickness**, thickness per sheet, calculated from that of 10 superimposed sheets
  - Includes surface roughness (dents)

JISでも坪量＝**Grammage** (g/m^2)になった。
single sheet thickness
bulking thickness

Paper structure – basic properties

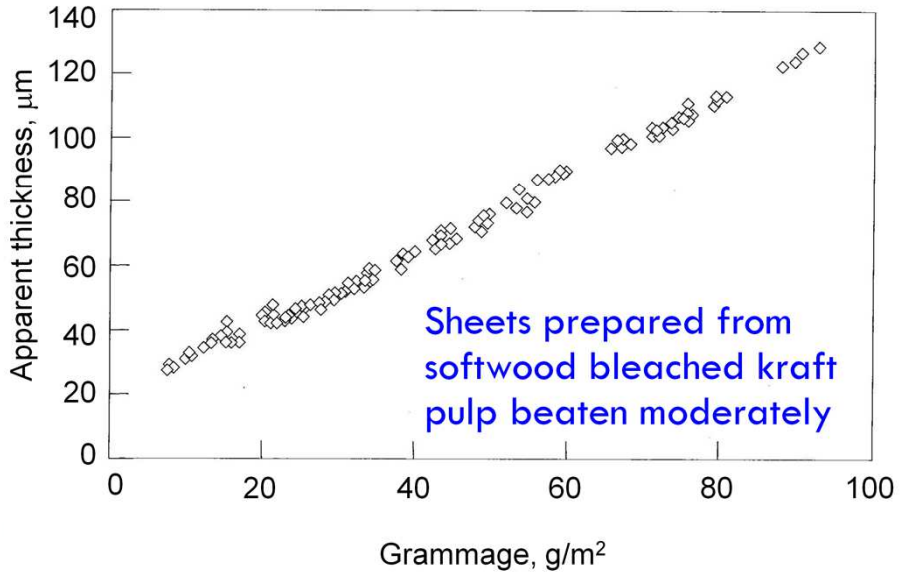
Q. Which is higher, single sheet thickness or bulking thickness?

- Density
  - Mass per unit volume in g/cm^3 calculated from grammage divided by thickness

JISでも坪量＝**Grammage** (g/m^2)になった。
single sheet thickness
bulking thickness

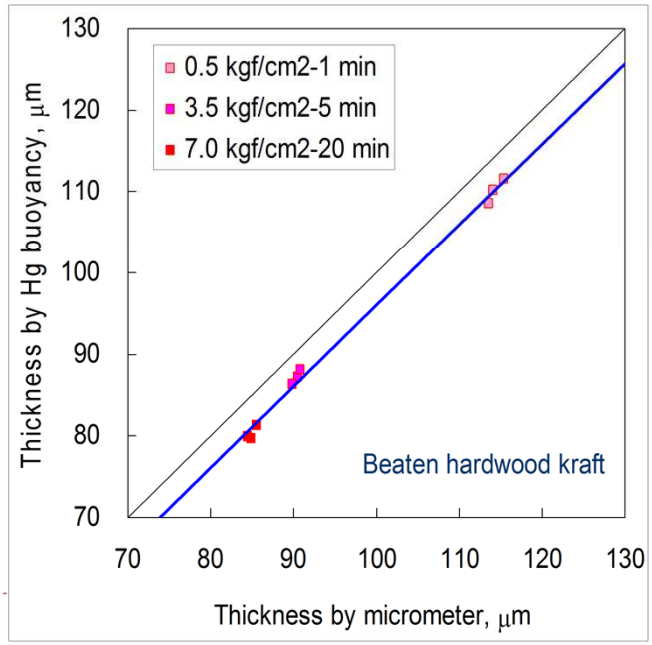
Paper structure – basic properties

- Density (grammage/thickness) affected by grammage!?

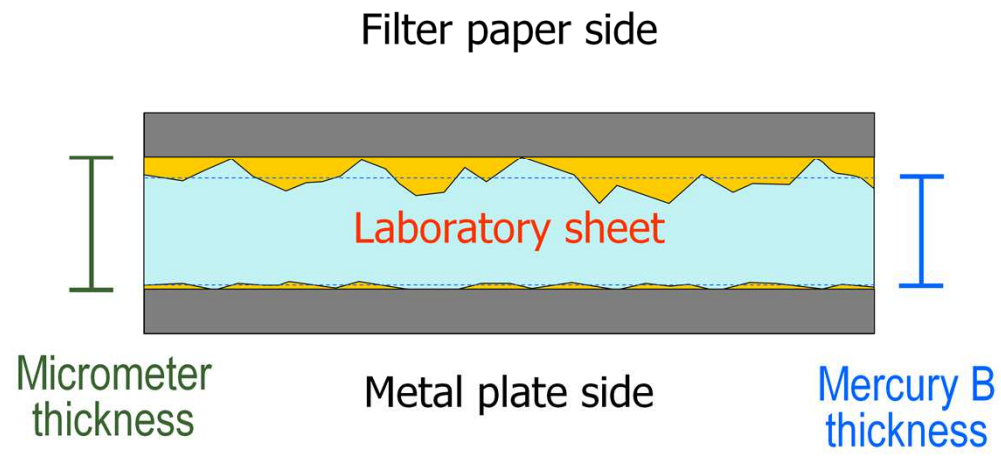


Paper structure – thickness measurement

- Micrometer
- Mercury buoyancy method

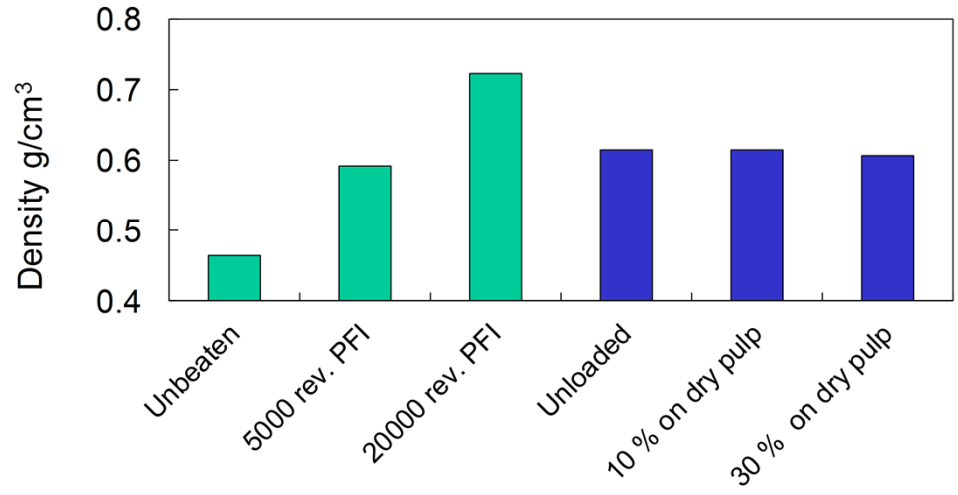


Paper structure – Why is the thickness different between the two methods?



Paper structure – Factors affecting density

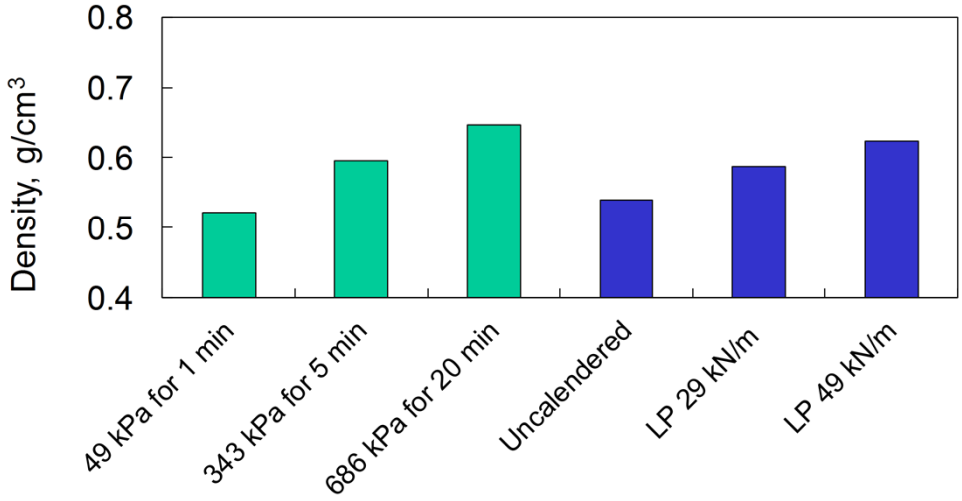
- Beating and filler loading



Beating rev. (PFI mill) Calcium carbonate addition

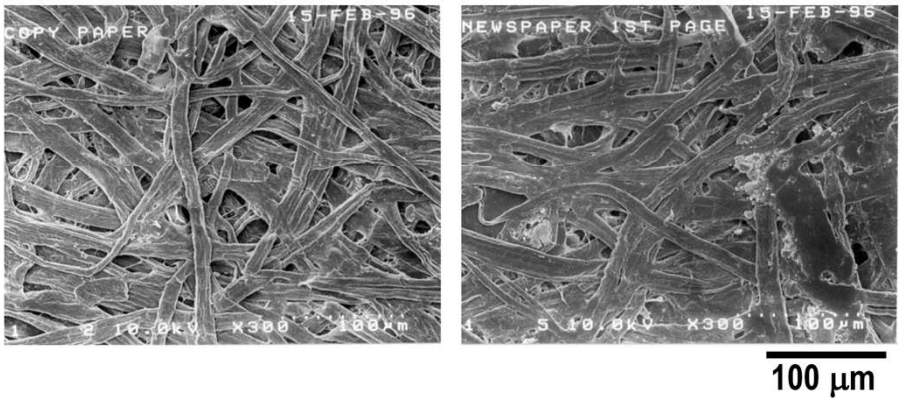
Paper structure – Factors affecting density

- Wet press and calendering



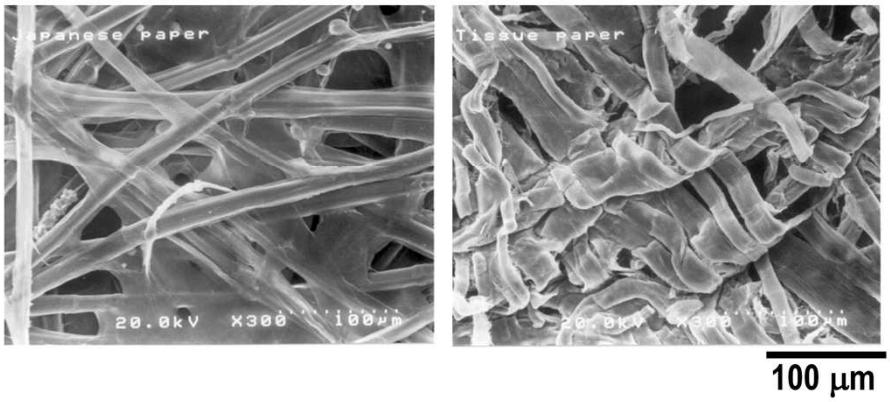
Wet press Calendering- linear pressure

Paper structure-Scanning electron microscope(1)



