Sizing of Paper and Board

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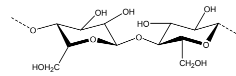
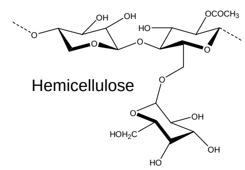
Chemistry of the Wood Fibre

- Carbohydrates
  - Cellulose (40-45 wt.%)
  - Hemicelluloses (20-30 wt.%)
- Lignin (20-30 wt.%)



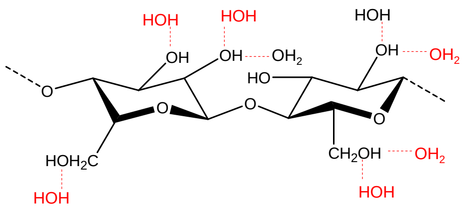
Cellulose



Hemicellulose

Carbohydrates: $C_n(H_2O)_m$

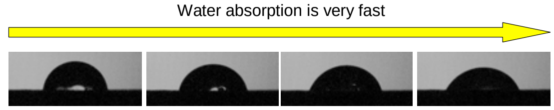
Carbohydrates Are Quite Hydrophilic



Heat of formation is 2 - 4 kcal per 1 mole of bonded water

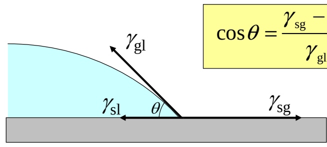
… and so is Paper

Water absorption is very fast



Contact Angle and Surface Energy

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{gl}}$$



Experiments show that, for unsized paper, the contact angle with water is zero.

that's because one says that unsized paper has high surface energy

$$\underbrace{\overbrace{\gamma_{sg} - \gamma_{sl}}^{\text{high}}}_{} \geq \gamma_{gl}$$

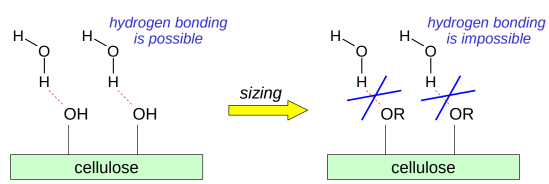
high

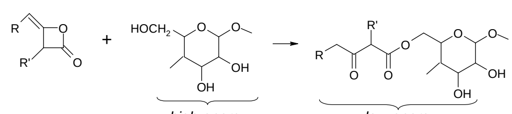
72 mJ/m²

unknown

likely quite negative due to hydration

The Idea of Sizing





Once again, What's High, What's Low?

Experiments show that, for sized paper, the contact angle with water is over 90º.

that's because sized paper is said to have low surface energy

$$\underbrace{\gamma_{\rm sg}-\gamma_{\rm sl}}_{\text{low}} << \gamma_{\rm gl}$$

low

72 mJ/m²

unknown

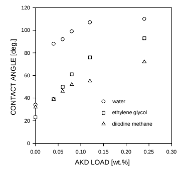
a large positive value as there's no hydration

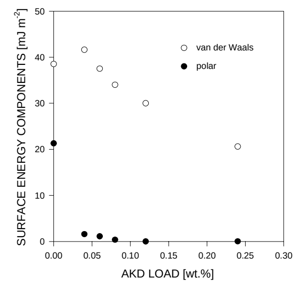
So, Sizing Reduces the Surface Energy

and the Oss-(not so)Good equation may be used to illustrate this,

$$\gamma_i(1+\cos\theta_i)=2[\sqrt{\alpha_i\gamma_{\rm vdW}}+\sqrt{\beta_i\gamma_{\rm pol}}] \qquad (i=1,2,...)$$

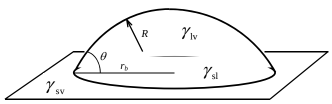
Wetting tests are done with water and ethylene glycol as test liquids.





