Basics of Bleaching Chemical Pulps

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Definition

Chemical treatment to:

- Increase brightness
- Improve cleanliness
- Improve brightness stability
- Remove hemicellulose
- Remove extractives

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Bleaching: A Working Definition

- Removal of colored residual lignin from chemical pulp (usually kraft) to increase its brightness, cleanliness and other desirable properties, while preserving the strength (cellulose integrity) and carbohydrate yield (cellulose and hemicellulose) of the unbleached fiber, with due regard for potential effects on the environment

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Bleaching vs. Pulping

- Compared to pulping, bleaching
  - is also a delignification process
  - is more selective in terms of yield and d.p.
  - is more expensive per unit of lignin removed
  - removes less lignin
  - produces problematic effluent

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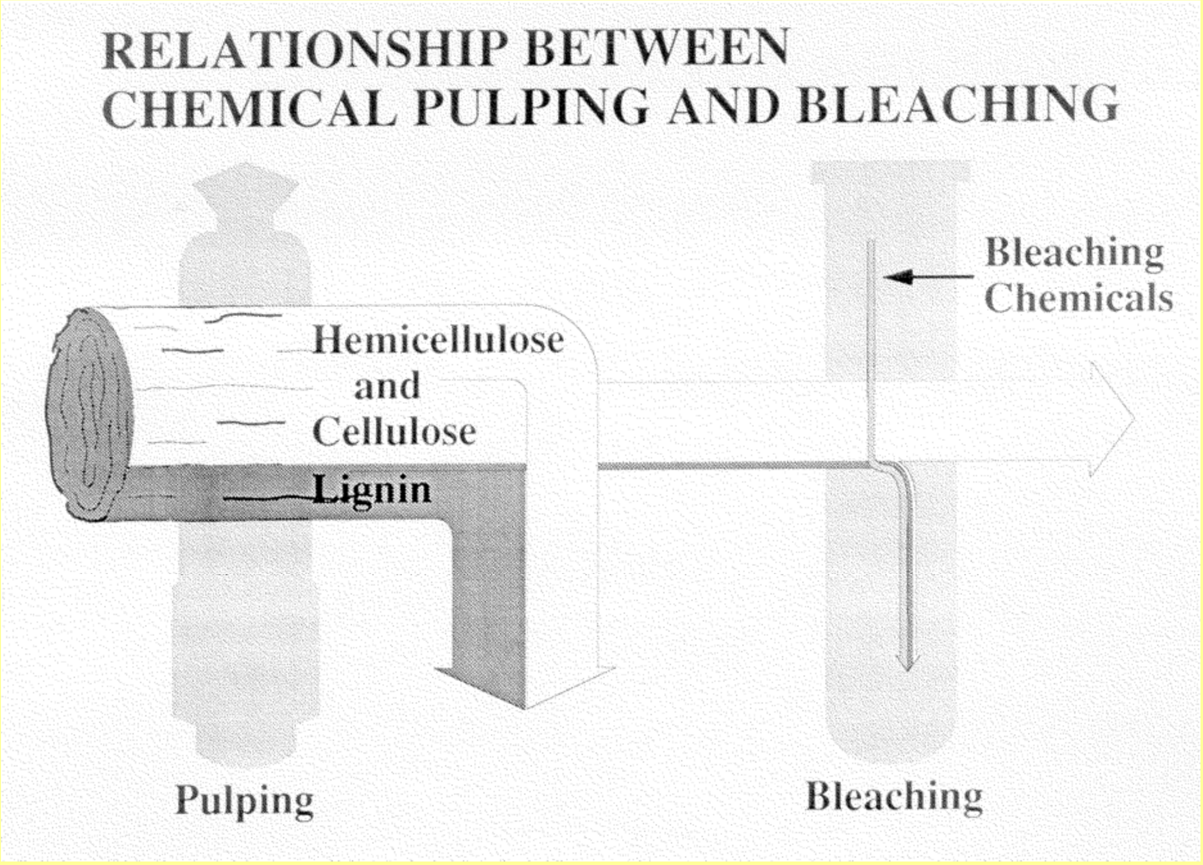
Bleaching vs. Pulping



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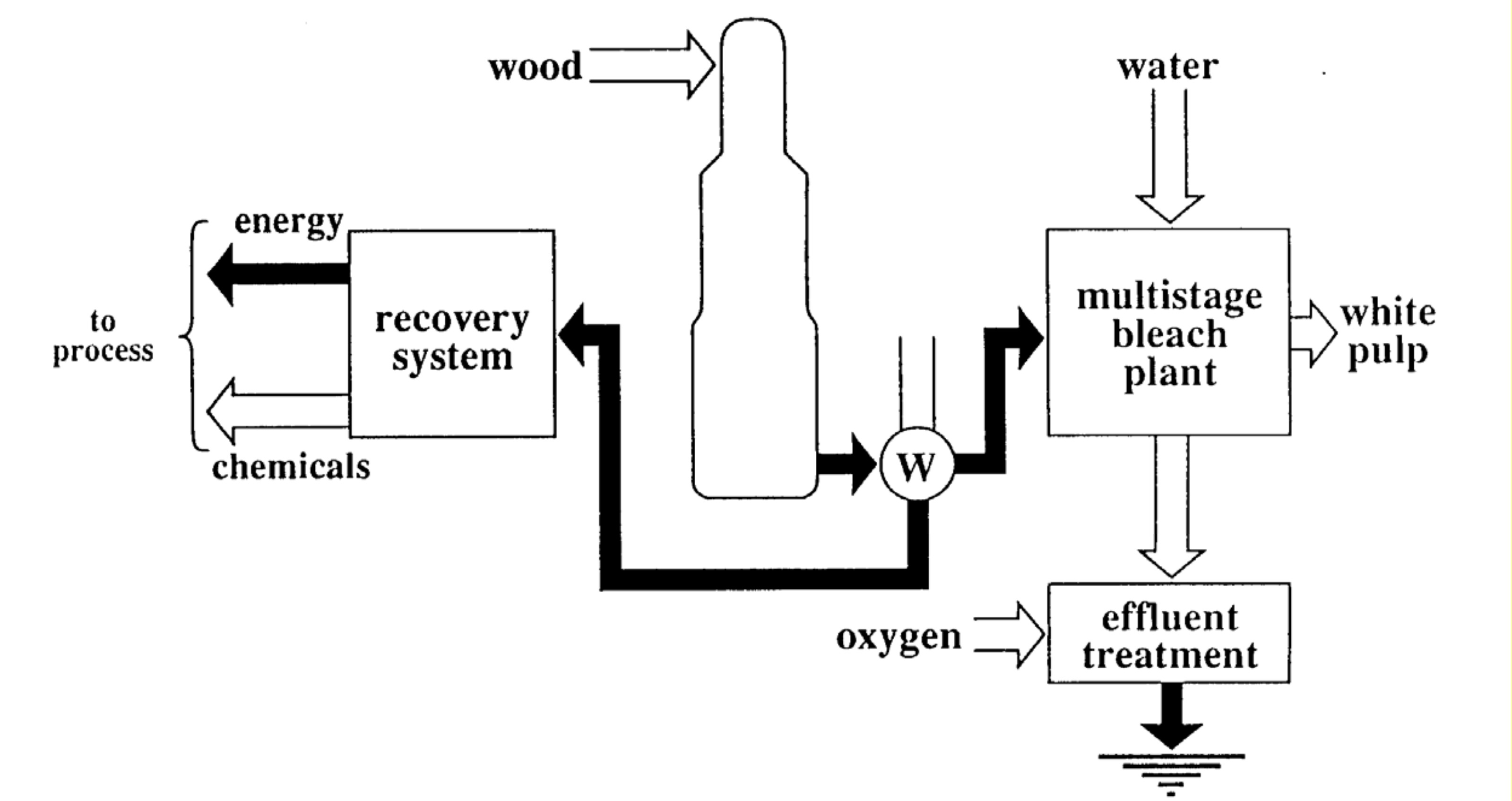
Bleaching Effluents: Processed in an Environmental Acceptable Manner