Copy paper Newspaper

Paper structure-Scanning electron microscope(2)



Japanese paper Tissue paper

Paper structure – Smoothness

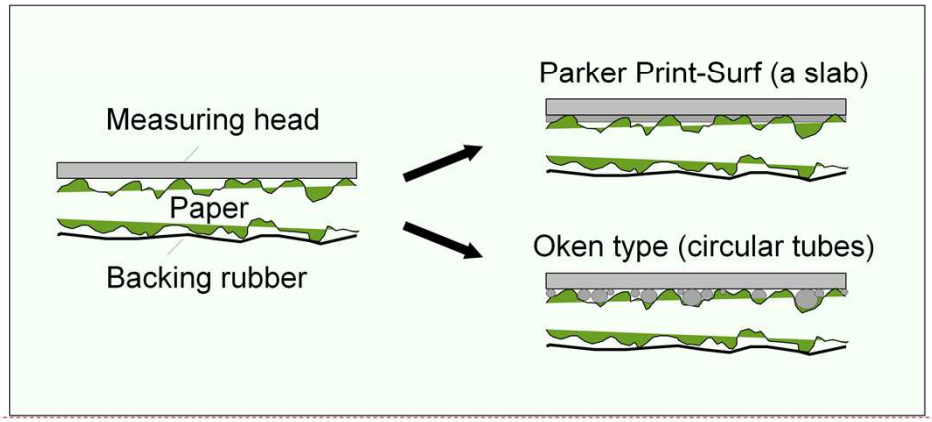
- Air leak method
  - Air flow rate through a gap between paper surface and smooth metal plate
- Surface profile (Microscopy)
  - Measurement method
    - Stylus profilometry
    - Scanning Probe Microscope
    - Confocal Optical Microscope
    - Interferometric Optical Microscope
    - Multi-detector Scanning Electron Microscope
  - Expression of surface roughness

Paper structure – Smoothness

- Air leak method
  - Air flow rate through a gap between paper surface and smooth metal plate
- Surface profile (Microscopy)
  - Surface shape measured using profilometry such as stylus profilometry, confocal optical microscope.
  - Several ways of expressing surface roughness

Paper structure – Smoothness

- Air leak method
  - Print surf roughness (μm)
  - Bekk smoothness, Oken smoothness (s)

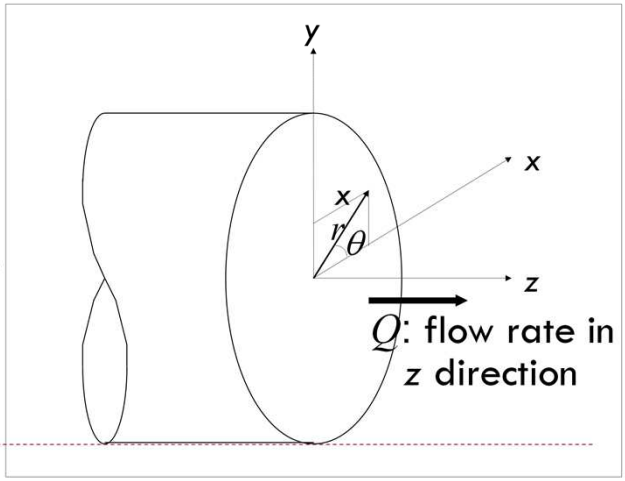


Paper structure – Smoothness

- Theory of air leak method
  - Hagen-Poiseuille flow

$$Q=\frac{\pi\Delta P}{8\mu}\frac{r^4}{l}$$

Q: volumetric flow rate
ΔP: pressure difference
μ: dynamic viscosity
r: radius of tube
l: length of tube



Bekk smoothness
50 kPa
10 mL
Viscosity of air; $1.8*10^{-5}$ Pa*s

Q=3.1416*50/(8*1.8*10^{-5}) *r^4/*L*
=

Paper structure – Smoothness

- Surface profile can be measured in 2D or 3D.
- Stylus, light beam, electron beam, or probe
  - Centerline average roughness (arithmetic average)

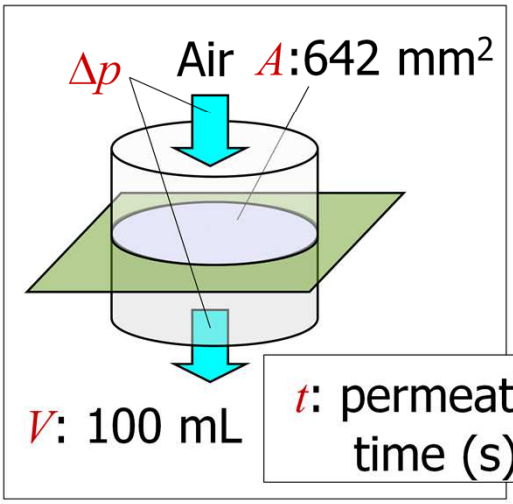
$$R_a = \frac{1}{\ell}\int_0^{\ell} |y| dy$$

  - Root mean squared roughness

$$RMS = \sqrt{\frac{1}{\ell}\int_0^{\ell} y^2 dy}$$

Paper structure – Air permeance

- Method
  - Gurley tester



Air permeance

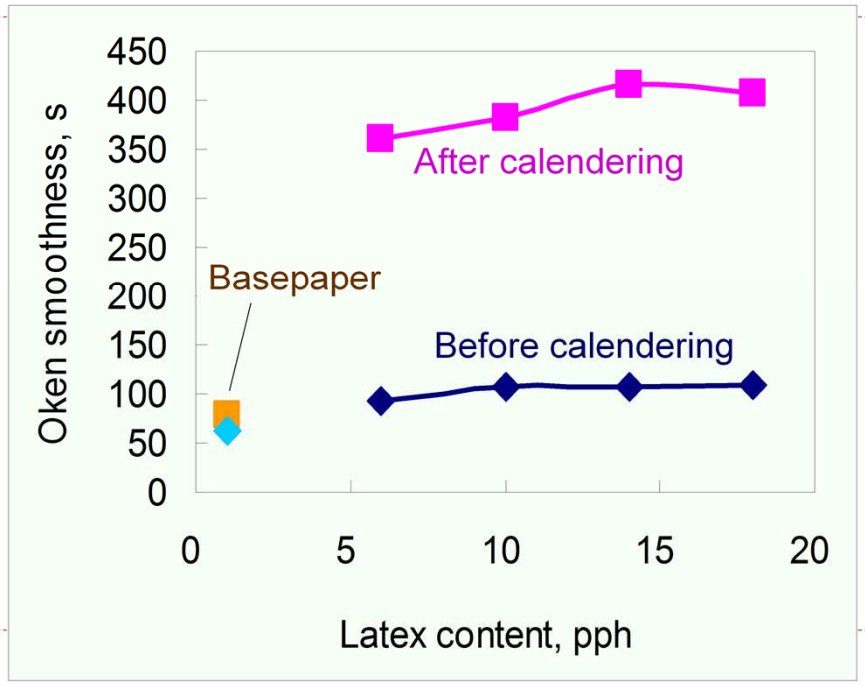
P [mm/(Pa·s)]

$$P = \frac{V}{1000 \times A \, \Delta p \, t}$$

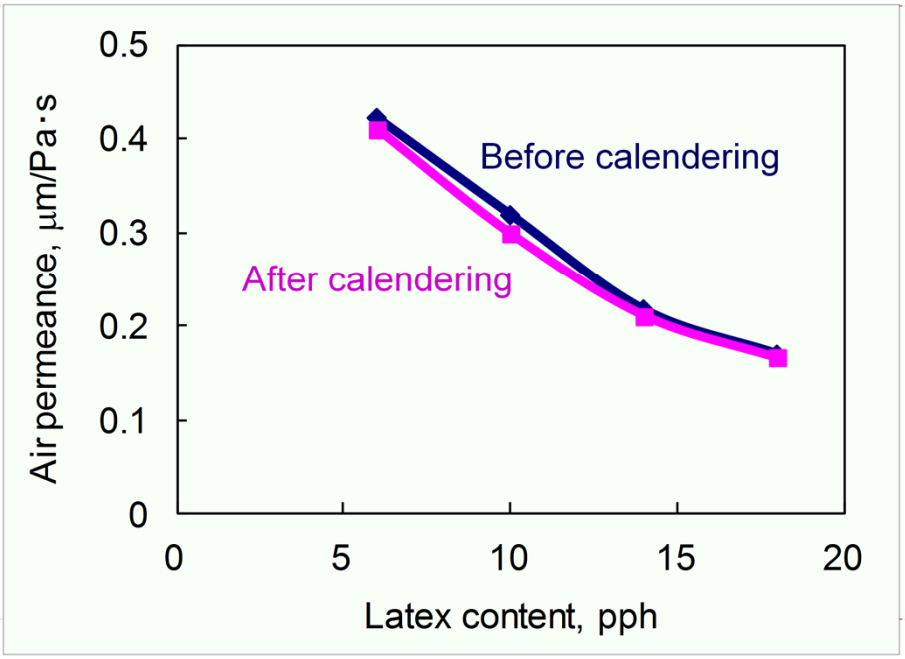
Universal air permeance

t: permeation time (s) = Air resistance (Gurley)

Paper structure –Smoothness of coated paper



Paper structure –Air permeance of coated paper

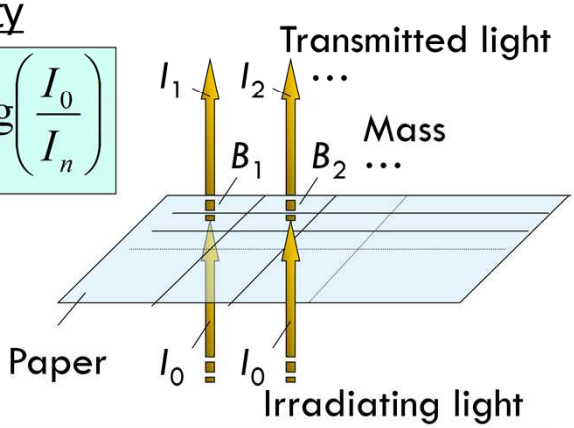


Paper structure - Formation

- Formation
  - [Definition 1] Unevenness sensed visually when white light is transmitted through paper – STD or CV of optical density