Difficulties:
- Surface roughness/porosity;
- Extractives

Relation between Contact Angle and Surface Energy



Young-Dupré equation (energy-wise)

$$F=F_{\rm lv}+F_{\rm sl}+F_{\rm sv}$$
$$F_{\rm lv}=\gamma_{\rm lv}S_{\rm lv}=2\pi R^2\gamma_{\rm lv}(1-\cos\theta)$$
$$F_{\rm sl}=\gamma_{\rm sl}S_{\rm sl}=\pi R^2\gamma_{\rm sl}\sin^2\theta$$
$$F_{\rm sv}=\gamma_{\rm sv}S_{\rm sv}=const-\pi R^2\gamma_{\rm sv}\sin^2\theta$$

find the drop shape corresponding to a minimum of the excess free energy

$$\min_{\{\theta\}} F|_{V=const}$$

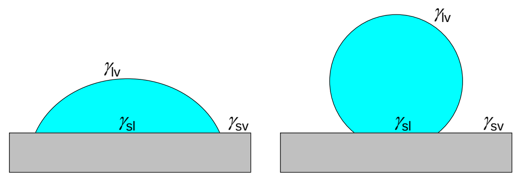
$$R(\theta)=\sqrt[3]{\frac{3V}{\pi(2-3\cos\theta+\cos^3\theta)}}$$

$$\boxed{\cos\theta=\frac{\gamma_{\rm sv}-\gamma_{\rm sl}}{\gamma_{\rm lv}}}$$

Thermodynamics of the Sizing Effect

A liquid drop will spontaneously spread over a surface as long as

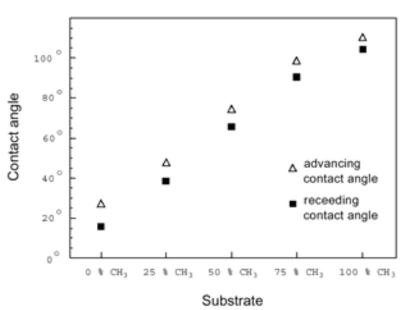
$$dF=d(\sum_1^3 S_{ij}\gamma_{ij})<0$$



not sized (hydrophilic)

sized (hydrophobic)

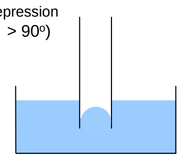
Relation between Contact Angle and Degree of Hydrophobization



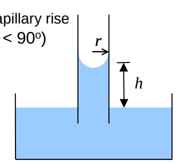
Fully alkylated (paraffin) surface has a contact angle of about 110º.

Capillarity and Wetting

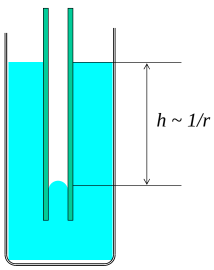
Depression
(θ > 90º)



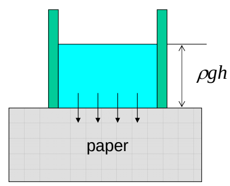
Capillary rise
(θ < 90º)



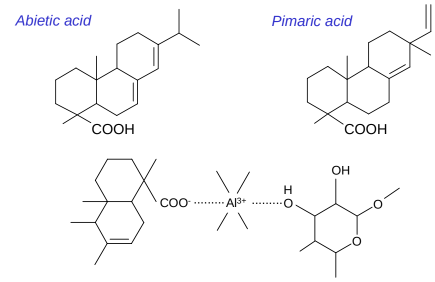
Hydrophobic Plug and Cobb Test



Cobb test
(h = 100 cm^3 / 100 cm^2):

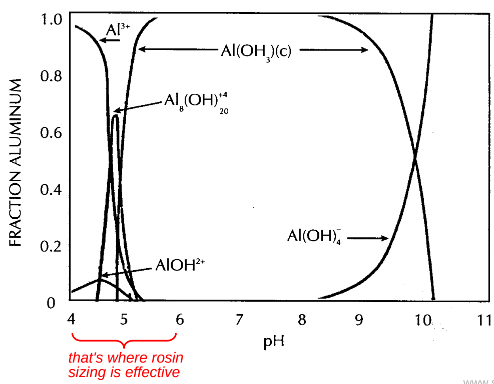


Rosin Sizing



- Rosin sizes are alkali metal salts of rosin (rosin is insoluble in water).
- Alum is essential for rosin bonding as rosin first react with aluminum ions and then aluminum rosinate is coordinationally attached to an OH group of cellulose.
- The best sizing effect is achieved at pH 4.2 to 6.5.