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Relevant Statistics

- 70 million tons/year bleached
- 28 million tons in USA
- 12 million in Canada
- Most used in grades needing strength
- Proportion of pulp used on site is
  - 74% in USA
  - 30% in Canada

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Why Kraft Pulp Needs To Be Bleached

- Dark color of unbleached pulp is due to residual lignin, which remains in the pulp because of its
  - high molecular weight
  - hydrophobic nature
  - chemical bonds to carbohydrates

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Bleaching Chemistry

- Bleaching chemicals are oxidizing agents that
  - break up the lignin molecule
  - introduce solubilizing groups into the fragments
  - disrupt lignin-carbohydrate bonds, allowing fragments to dissolve

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Important Pulp Properties

Macroscopic

- Kappa Number
- Brightness
- Opacity
- Tear Strength
- Viscosity
- Dirt Content

Microscopic

- Residual Lignin Content
- Light Absorption Coefficient
- Scattering Coefficient
- Fiber Strength
- Cellulose Mol. Wt.

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Kappa Number

- Amount of oxidizing agent ($KMnO_4$) consumed by 1 gram of pulp
- Measures lignin content linearly
- Kappa No. = 6.7 times lignin content in %
- Successor to K no.
- K no. = 2/3 Kappa no.

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Light Absorption Coefficient

- Light passing through a solution can be either absorbed or transmitted
- Capacity of solute to absorb light of given wavelength given by Beer's law
- Molar extinction coefficient is characteristic of solute
- Different wavelengths are absorbed differently

$$\log\left(\frac{I_0}{I}\right) = \varepsilon \cdot c \cdot l$$

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Light Absorption by Pulp Sheets

- The product of molar extinction coefficient and concentration is replaced by *k*, the *absorption coefficient*
- The visible light absorbed by lignin is in the blue range (400-500 nm), making it appear yellow.
- Bleaching removes lignin and therefore decreases the absorption coefficient in this range. It is measured at 457 nm.

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Light Scattering by Pulp Sheets

- Pulp sheets are physically more complex than solutions so they can *scatter* light as well as absorb or transmit it.
- The tendency of a sheet to scatter light can be quantified in terms of *s, the scattering coefficient*
- *s* depends on free surface within sheet, and therefore on degree of bonding

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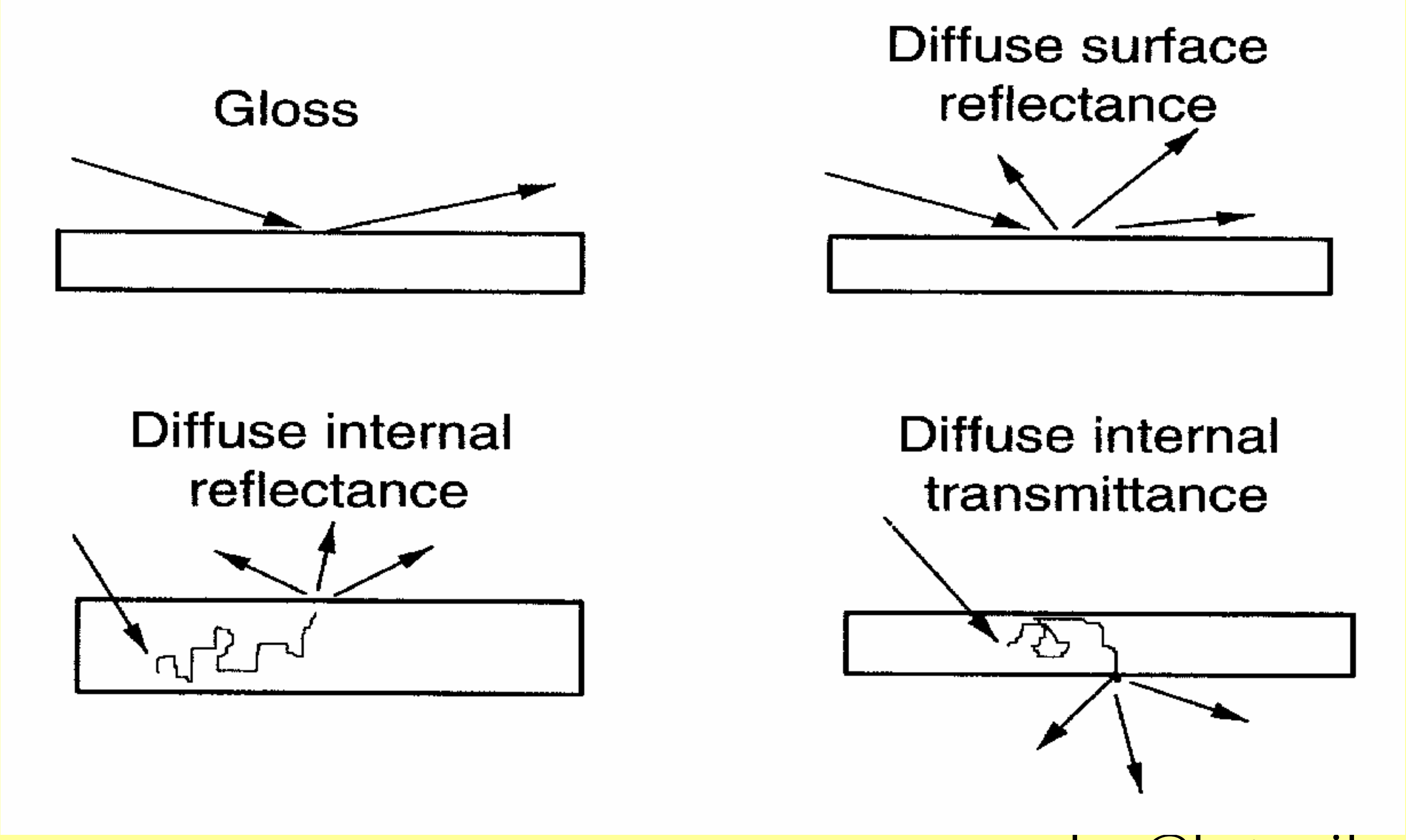
Fate of Light Shining on Paper



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Fate of Light Shining on Paper

- Light shining on a sheet of paper can
  - be specularly reflected, to the extent that the sheet is glossy
  - be reflected and scattered, to the extent that the sheet is opaque
  - be transmitted, i.e., pass right through the sheet, to the extent that the sheet is translucent (lacks opacity)
  - be absorbed, to the extent that the sheet is colored

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The Kubelka-Munk Theory

The fraction of light reflected by a thick sheet of paper, called **reflectance**, can be calculated from 2 basic properties - absorption coefficient, k, (color) and scattering coefficient, s (content of reflecting surfaces within the sheet). The absorption coefficient is a measure of how much light is absorbed and the scattering coefficient a measure of how much is reflected and scattered. Reflectance decreases as k increases and increases as s increases.