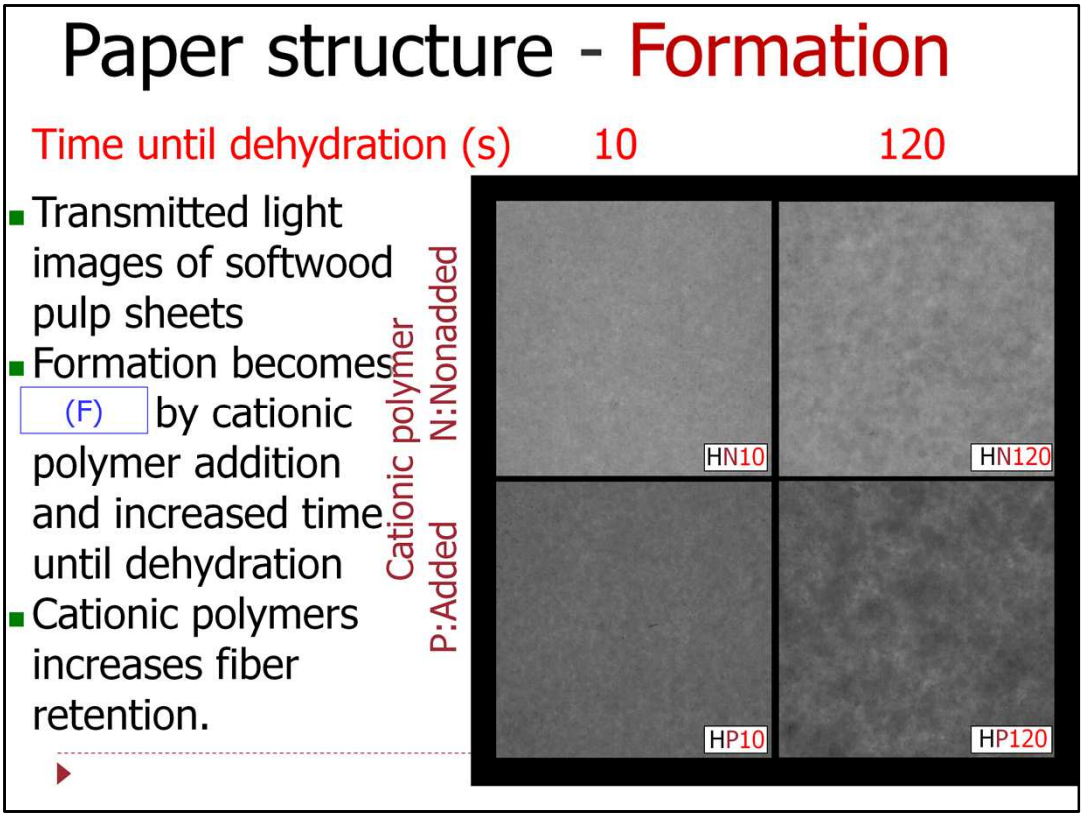
$$\log\left(\frac{I_0}{I_n}\right)$$

  - [Definition 2] Distribution of local mass B_n – STD or CV of local mass



- STD=Standard deviation, CV= coefficient of variation

質量分布は、カレンダリングなどの処理を行ってもほとんど変化がなく扱いやすい量である。透過光は繊維間の結合量や接触距離によって散乱の程度が変化するので、カレンダリングや吸水･乾燥により変化するので扱いにくいが、視覚的に一致する。



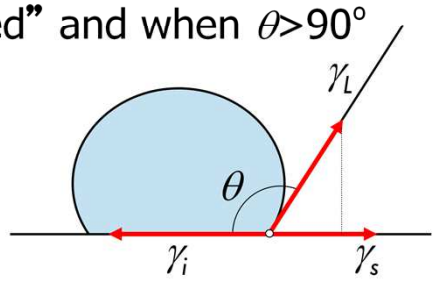
Q. In (F) better or worse?
A. worse

Interaction- between paper and water (liquid)

- Wetting
- Contact angle
- Surface energy
- Sizing degree
- Liquid penetration
- Swelling

Surface chemistry - Contact angle

- Contact angle (θ)
  - The angle made by the solid and liquid surfaces when a liquid droplet is placed on a solid surface.
  - When $0° < \theta < 90°$, "wetted" and when $\theta > 90°$ "unwetted".
- Young equation
  - When the contact angle is constant, horizontal components of forces are balanced.



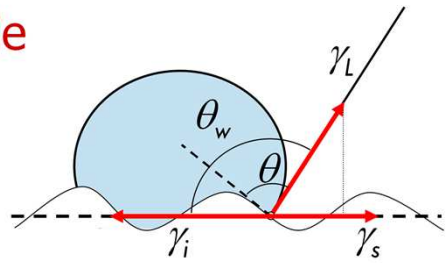
$$\gamma_i - \gamma_s + \gamma_L \cos\theta = 0$$

$\gamma_S > \gamma_i + \gamma_L$であると、このような接触角は存在せず、液体は固体表面を自然に拡がって完全に濡らしてしまう。

Surface chemistry - Contact angle

- Contact angle on a rough solid surface
  - Supposed that the area including microscopic structure is ***r*** times larger than the apparent one,
  - Wenzel's contact angle

$$\cos\theta_w = r\cos\theta$$



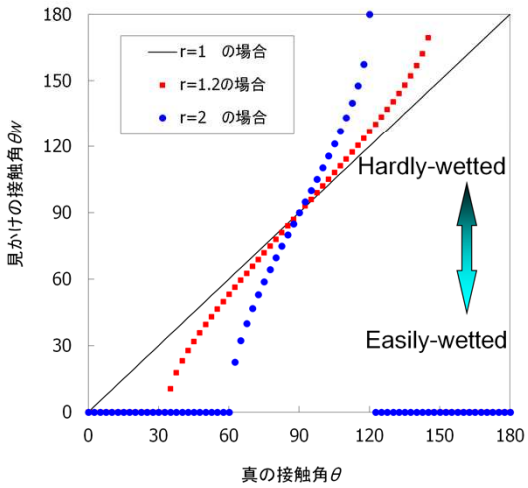
θ＝60° とし、r＝1.414（√2）とするとθwは何度か？
cosθw＝√2×cos60° ＝√2×1/2＝1/√2
よって、θw＝45°
同一の条件で、θ＝120° の場合はどうか？
cosθw＝√2×cos120° ＝√2×（-1/2）＝-（1/√2）
よって、θw＝135°

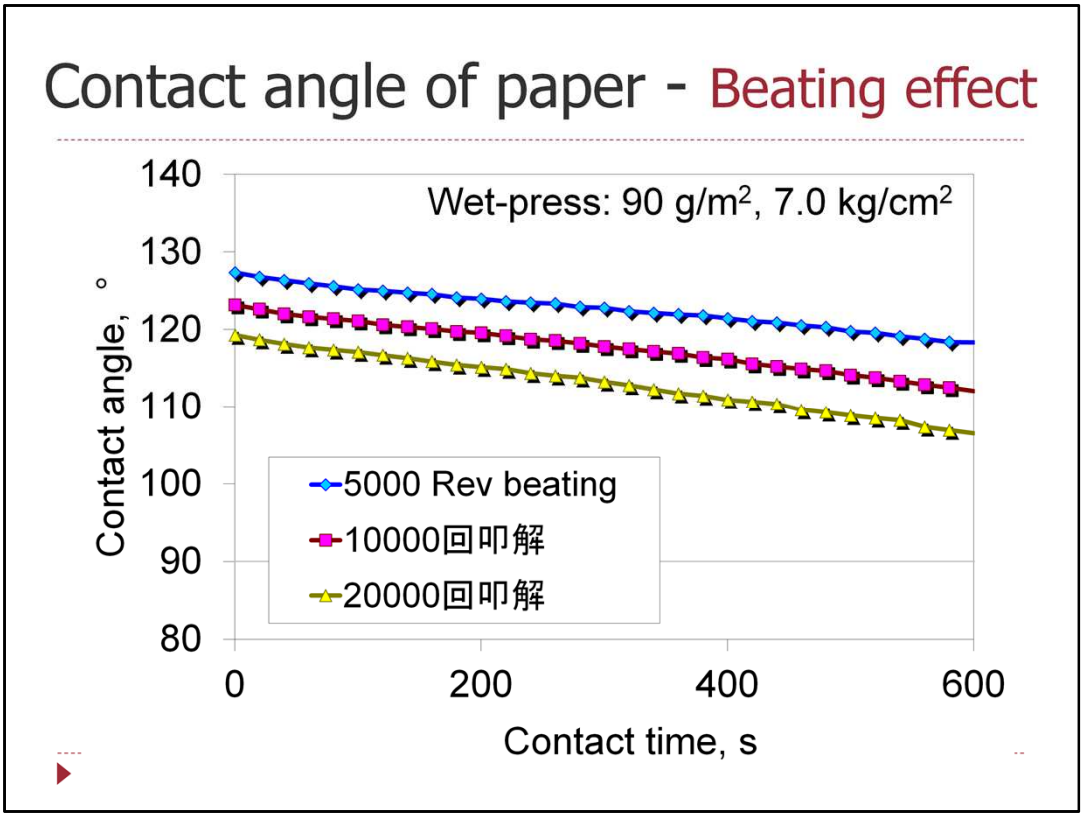
Surface chemistry - Contact angle

Wenzel's equation

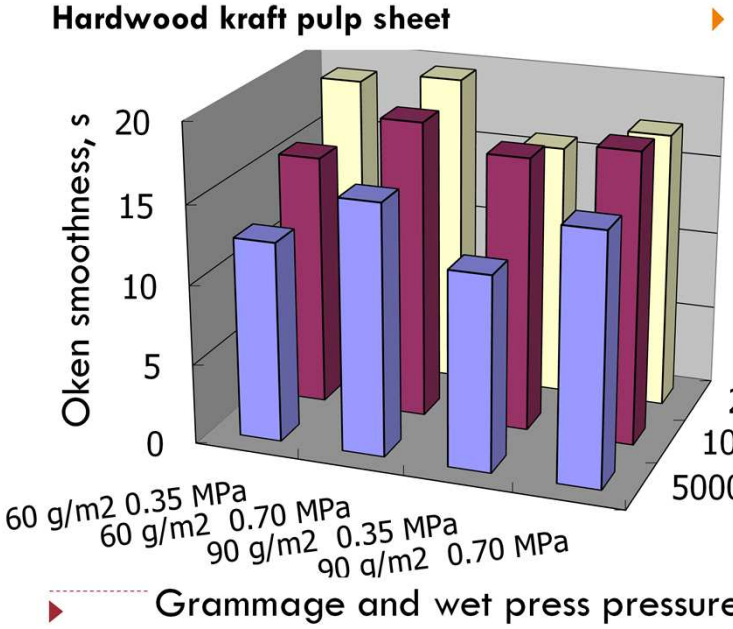
- On a rough surface, when $\theta_w < \theta$ at $\theta < 90^\circ$, easily-wetted surfaces become more easily-wetted. But, when $\theta_w > \theta$ at $\theta > 90^\circ$, hardly-wetted surfaces become more hardly-wetted.

$$\cos\theta_w = r\cos\theta$$




Contact angle of paper - Beating effect
Wet-press: 90 g/m2, 7.0 kg/cm2
Contact angle, °
140
130
120
110
100
90
80
0
200
400
600
Contact time, s
5000 Rev beating
10000回叩解
20000回叩解

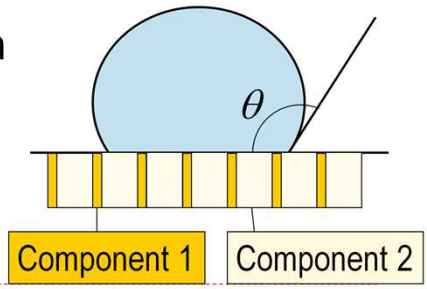
Beating and smoothness



- Surfaces smoothed by beating became easily-wetted.