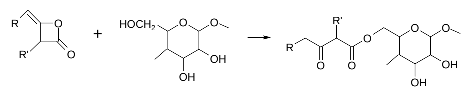
Alum Chemistry



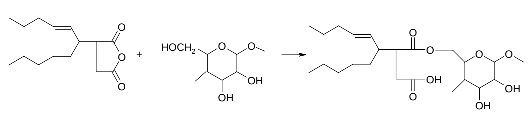
Cellulose-Reactive Sizes

Water is more reactive than cellulose

AKD sizing



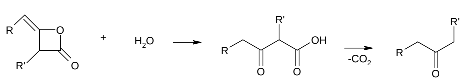
ASA sizing



Side Reactions

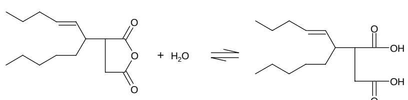
Size Hydrolysis

AKD



lactone *β-keto acid* *ketone*

ASA



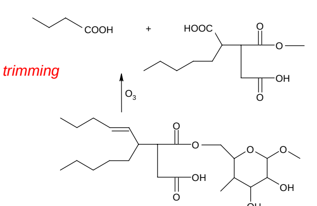
2,5-furandion ring *alkenyl succinic acid*

Mechanism: nucleophilic attack (S_N2)
Kinetics: 2nd order (autocatalytic effect is possible)

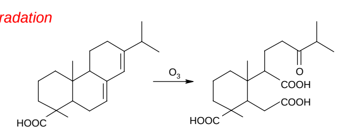
Side Reactions

Size Oxidation

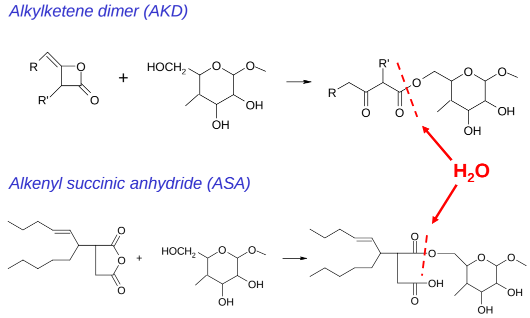
ASA chain trimming



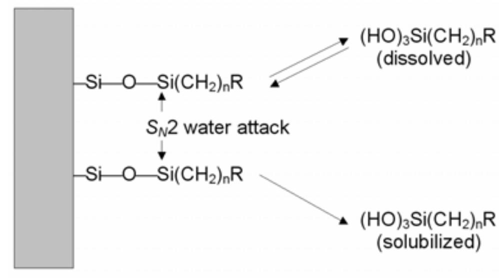
Rosin degradation



Surfactant-Induced Sizing Loss



That's How Surfactant Speeds Up Degradation of Hydrolyzable Hydrophobic Layers

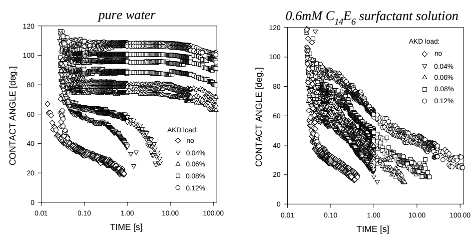


B. Zhmud et al., SILICA-2001, Mulhouse, France, September 1-5, 2001.

Surfactant-Induced Wetting ≠ Sizing Loss

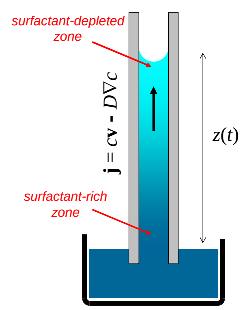
$$\cos\theta(c) = \frac{\gamma_{sv} - \gamma_{sl}(c)}{\gamma_{lv}(c)} = \frac{\gamma^0_{sv} - \gamma^0_{sl} + RT\int\Gamma_{sl}(c)d\ln c}{\gamma^0_{lv} - RT\int\Gamma_{lv}(c)d\ln c}$$

$$= \cos\theta(0)\left\{1 + \frac{RT}{\gamma^0_{lv}}\int[\Gamma_{sl}(c) + \Gamma_{lv}(c)]d\ln c + \ldots\right\} > \cos\theta(0)$$



Some Remarks on Wetting Dynamics of Sized Paper

Capillary Rise of Surfactant Solutions in Hydrophobic Capillaries



The concentration gradient near the meniscus,

$$\left.\frac{\partial c}{\partial \zeta}\right|_{\zeta=z} \approx -\frac{c_b}{\sqrt{Dt}}$$