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The Kubelka-Munk Equation

The fraction of light reflected by a thick sheet of paper can be calculated from 2 basic properties - absorption coefficient, *k*, and scattering coefficient, *s*. Reflectance decreases as *k* increases and increases as *s* increases.

$$R_\infty = 1 + \frac{k}{s} - \sqrt{\left(\frac{k}{s}\right)^2 + 2\left(\frac{k}{s}\right)}$$

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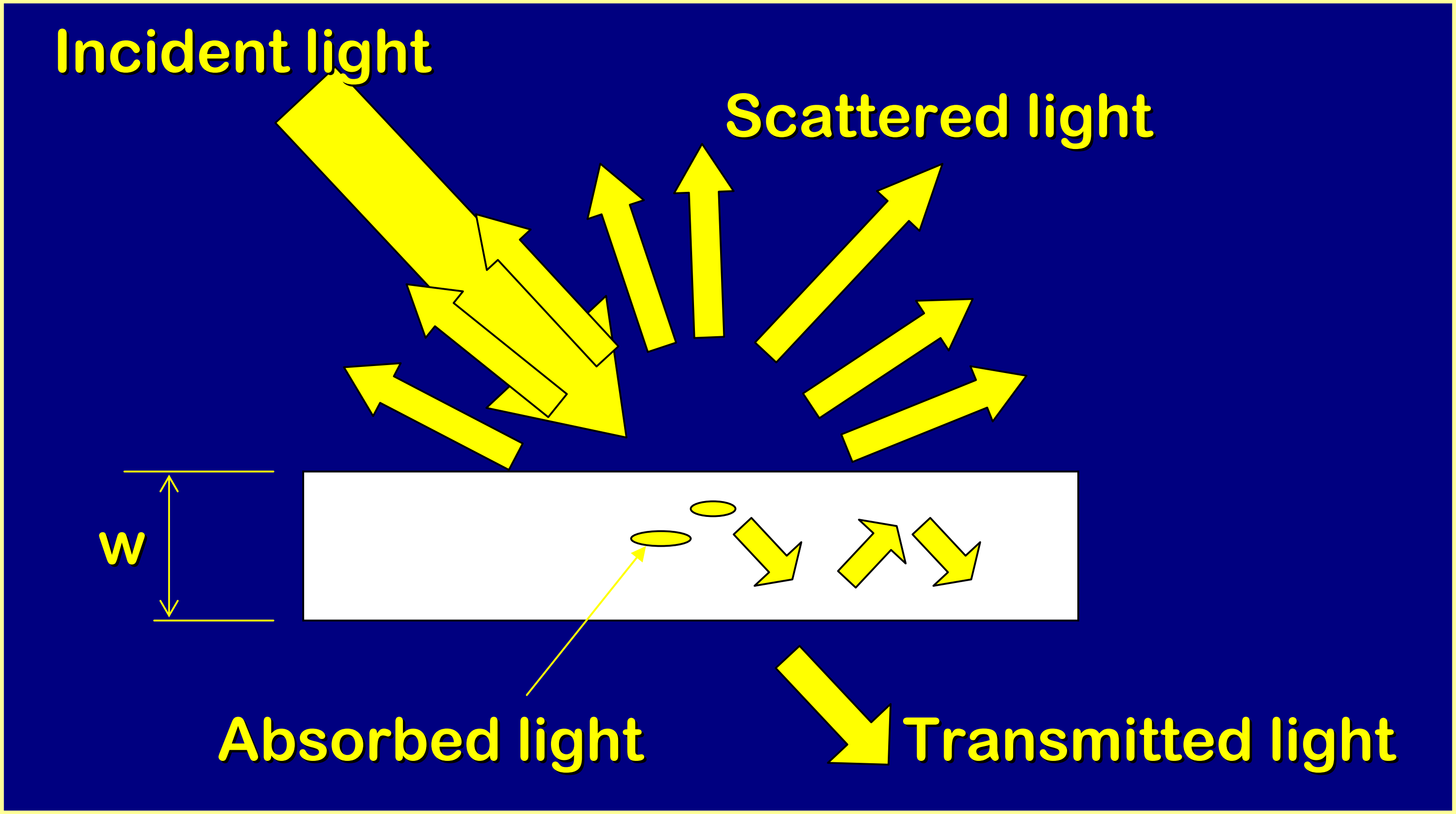
Light Scattering and Absorption



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Brightness

- Reflectance of blue (457 nm) light from a thick sheet
- Sheets having a low brightness appear yellow or brown; those having a high brightness appear white.
- Brightness may be increased by decreasing the absorption coefficient (color intensity)
- Brightness may be increased by increasing the scattering coefficient (e.g. snow vs. water)

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TAPPI Brightness

- TAPPI Test method T452
- 45º illumination and 0º (perpendicular) viewing
- Expressed as % of MgO reflectance

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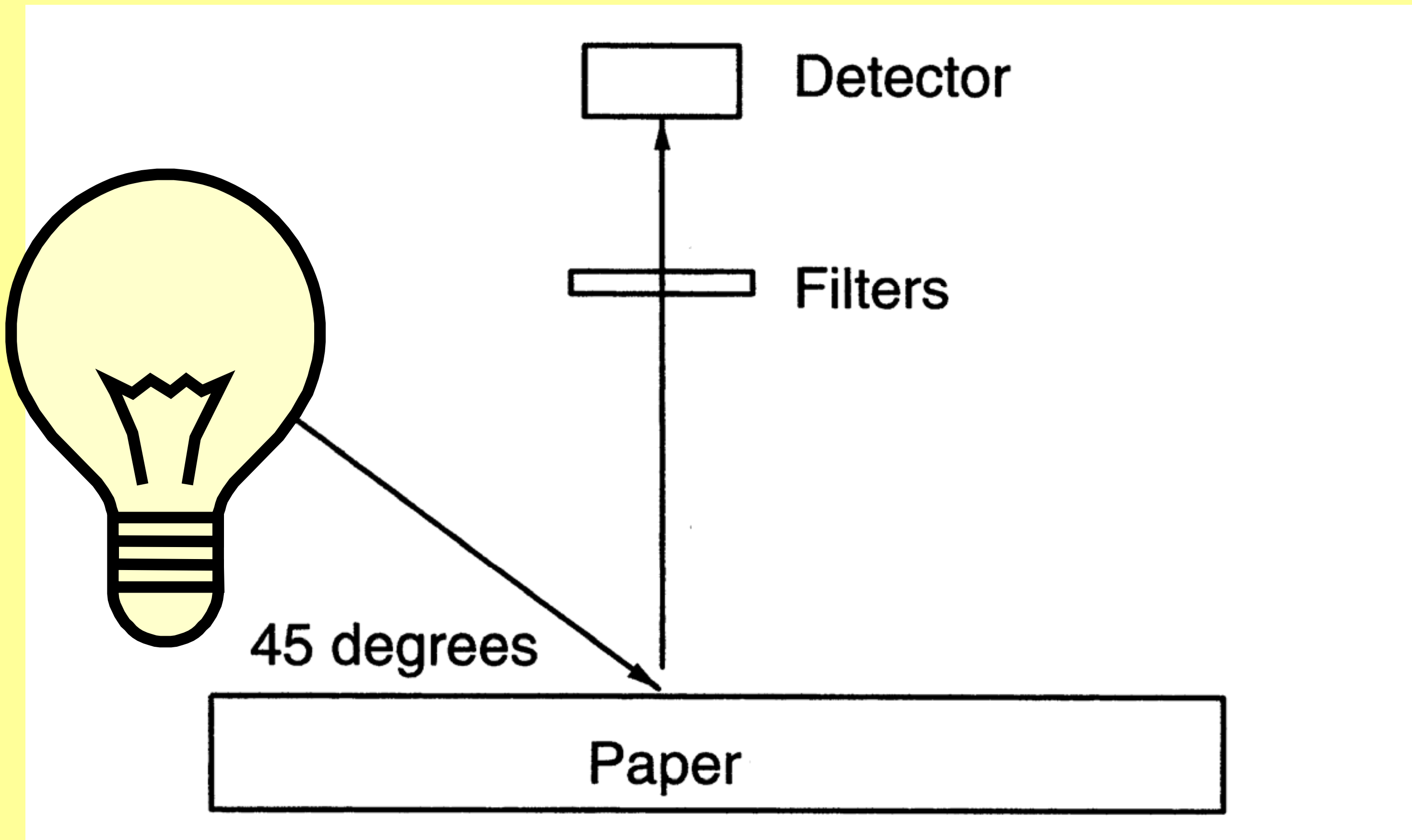
TAPPI Brightness Measurement Geometry