Surface chemistry - Contact angle

- On composite surfaces
  - The effective contact angle θ_C is dependent on the areal ratio of each component.
- Cassie's law
  - is stated as $\cos\theta_C = Q_1 \cos\theta_1 + Q_2 \cos\theta_2$, where θ_1 is the contact angle for component 1 with areal fraction Q_1 and θ_2 is the contact angle for component 2 with areal fraction Q_2 ($Q_1 + Q_2 = 1$).



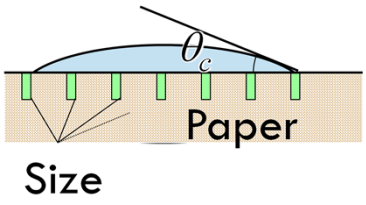
Surface chemistry - Contact angle

Q. What is the contact angle θ_c of sized paper?

- Sizing agent need not cover the whole surface of fibers for repelling water. If a sizing agent covers 5% of the whole surface, what is the contact angle θ?
- Assume that θ is 0° for unsized fibers and 120° for the covering size.
- $\cos\theta_c =$ (G) $\times \cos 0° +$ (H) $\times \cos 120°$

  $\cos\theta_c =$ (I) $= 0.925$

  $\theta_c =$ (J)



Surface chemistry - Contact angle

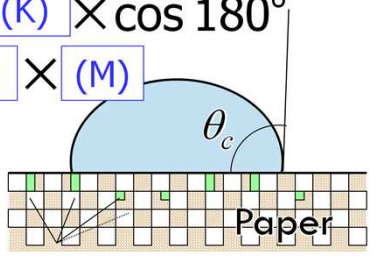
Q2. What is the contact angle θ_c of sized paper?

- Half the volume of paper is air. If 50% of paper surface is air, what is the θ_c?
- Assume that θ_c of a true surface of sized paper is 22.3° and θ of air is 180°.
- $\cos\theta_c =$ (K) $\times \cos 22.3° +$ (K) $\times \cos 180°$

$\cos\theta_c =$ (K) $\times$ (L) $+$ (K) $\times$ (M)

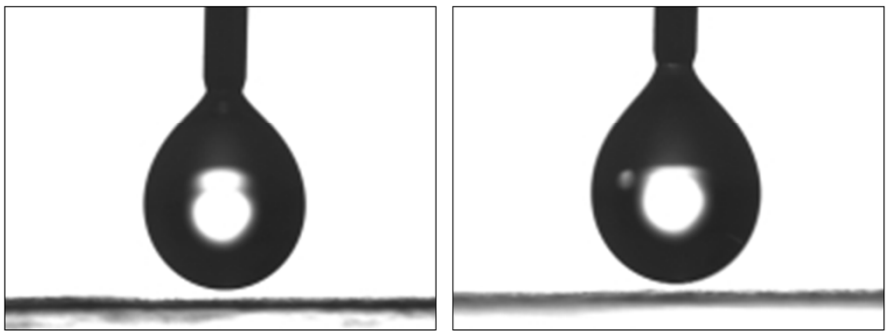
$=$ (N)

$\theta_c =$ (O)



Surface chemistry - Contact angle

- **Comparison in Water absorption**



Parchment **Wood-containing paper**

- "wood-containing" means "made from mechanical pulp"

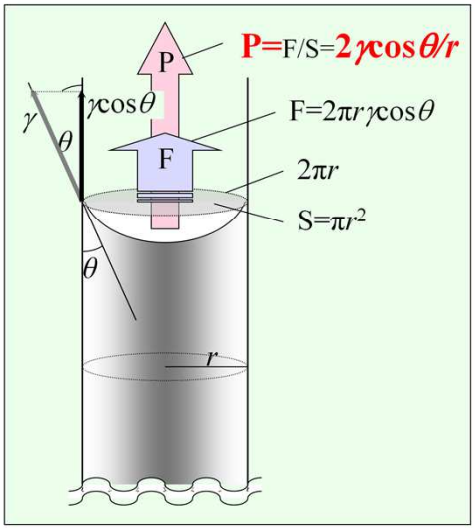
Liquid absorption theory - Capillary model

- Force developing around a meniscus of a liquid in a capillary (pipe)
- Steady flow in a pipe

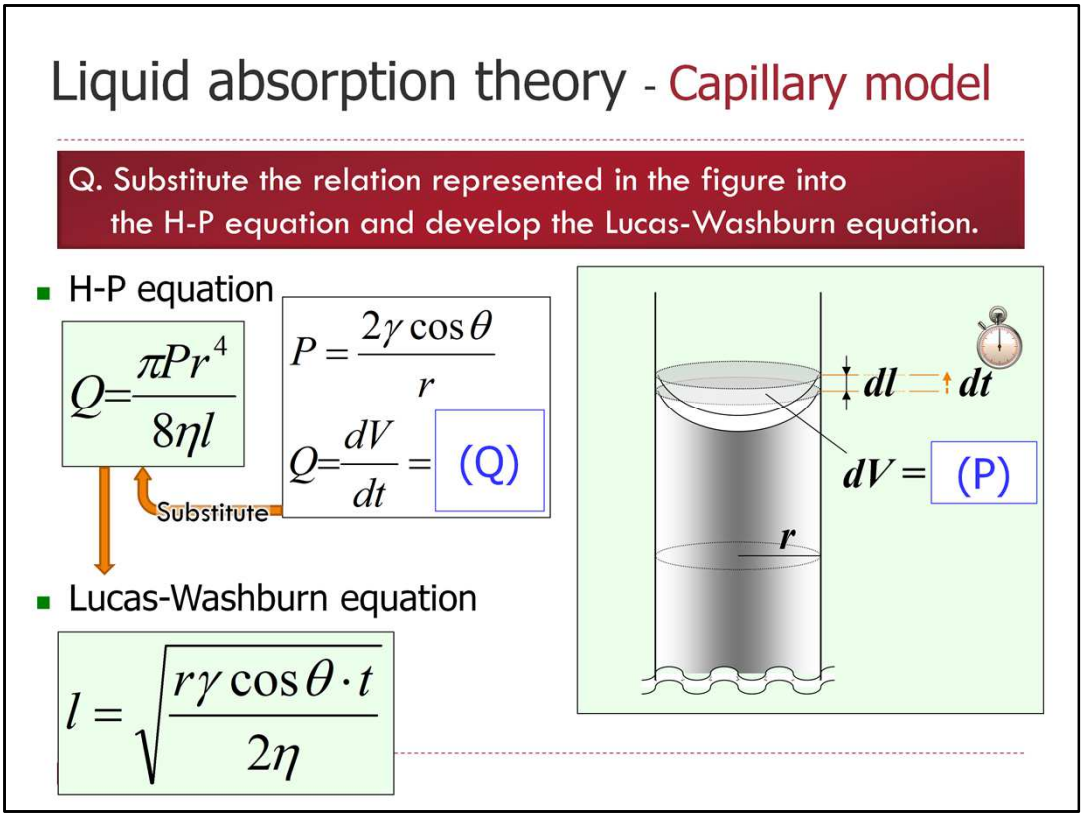
$$Q=\frac{\pi P r^4}{8\eta l}$$

l: **Capillary length**
r: **Capillary radius**
η: **Liquid viscosity**
Q: **Volumetric flow rate**

(Hagen-Poiseulle equation)



P=F/S=2*γcosθ/r*をHagen-Poiseulleの式に代入して、
Q=（π× **2*γcosθ/r*×*r*⁴）／**8η*l*=** π ***r*³ *γcosθ*／4η*l***
ここで、***Q=dV/dt*、*dV=*** π ***r*²** d*l*なので
d*l* =（***rγcosθ/4η*）dt**となる。辺々積分して、
l=sqrt（（***rγcosθ/2η***）/t）となり、Lucas-Washburnの式となる。

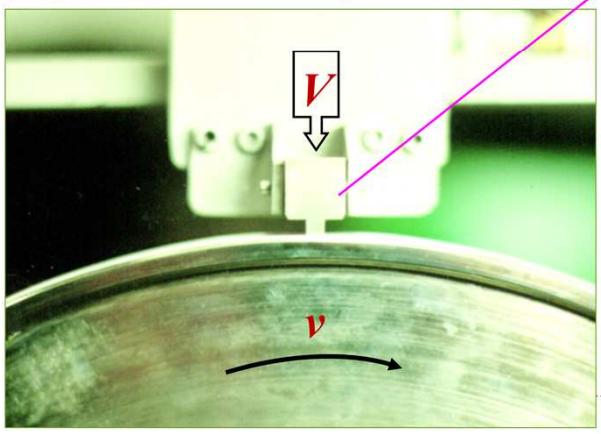


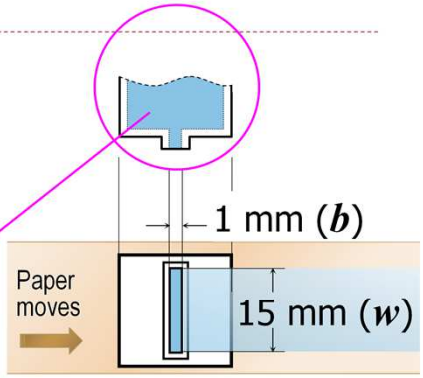
P=F/S=**2**γ***cos*** θ***/r***をHagen-Poiseulleの式に代入して、
Q=（π× **2**γ***cos*** θ***/r*×*r*⁴）／**8**η***l***=π ***r***³ γ***cos*** θ／**4**η***l***
ここで、***Q=dV/dt***、***dV***=π ***r***² d*l*なので
*l*d*l* =（***r***γ***cos*** θ***/4***η）**dt**となる。辺々積分して、
l=sqrt（（***r***γ***cos*** θ***/2***η）/t）となり、Lucas-Washburnの式となる。

Water absorption rate - How to measure

- Bristow's apparatus

A liquid supply head filled with a liquid of volume V scans paper at various speeds v.

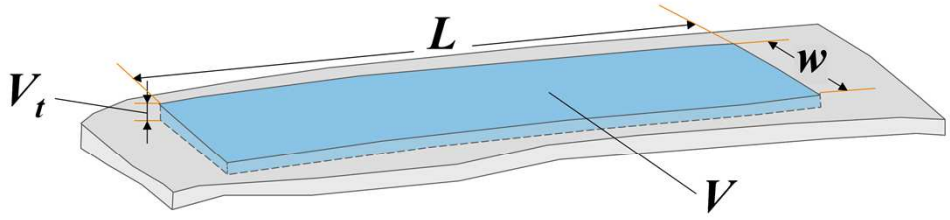




- **Contact time** $t = b / v$
  - Scan speed v
  - Slid width b
- **Transfer Vol** $V_t = V/(wL)$
  - Liquid volume V
  - Slit width w
  - Trace length L

Water absorption rate – How to measure

- Calculate transferred volume per unit area V_t



Contact time $t = b/v$

Scan speed	v
Slid width	b

Transfer Vol $V_t = V\ (wL)$

Liquid volume	V
Slit width	w
Trace length	L

Vt = depth of penetration

Water absorption rate – Water and oil

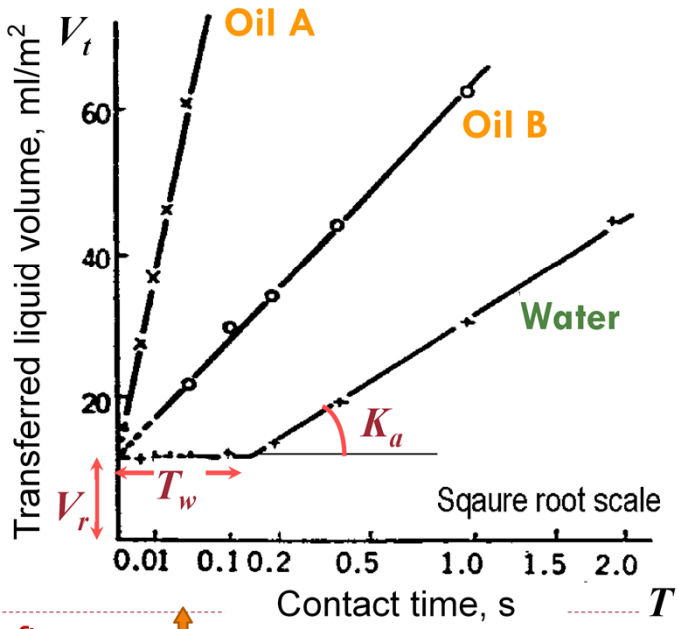
- For water,

$$V_t = V_r + K_a\sqrt{T - T_w}$$

V_r Roughness index
T Contact time
T_w Wetting delay
K_a Absorption coeff.

- For oil, $T_w = 0$. Then,

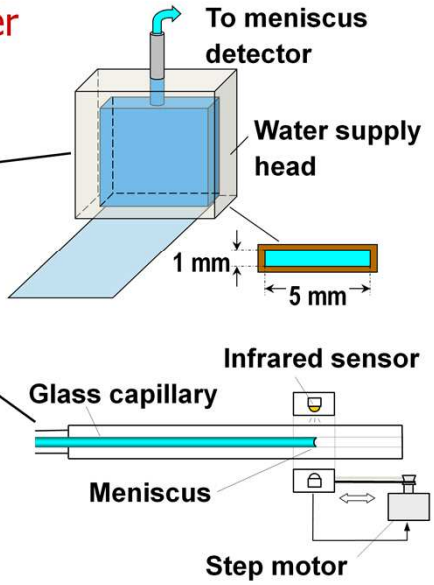
$$V_t = \boxed{\text{(Q)}}$$



▸ Bristow's plot of kraft paper

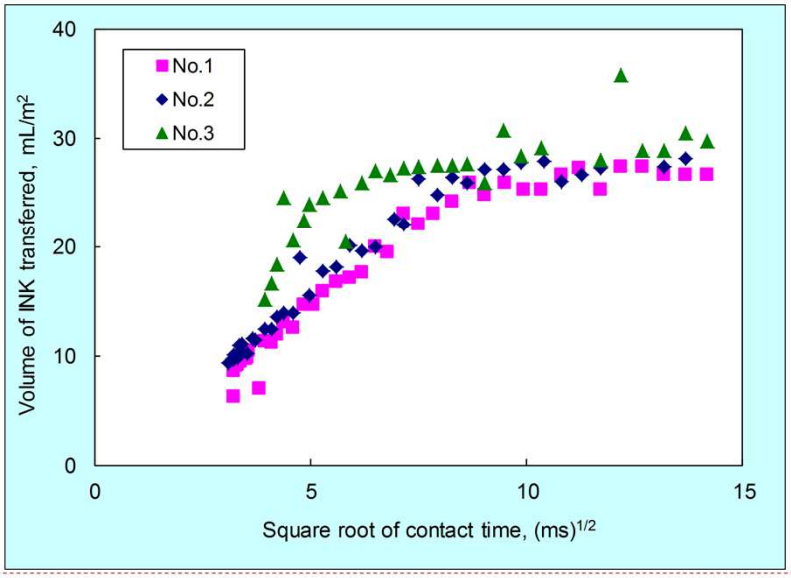
Water absorption rate - How to measure

- Automatic Scanning Absorptometer (Spiral-scan Bristow's apparatus)
  - Scanning speed changes stepwise during measurement

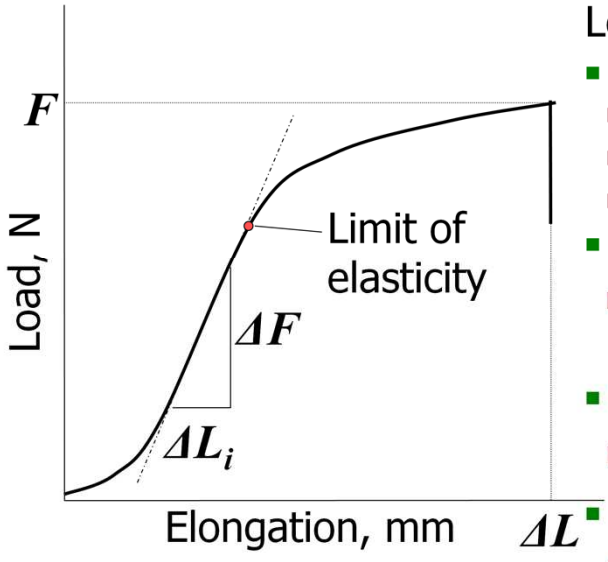


- ASA

Water absorption rate of ink jet paper -ASA



Mechanical properties –Tensile strength

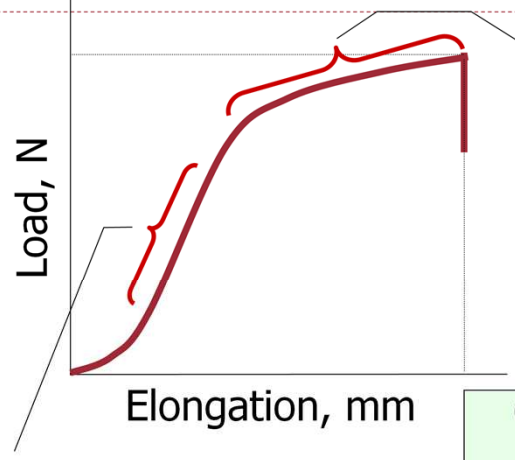


Load-elongation curve

- Method
  - 15 mm in width
  - 100 mm in span
  - 10 mm/min elong speed
- Tensile index I
  - $I = \frac{F}{wg}$
    (w: width g: grammage)
- Strain at break ε_T
  - $\varepsilon_T = \frac{\Delta L}{L}$
- Modulus of elasticity E^*
  - $E^* = \frac{\Delta F}{\Delta L i w T}$ (T: thickness)

F=50N
ΔL＝5mm
弾性挙動10～34N、伸びは1～2mm
で計算させる

Mechanical properties –Tensile strength

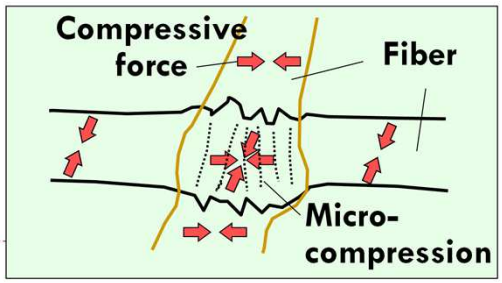


Plastic region

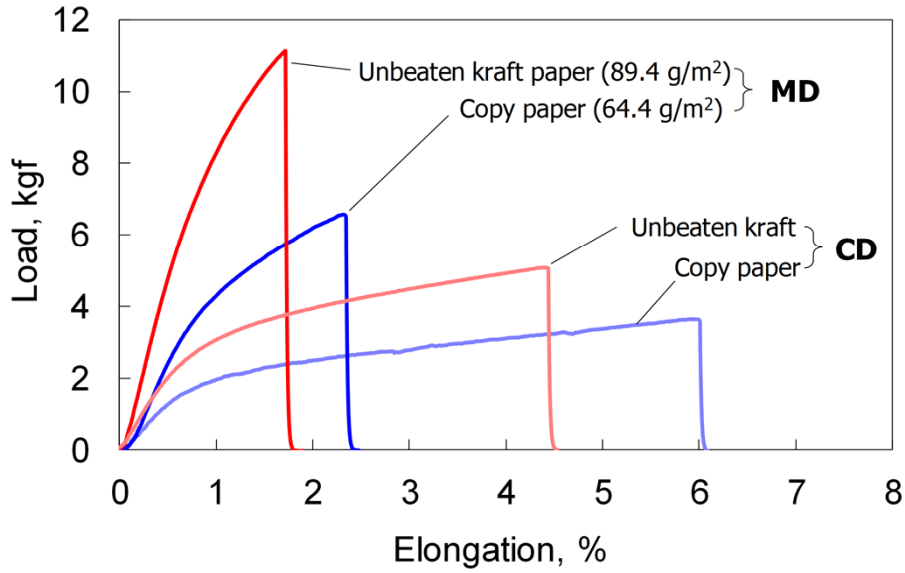
- Extension of curl
- Extension of micro-compression
- Breakage of inter-fiber bonds
- Breakage of fibers

Elastic region

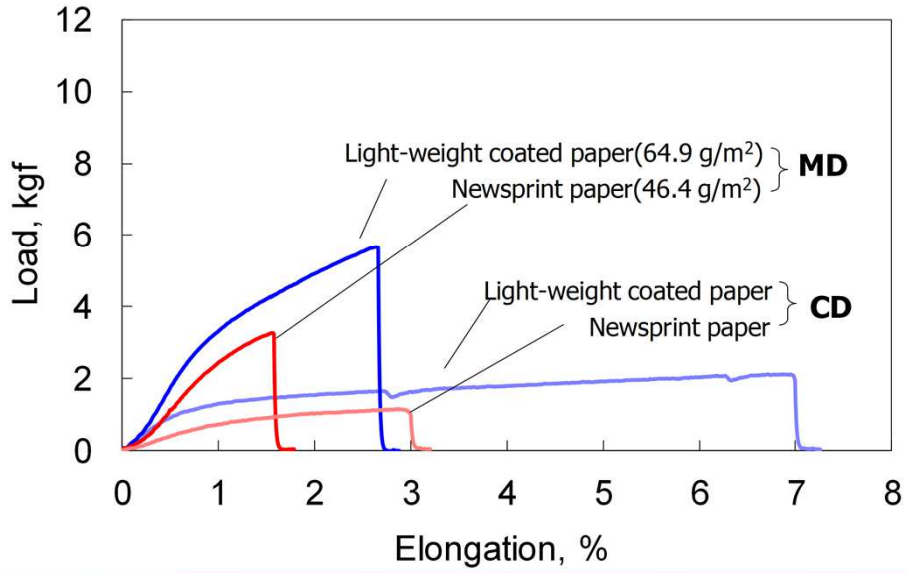
- Elastic elongation of fibers
- Elastic elongation of fiber network