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ISO Brightness

- Diffuse illumination, 0^o viewing
- Expressed as absolute reflectance
- Less dependent on surface characteristics

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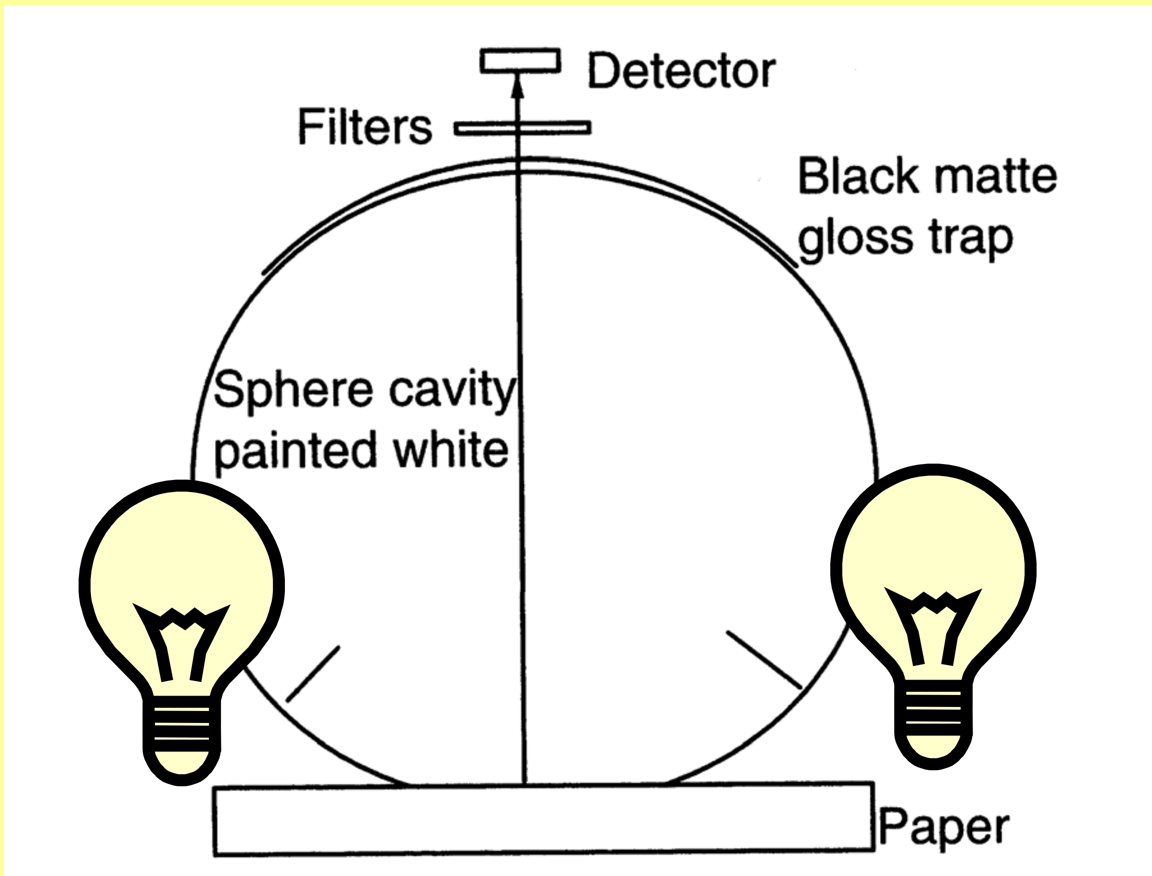
ISO Brightness Measurement Geometry



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Brightness Stability

- *k* increases on exposure to heat or light
- Phenomena known as *reversion*, *brightness reversion*, *color reversion*, *thermal reversion*, *yellowing*, *photoyellowing*
- Can be expressed as *post color number*, the change in *k/s*.

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

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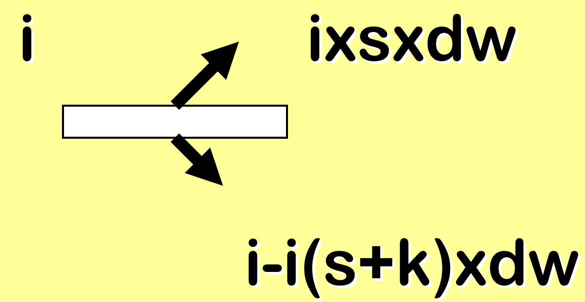
Kubelka-Monk Theory

Theory of light scattering. Developed for paint films. Assumes homogenous material small particles considers diffuse reflectance and transmittance of light

2 material properties describe scattering of light



k = absorption coefficient

s = scattering coefficient

i = intensity of light

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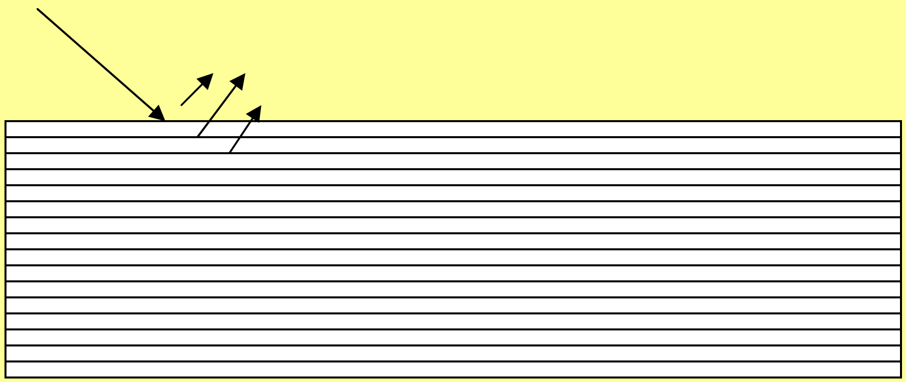
Reflectivity

Reflectivity is a measure of reflected light

R_∞ =Total reflectivity from a thick pile of paper



Reflectivity depends only on scattering and absorption coefficients, s and k

$$R_\infty = 1 + k/s + [(k/s)^2+2k/s]^{0.5}$$

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Brightness

Brightness is the R_{∞} value measured using a blue light source having a wavelength of 457nm

R=100% corresponds to reflectance off magnesium oxide

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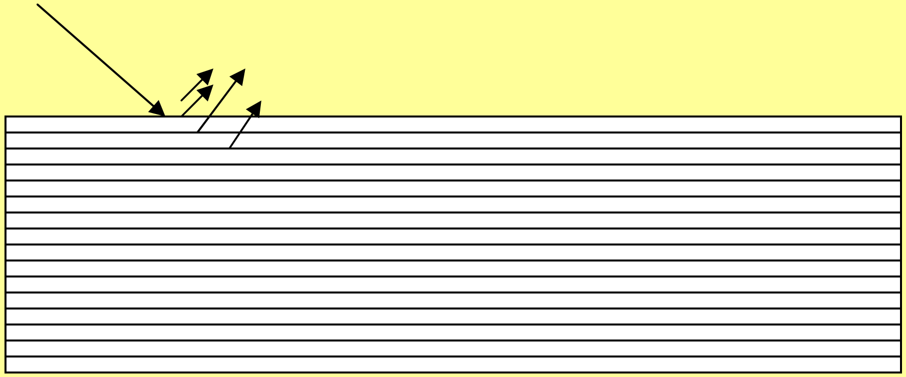
Reflectivity