Anisotropy–Tensile strength



Anisotropy–Tensile strength



Q. Why does light-weight coated paper elongate greatly?

Mechanical properties – Stiffness

- (Bending) stiffness ***S*** represents the degree to which paper resists bending

S=Mr

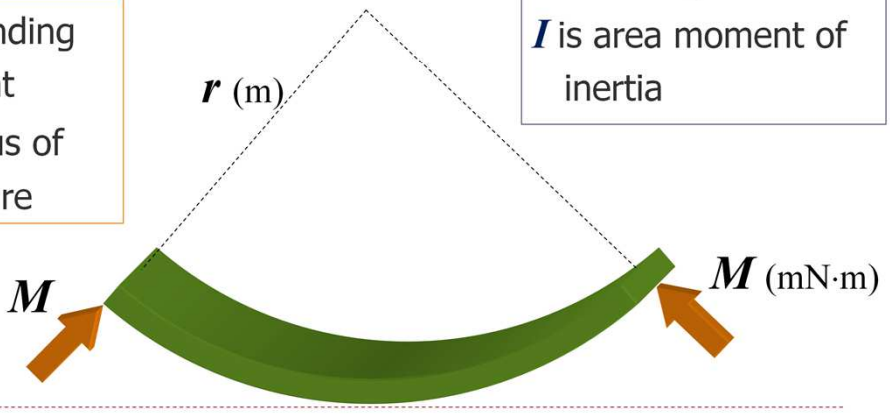
M is bending moment

r is radius of curvature

S=EI

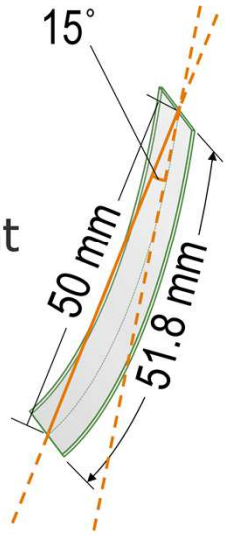
E is Young's modulus

I is area moment of inertia



Mechanical properties – Stiffness

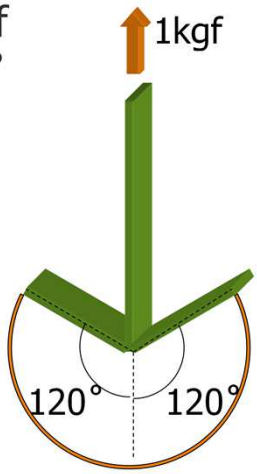
- **Taber Stiffness**
  - Bending moment when a test piece 38mm wide is bent to 15° and load length 50 mm
  - The unit is mN·m

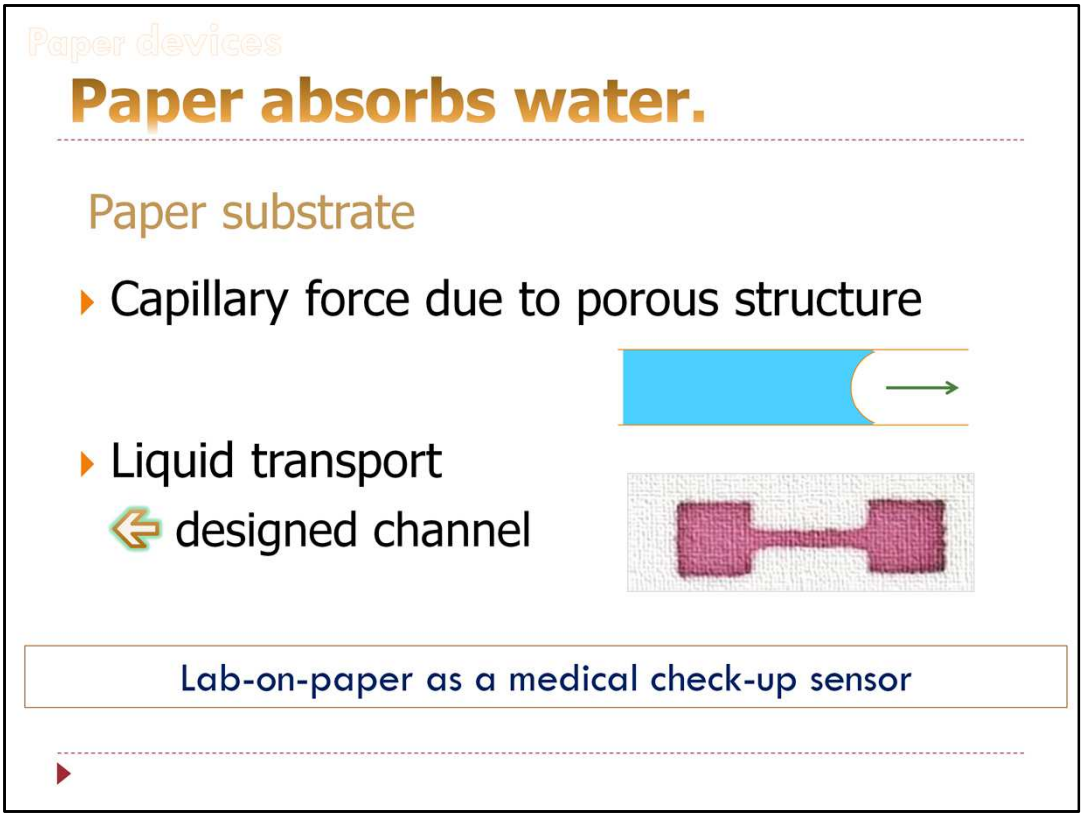



Taber tester

Mechanical properties – Folding endurance

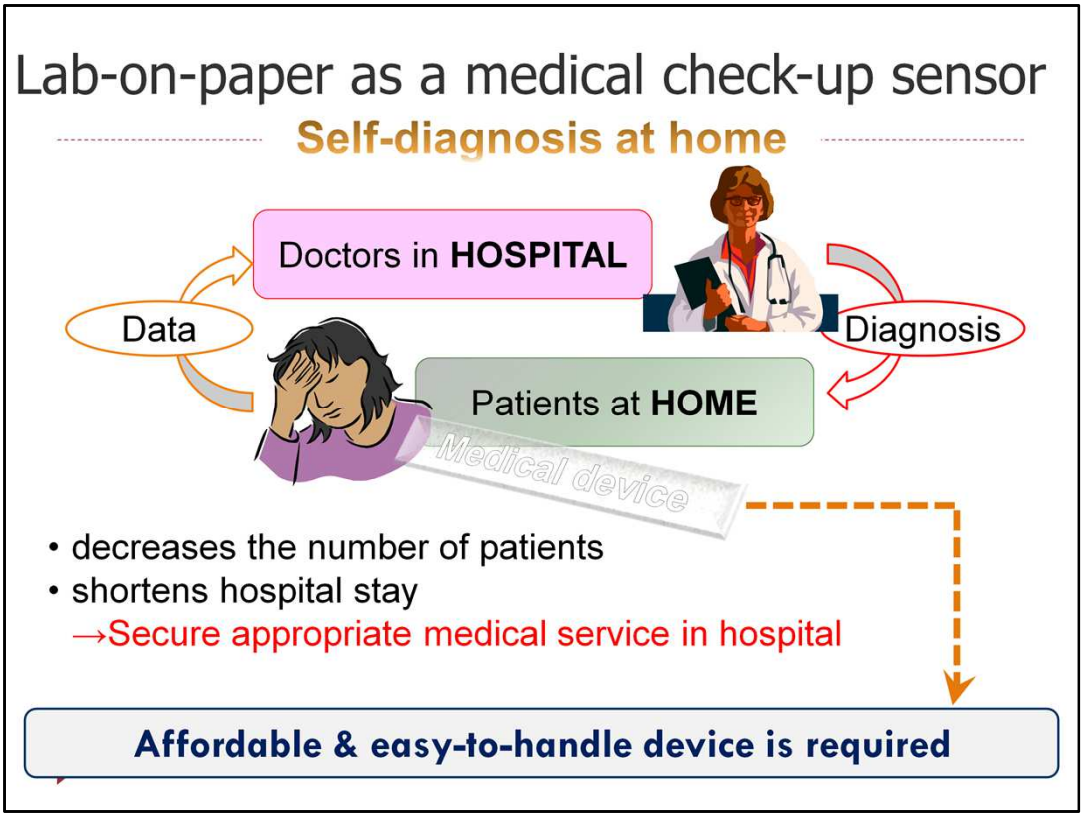
- Folding endurance
  - logarithm number of double folds at 120° on both sides that are required to make a test piece break
  - Longer fibers tend to show higher values.



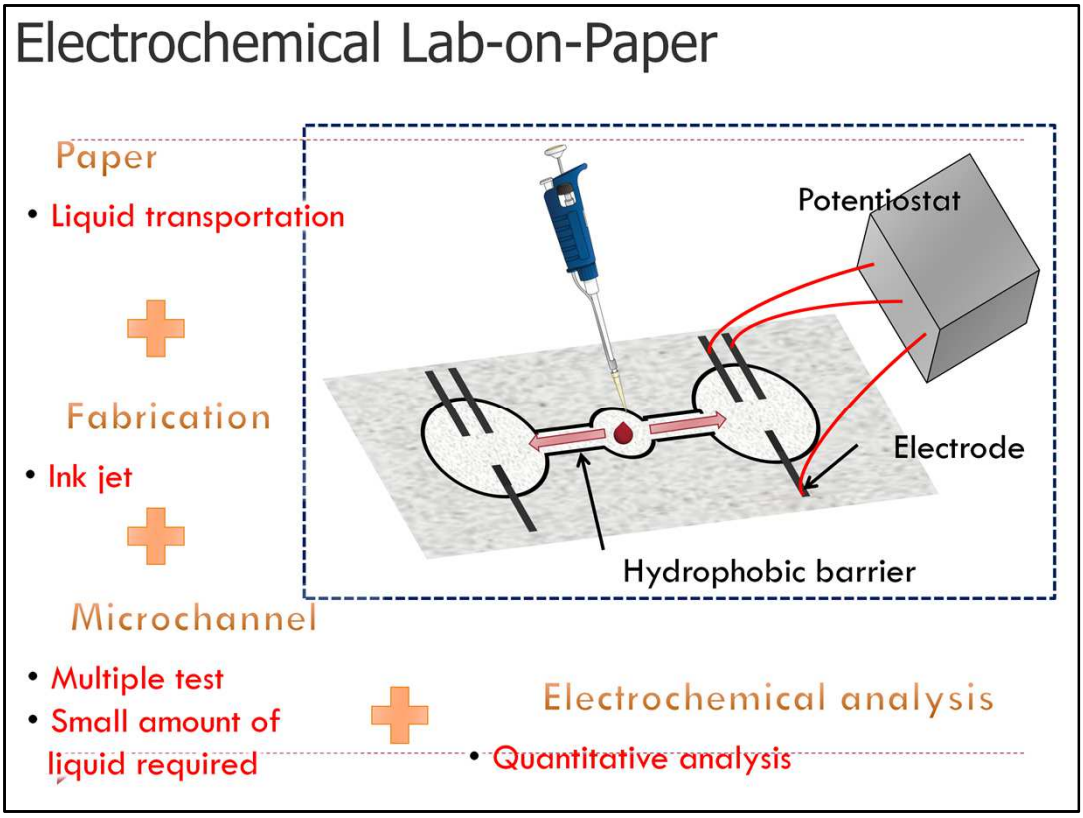


Micro-fluidic circuits、Micro-fluidic channelsなどと呼ばれる

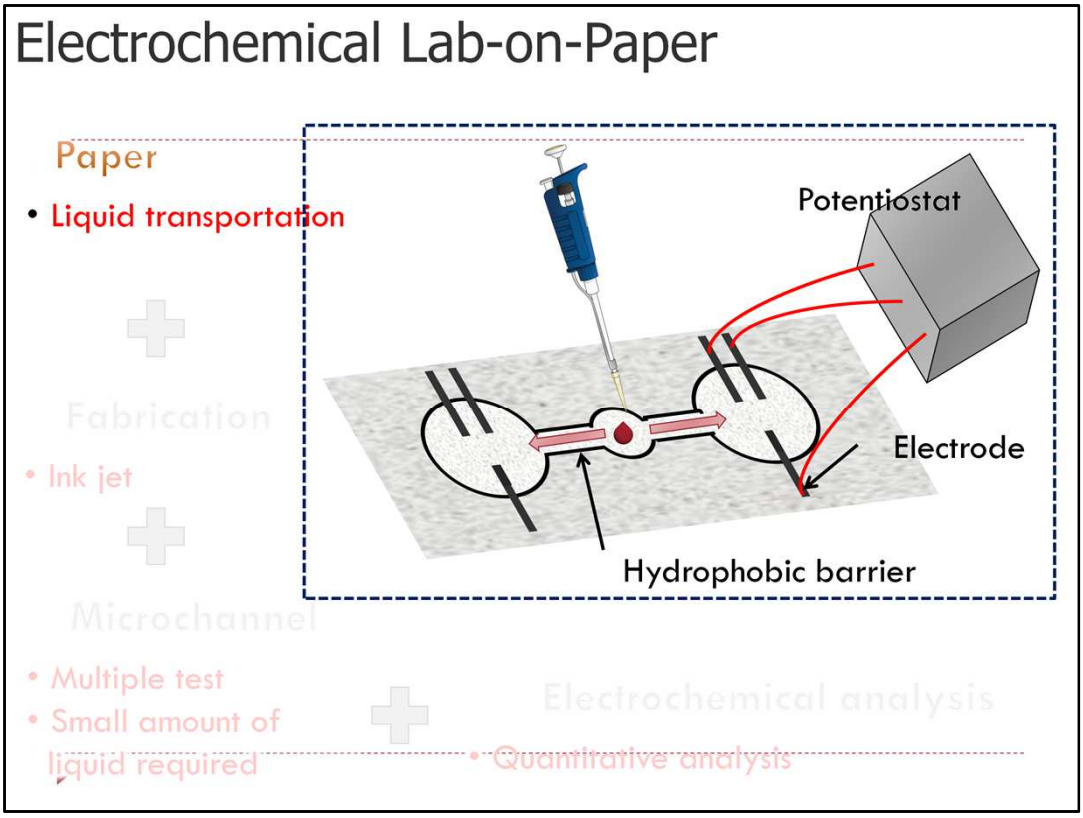
Patterningはpalにアクセント



in thesedays, self-diagnosis is more and more attractive because of the increasing demand of medical resources like doctors.
it requires inexpensive and easy-to-handle medical device.
In-patients 入院患者
Home patients 在宅患者



it is the concept of our work.
by integrating paper, microchannel & electrochemistry, a low-cost smart multiple assay can be obtained.



it is the concept of our work.
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Paper Preparation

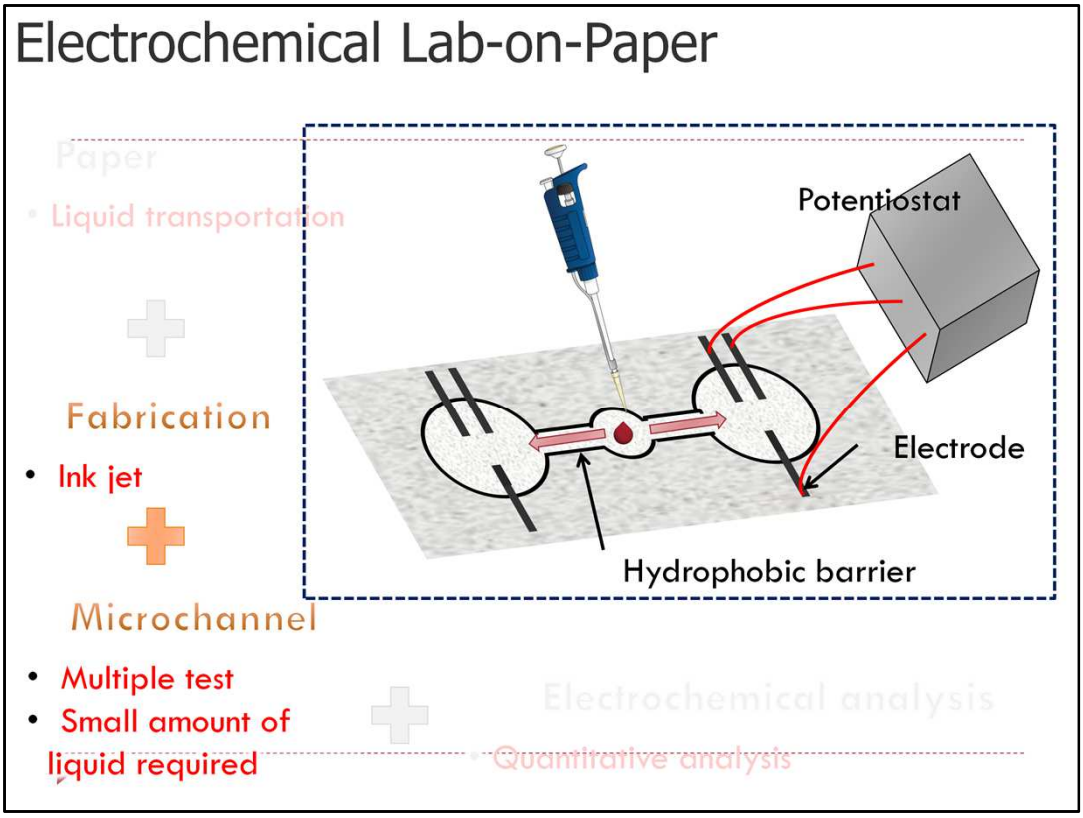
Improve printability

- Decrease pore size→ prevent ink bleeding
- Materials…cotton pulp→almost none of impurities

#	Beating (Revolution, PFI mill)	Density of paper (g/cm^3)
1	10000	0.568
2	20000	0.622
3	30000	0.641

Beating increases paper density

Paper substrate was successfully designed



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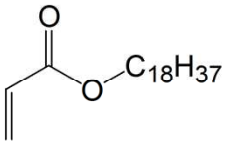
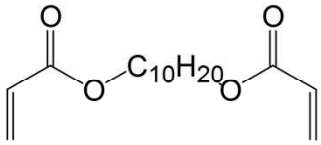
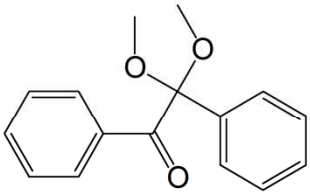
189

UV curable ink for hydrophobic barrier

- Polymerized by UV-light irradiation
- Monomers, oligomers, initiators in **ethanol** → VOC-free