R_0 =Total reflectivity from a single sheet with a black background



$$R_\infty = 1 + k/s + [(k/s)^2+2k/s]^{0.5}$$

Reflectivity depends only on scattering and absorption coefficients, s and k

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R_0 and R_∞ are used to measure s and k

$$k/s = (1-R_\infty)^2/2R_\infty$$

$$s = (1/b)[R_\infty/(1-R_\infty^2)]\ \ln[R_\infty(1-R_0R_\infty)/(R_\infty - R_0)]$$

b = grammage

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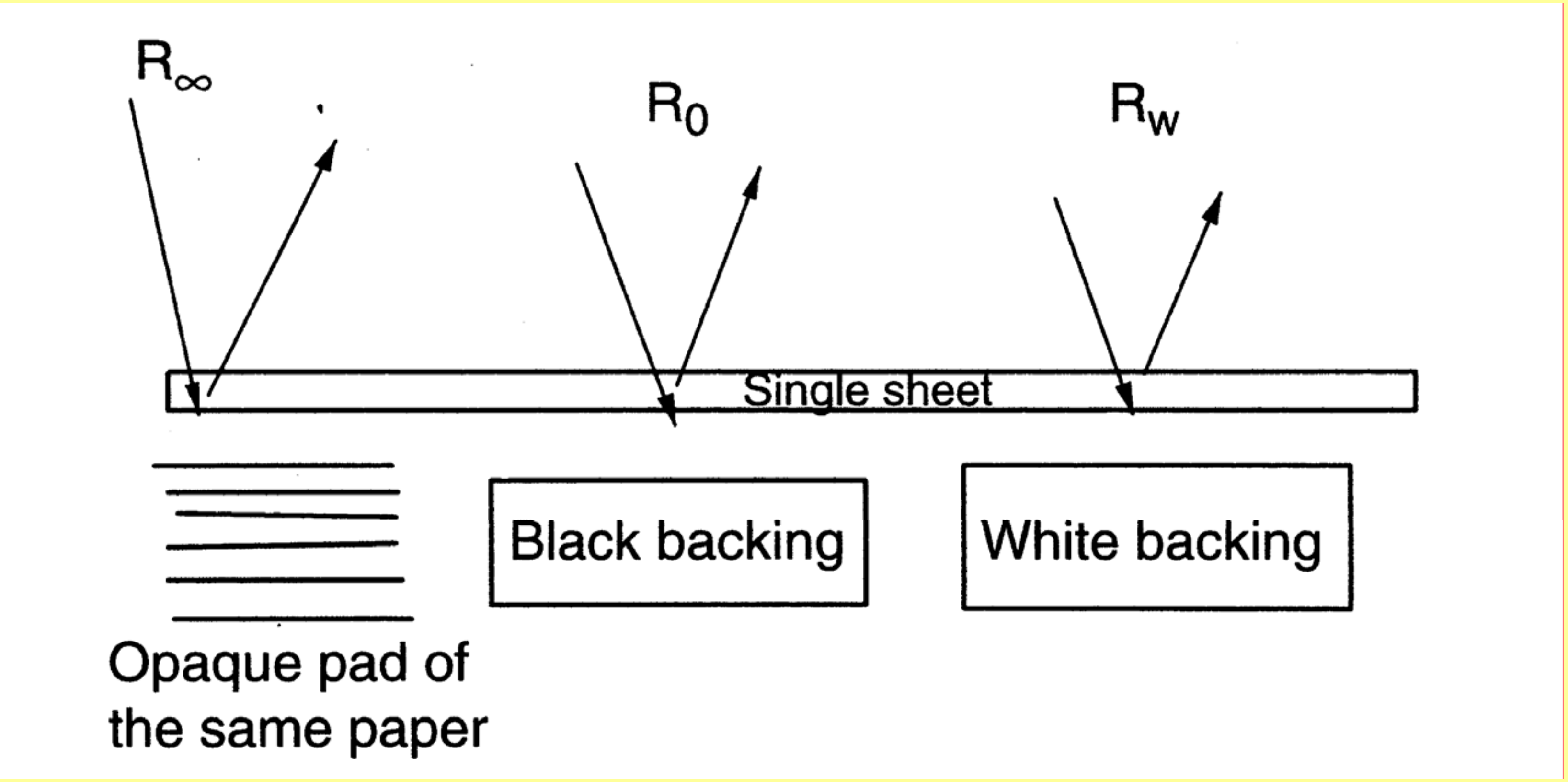
Effect of Backing on Reflectance



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Opacity for Paper

When you Increase	Opacity Will
Basis Weight	Increase
density	Decrease
% filler	Increase
coating weight	Increase

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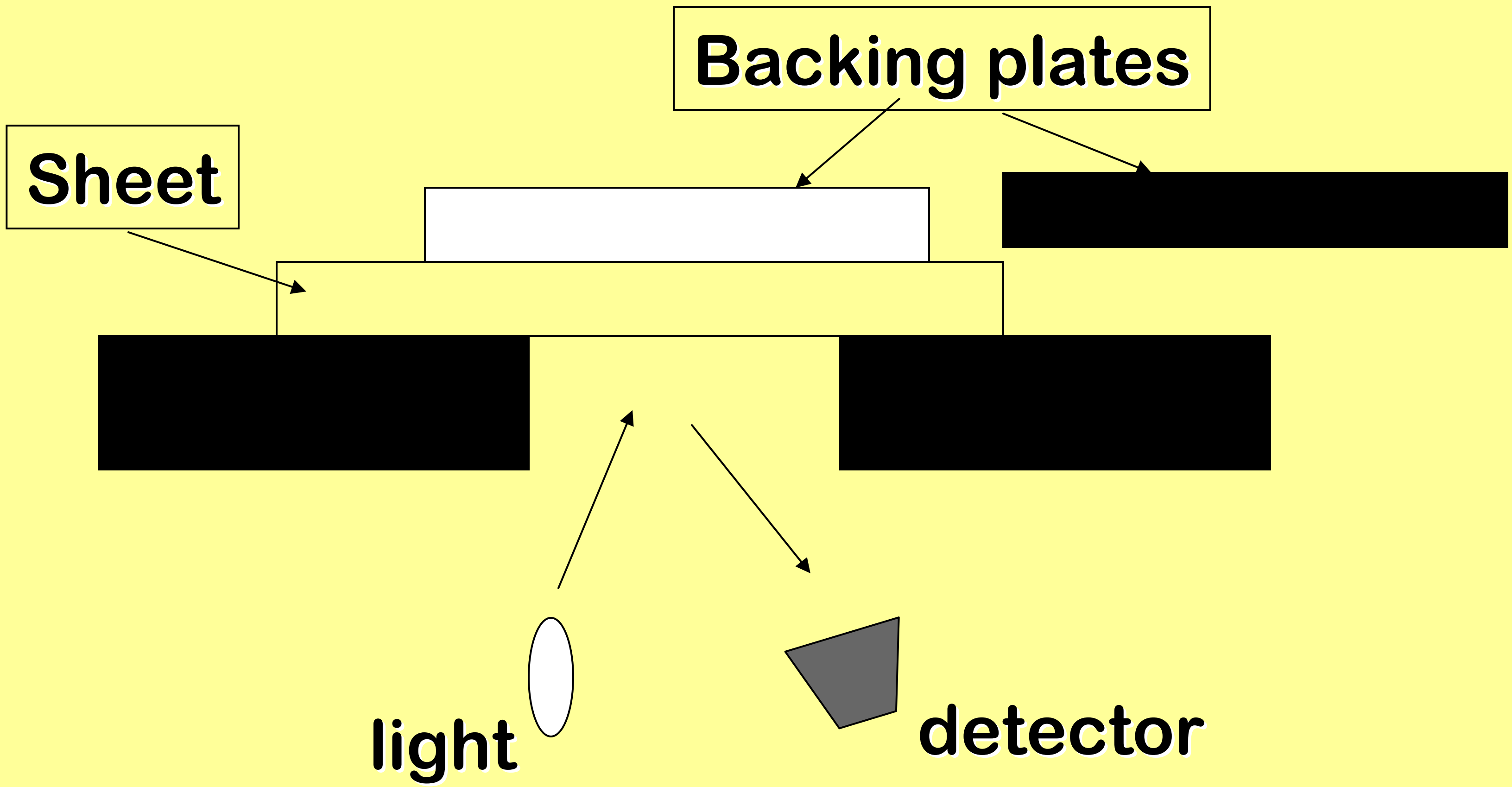
Opacity Measurements