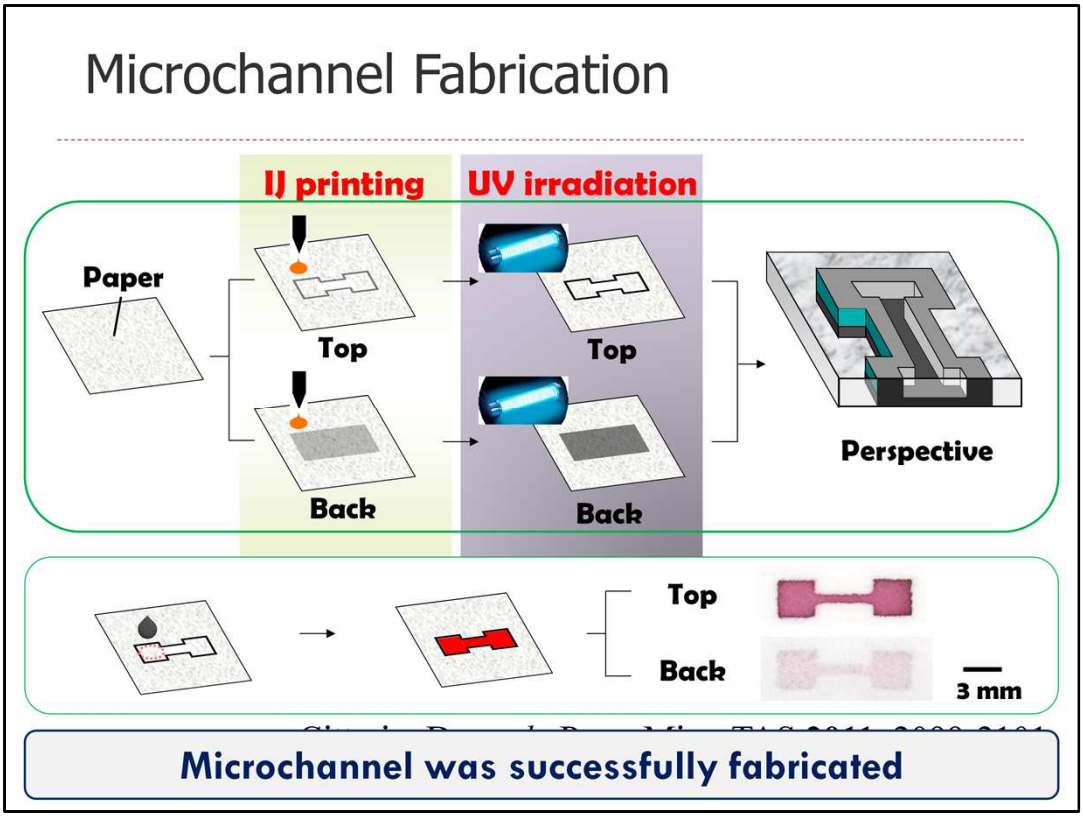
Ingredients of UV ink

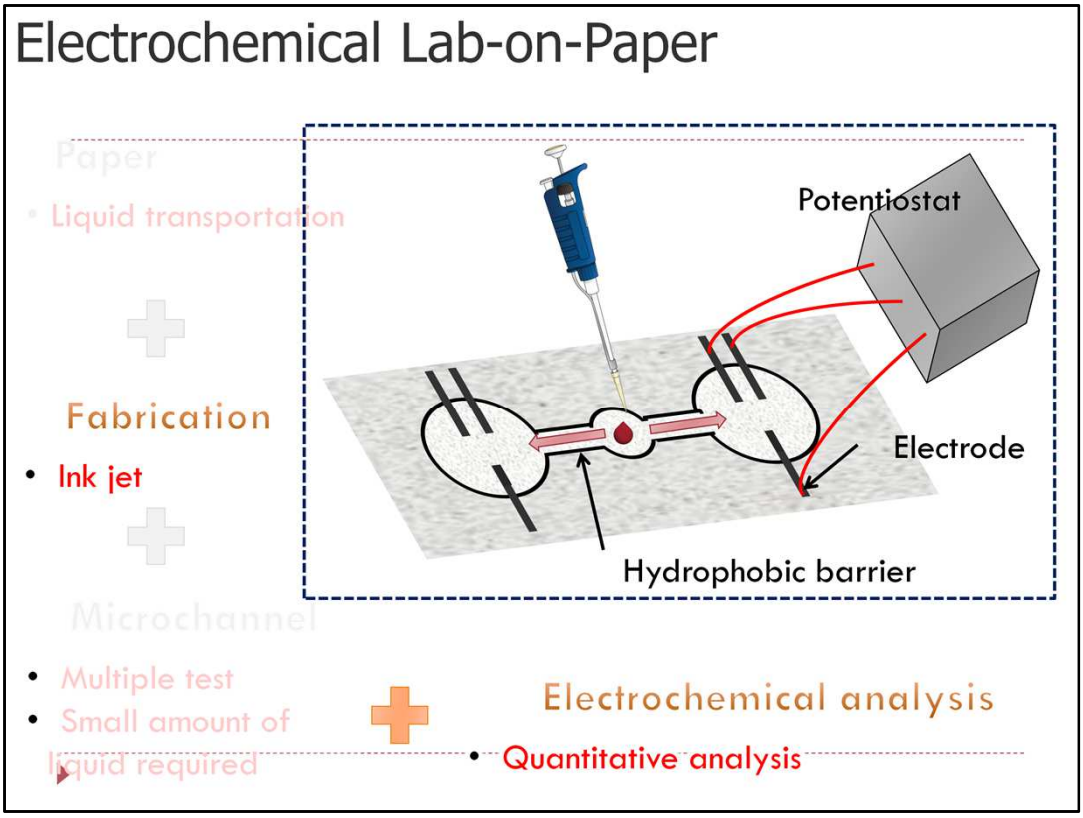
		
Octadecyl acrylate	1,10-decanediol acrylate	Irgacure 819
59.5%	25.5%	15.0%

(m/m)

Solvent-free & Green Material

Citterio, D. *et al.*, Proc. MicroTAS **2011**, 2099-2101


Microchannel Fabrication
IJ printing
UV irradiation
Paper
Top
Back
Top
Back
Perspective
Top
Back
3 mm
Microchannel was successfully fabricated



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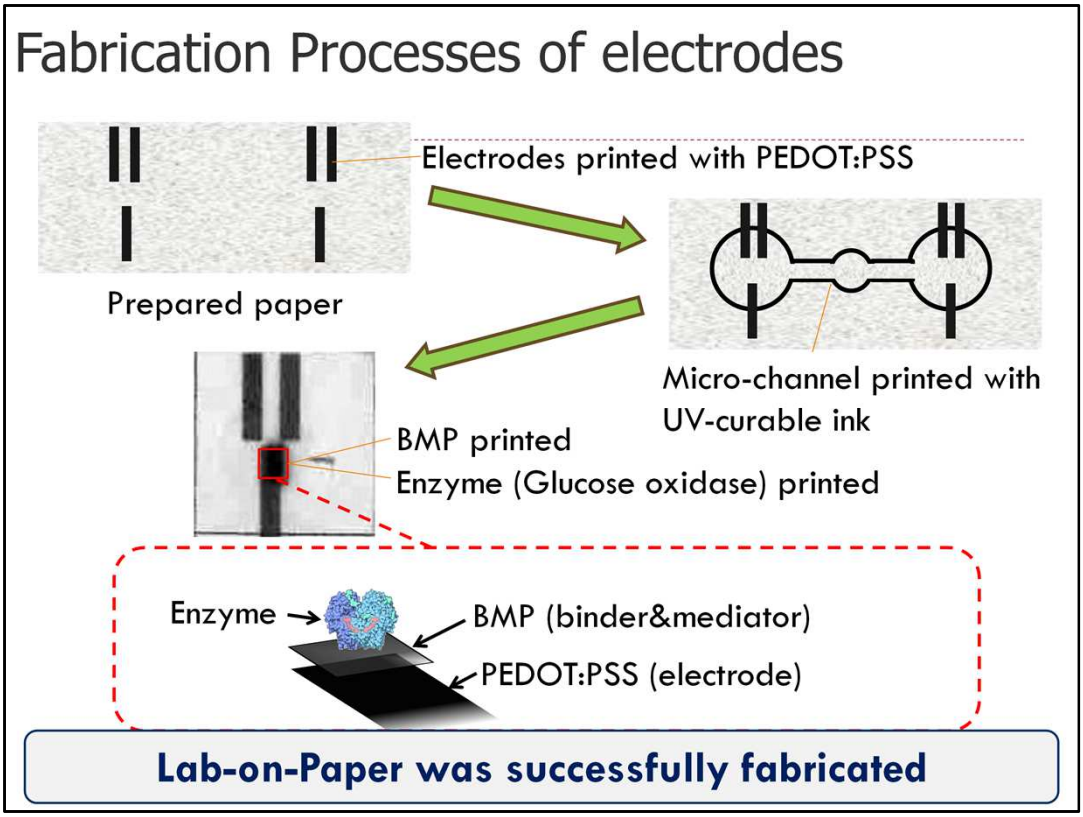
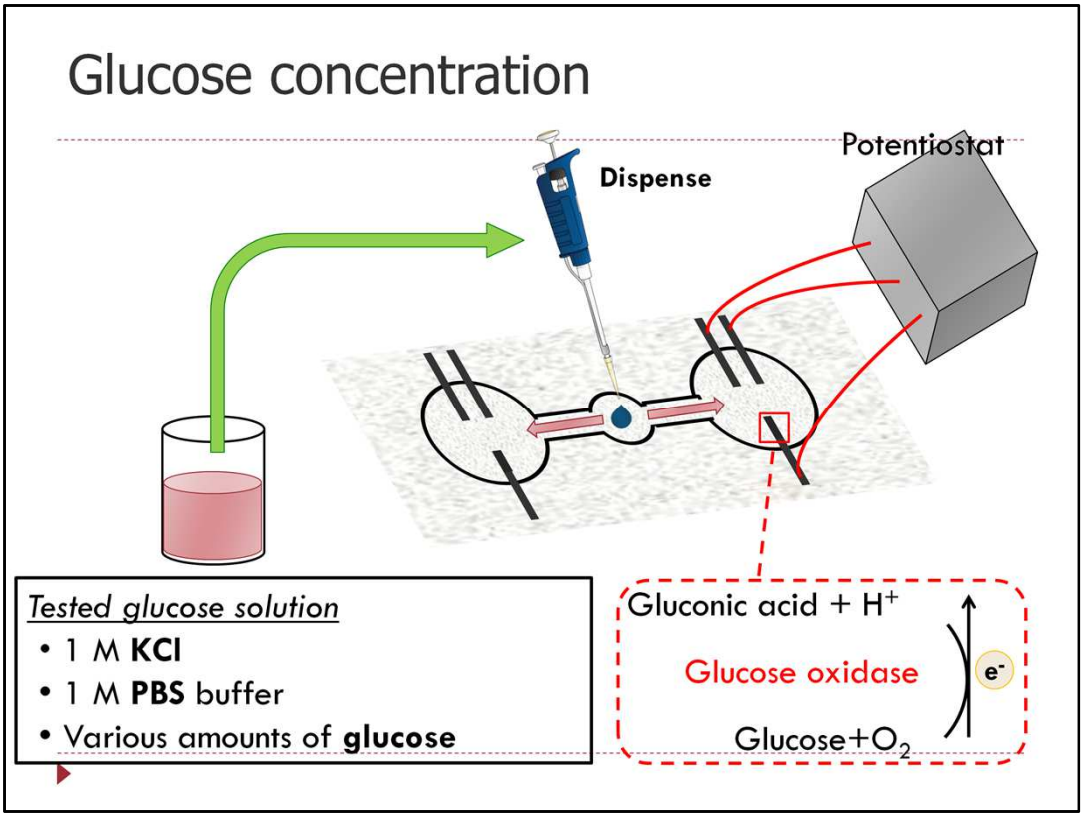

Fabrication Processes of electrodes
Electrodes printed with PEDOT:PSS
Prepared paper
Micro-channel printed with
UV-curable ink
BMP printed
Enzyme (Glucose oxidase) printed
Enzyme
BMP (binder&mediator)
PEDOT:PSS (electrode)
Lab-on-Paper was successfully fabricated

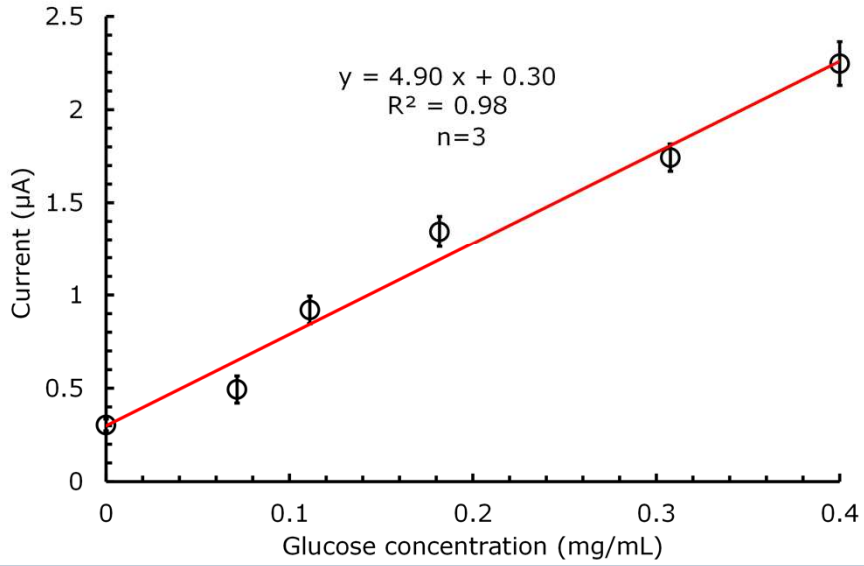


Blood glucose level

Chronoamperometry for Glucose Test

Current value at 0.5 V

(vs. printed pseudo reference electrode)



Glucose conc. was successfully measured