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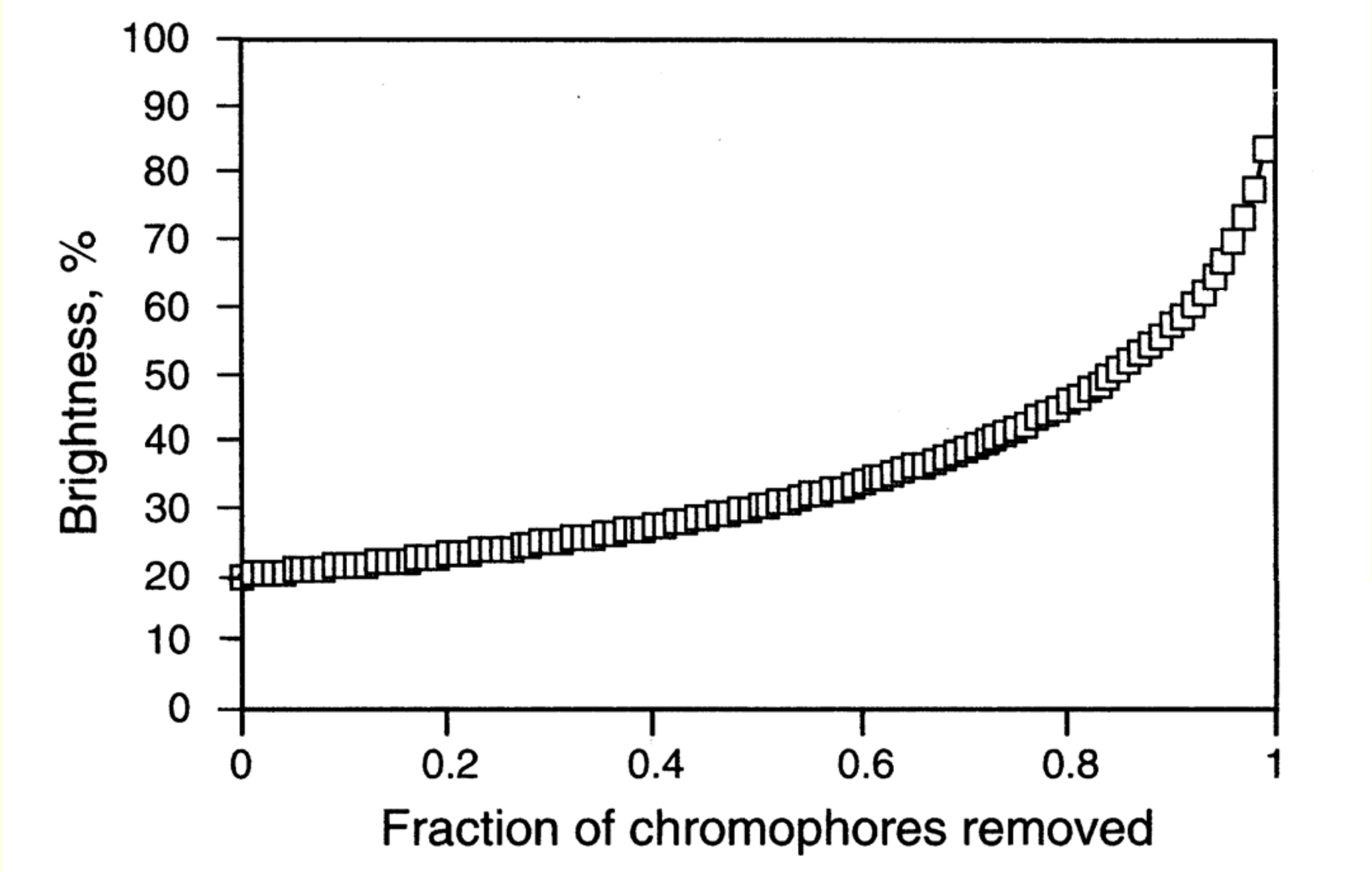
Non-Linear Relationship of Brightness to Chromophore Concentration



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Opacity

- Ratio of reflectance over black backing to reflectance over white backing, expressed as a percentage (TAPPI Methods T425 and T519)
- Increases as *s* increases
- Increases as *k* increases
- Affected by bonding and fillers
- Bleaching affects *k*, usually not *s*

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Opacity

$$\text{Opacity} = \frac{\text{Reflection factor of a sheet against a black backing}}{\text{Reflection factor of a large stack of sheets}}$$

$$\text{Tappi Opacity} = \frac{\text{Reflection factor of a sheet against a black backing}}{\text{Reflection factor of a sheet against a standard backing}}$$

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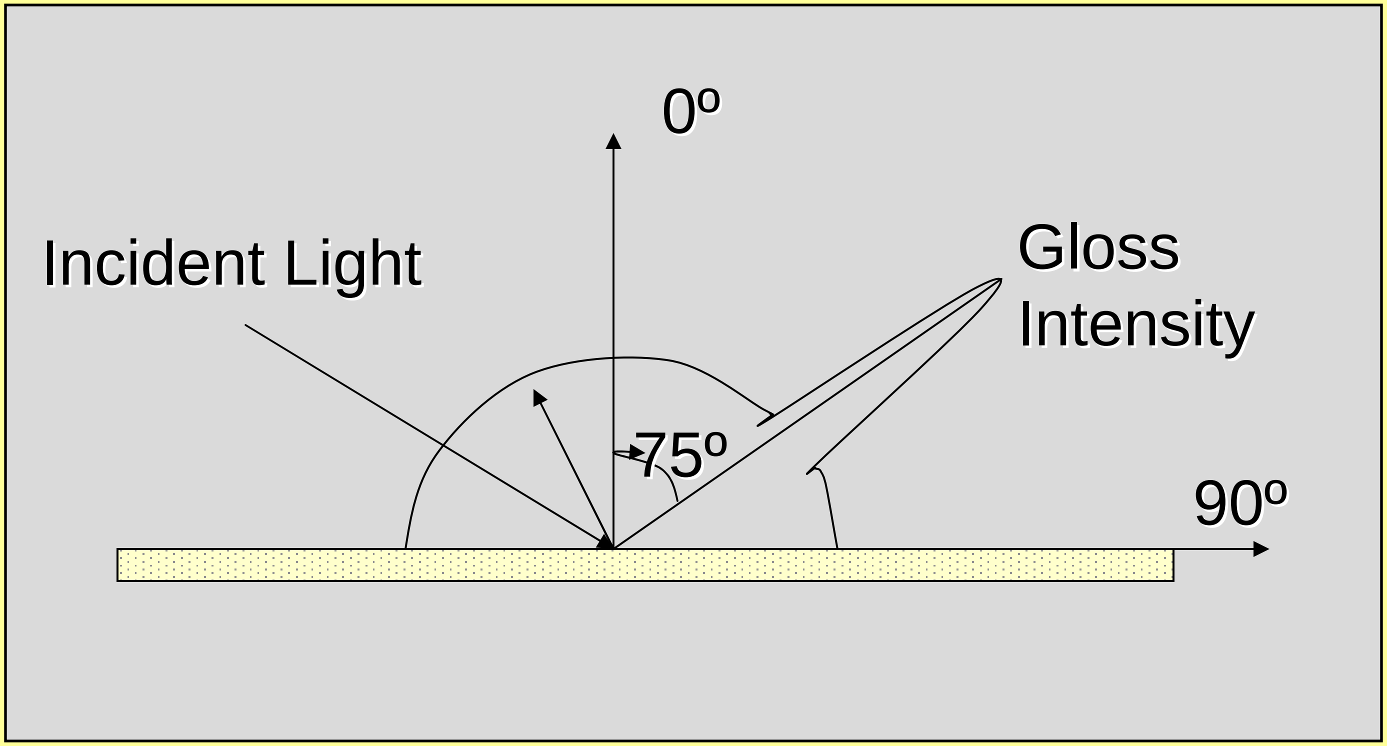
Gloss



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Optical Testing

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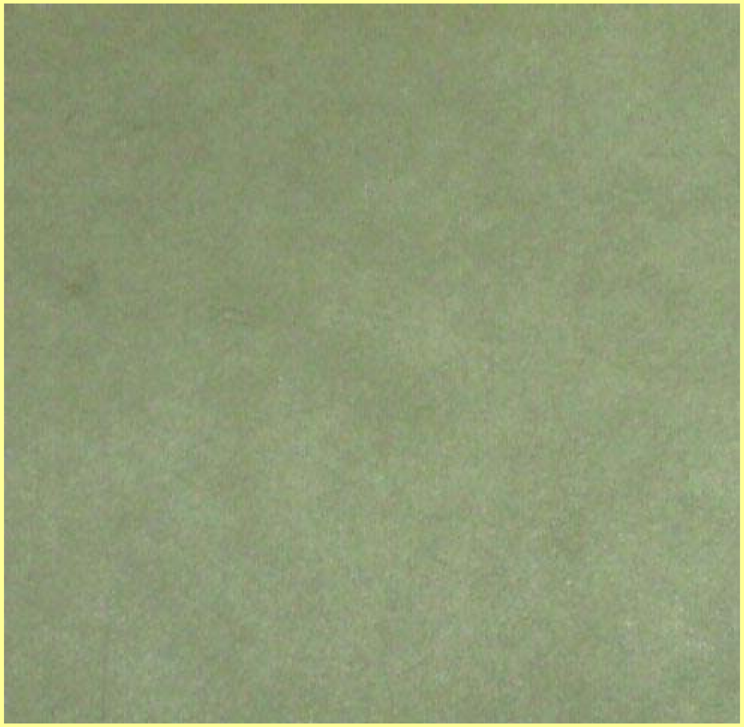
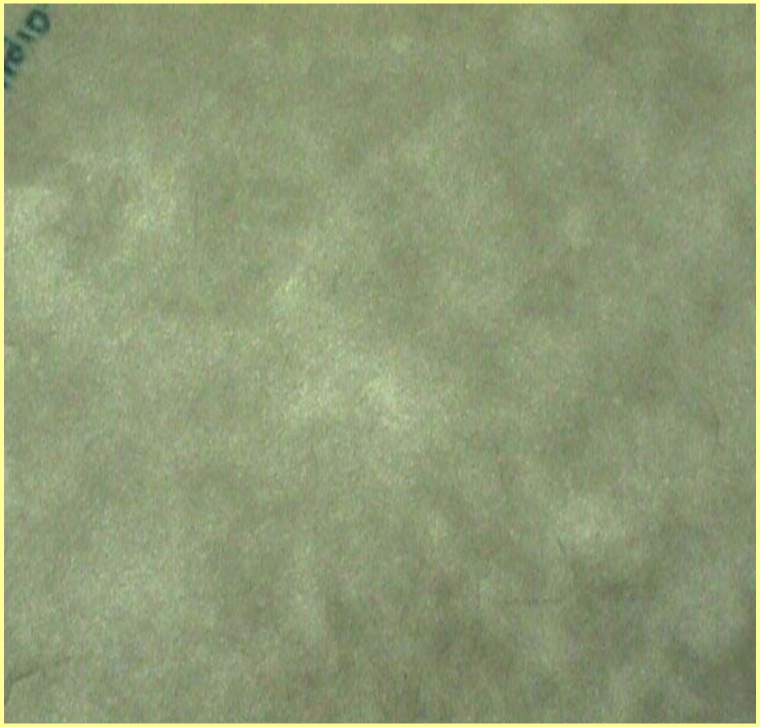
Examples of Formation





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Fiber Wall Structure

- Wood cells, and therefore pulp fibers, are hollow, elongated structures made up of cellulose microfibrils in a matrix of hemicellulose and lignin
- Microfibrils each consist of perhaps 36 parallel, hydrogen bonded cellulose molecules
- Microfibrils in the dominant wall layer, S2, are helically wound at a low angle

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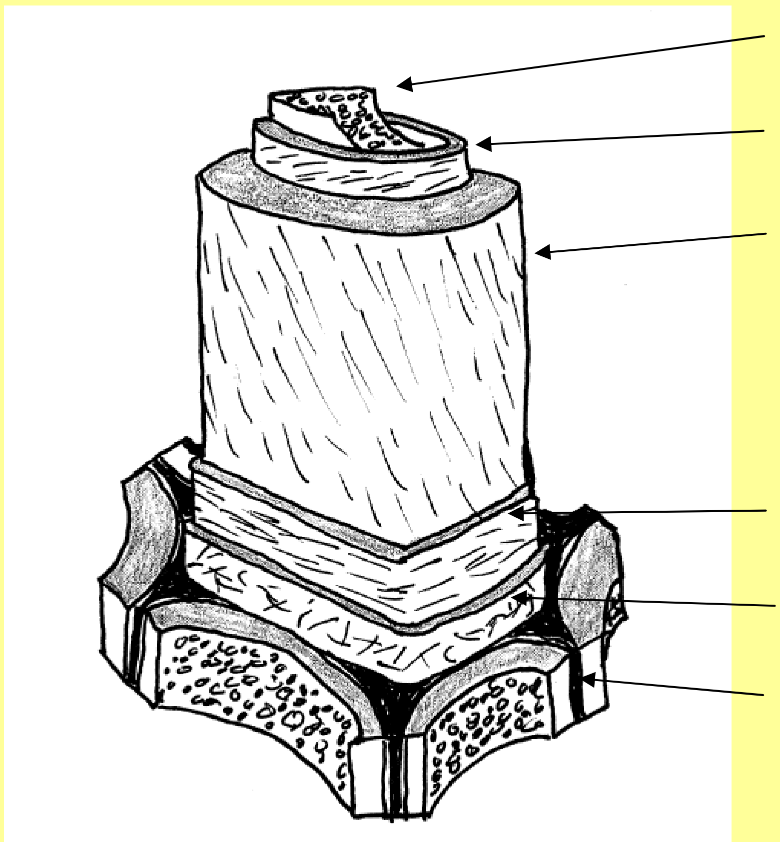
Fiber Wall Structure (2)



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Fiber Strength

- Tensile load on fiber is borne by microfibrils and therefore by cellulose molecules
- Strength of structure decreases as the length of its component molecules is decreased
- Cellulose chain cleavage by bleaching agents can therefore reduce fiber strength
- The relationship between cellulose d.p. and fiber strength is, however, nonlinear

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Fiber vs. Sheet Strength

- Fiber strength loss shows up first as loss in tear strength
- Tear failure usually involves fiber breakage, while tensile failure usually involves fiber pullout

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Monitoring Fiber Strength

- Single fiber testing
- Zero-span tensile strength
- Tear vs. tensile curves
- Viscosity

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Pulp Viscosity

- Measured by dissolving pulp fibers in CED and observing the time taken for the solution to pass through a standard capillary (TAPPI Test Method T230)
- Viscosity is expressed in centipoises (cp) or millipascal-seconds (mPa.s), which are numerically the same
- It is related to cellulose mol. wt. and indirectly to fiber strength

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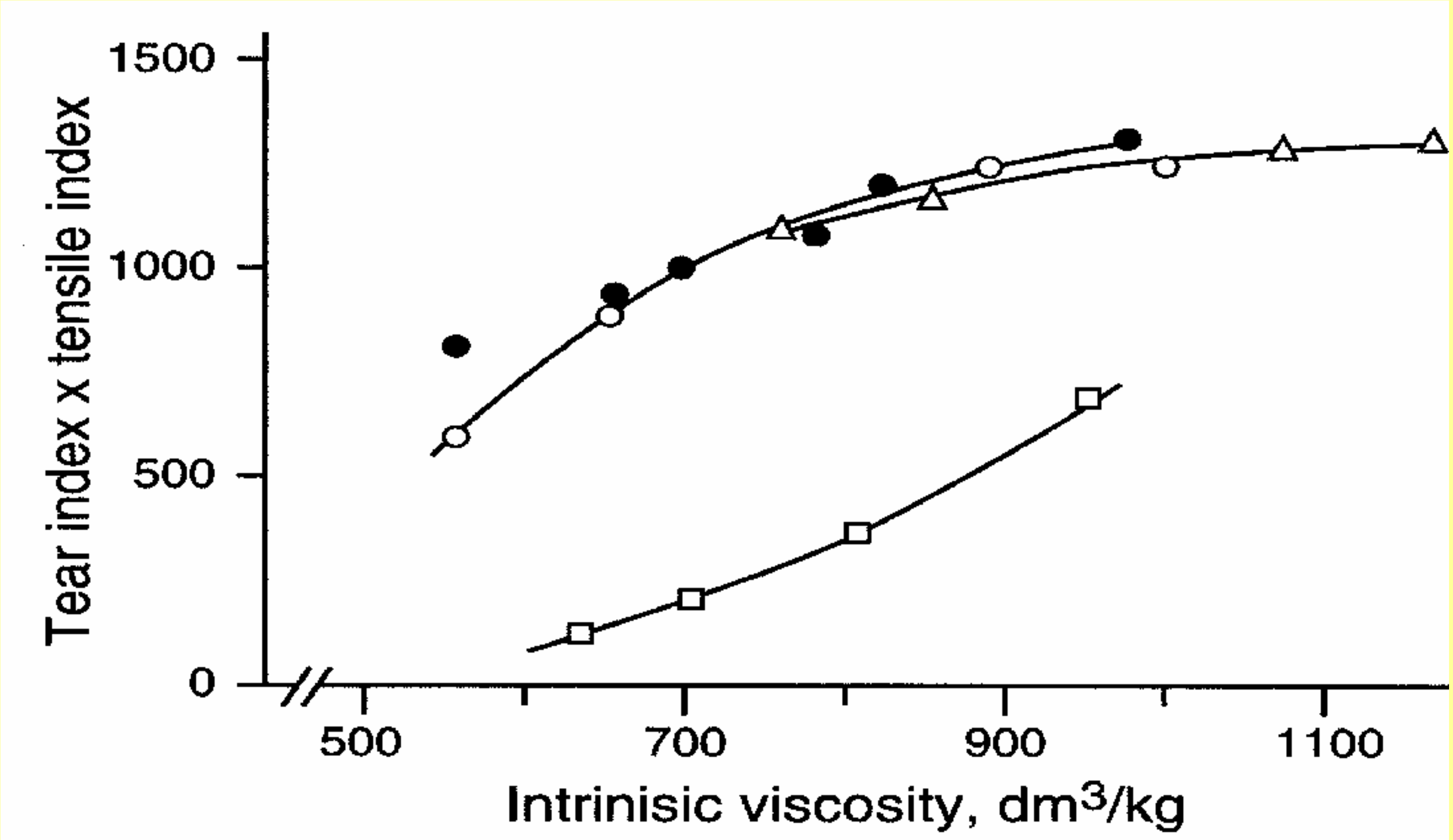
Non-Linear Relationship of Strength to Viscosity



Δ Conventional bleaching of conventional pulp

○ Conventional bleaching O-delignified pulp

□ Acid hydrolysis of bleached pulp

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Dirt

- Dark colored foreign matter
- Measured by T213 as equivalent black area
- From wood: bark, resin, sand, shives
- From process: carbon, sand, rust, rubber, scale
- Other: plastics, grease, fly ash

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Bleaching Chemicals

Name	Formula	Symbol
Chlorine	Cl_2	C
Chlorine Dioxide	ClO_2	D
Oxygen	O_2	O
Hydrogen Peroxide	H_2O_2	P
Sodium Hypochlorite	$NaOCl$	H
Hypochlorous Acid	$HOCl$	M
Ozone	O_3	Z
Sodium Hydroxide	$NaOH$	E

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Bleaching Chemical Characteristics

- Equivalent Weight
- Efficiency
- Reactivity
- Selectivity
- Particle Bleaching Ability
- Environmental Implications

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Equivalent Weight

- Bleaching is an oxidation process
- Bleaching chemicals are oxidizing agents
- One equivalent weight of a bleaching chemical is the weight of that chemical that is required to do a specified amount of oxidation.
- Equivalent weight is therefore an inverse measure of oxidizing power

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Equivalent Chlorine

- Equivalent chlorine is another way of expressing a bleaching chemical's oxidizing power
- It is defined as the number of pounds (or kg) of chlorine that has the same oxidizing power as one pound (or kg) of the bleaching agent in question
- Equivalent chlorine is therefore a direct measure of oxidizing power

Efficiency

- Some of the oxidizing power of a bleaching agent is always wasted in side reactions
- Some bleaching agents are more prone than others to undergo wasteful reactions; conversely, some use their oxidizing power more efficiently than others
- Efficiency is a measure of the degree to which a bleaching agent's oxidizing power is used in desirable, lignin-degrading reactions

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Equivalent Wt. and Efficiency

L=Low M=Med. H=High

Chemical	**Equiv. Weight**	**Equiv. Chlorine**	**Efficiency**
Cl_2	35.5	1.00	H
ClO_2	13.5	2.63	H
O_2	8	4.44	L
H_2O_2	17	2.09	L
NaOCl	37.2	0.93	M
O_3	8	4.44	H

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Equivalent Chlorine Charge

- ✓ The charge of chlorine or chlorine dioxide in the first bleaching stage that employs either is often expressed as **kappa factor**, sometimes also called **active chlorine multiple**

$$Kappa\ Factor = \frac{Percent\ Eq.\ Cl_2}{Kappa\ No.}$$

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Reactivity and Selectivity

- Reactivity may be defined in terms of the fraction of the residual lignin that the bleaching agent is practically capable of removing
- Selectivity is the degree to which the bleaching agent can remove lignin without dissolving or damaging the other components of the fiber, cellulose and hemicellulose

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Reactivity and Selectivity

L=Low M=Med. H=High

Chemical	Reactivity	Selectivity
Cl_2	H	H
ClO_2	M	H
O_2	L	M
H_2O_2	L	H
NaOCl	M	M
O_3	H	M

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Particle/Dirt Removing Ability and Environmental Implications

- Different bleaching agents differ in their ability to remove dirt particles, a very important characteristic
- For good dirt removal, chemical reaction with lignin must be slow enough to allow time for diffusion of chemical into particles
- Different bleaching agents engender different levels of concern for the environment; whether the concern is justified may be irrelevant

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Dirt and Environmental

L=Low M=Med. H=High

Chemical	Dirt Removal	Environmental Implications
Cl_2	H	H
ClO_2	H	M
O_2	M	L
H_2O_2	L	L
NaOCl	H	H
O_3	L	L

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