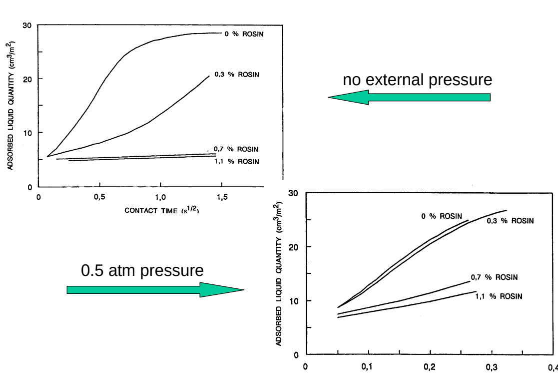
Mass conservation,

$$\underbrace{2\pi r\Gamma^m_{ls}\mathrm{d}z}_{\text{amount adsorbed to the wall}} \approx \underbrace{\pi r^2 D\frac{c_b}{(Dt)^{1/2}}\mathrm{d}t}_{\text{amount transported to the lv interface}}$$

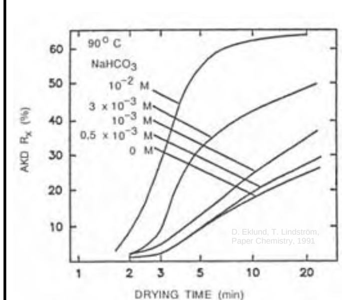
$$\boxed{z(t) \approx \frac{rc_b}{\Gamma^m_{ls}}(Dt)^{1/2}}$$

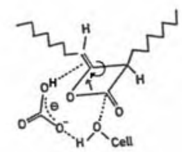
i.e. a pseudo-Lucas-Washburn behaviour!

Sizing Effect vs Size Load



Catalytic Effects in AKD Sizing

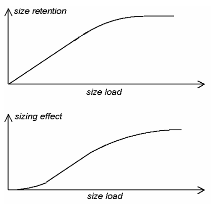


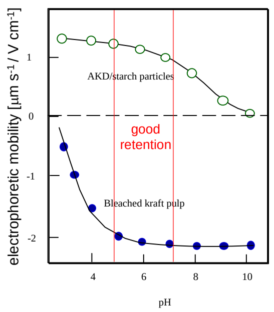


Size Retention:

Necessary But Not Sufficient Condition for Good Sizing

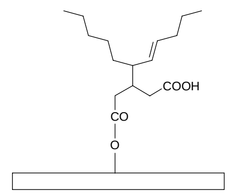
Retention mechanism:
- Charge flocculation
- Bridge flocculation



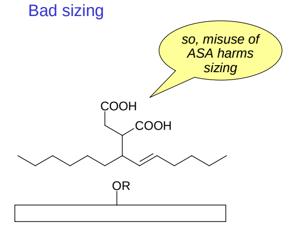


Molecular Criteria of Good Sizing

Good sizing



Bad sizing



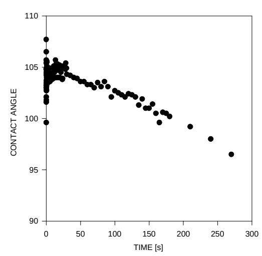
- Uniform surface coverage
- Proper molecular arrangement

- Non-uniform surface coverage
- Improper molecular arrangement

Persistence of the Sizing Effect

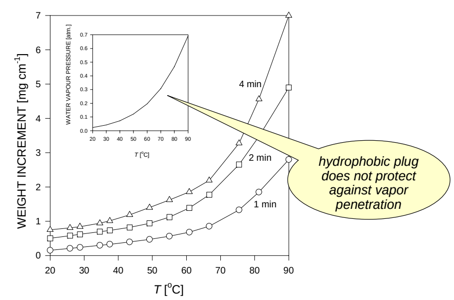
Sizing loss can occur due to

- Water vapours that cause hydrolysis of ester bonds and cleavage of hydrogen bonds in the cellulose
- Mechanical wear
- Size inversion or migration
- Size evaporation
- Surface-active compounds



Contact angle for water drops at the surface of a commercial AKD/rosin sized paperboard.

Effect of Temperature and Humidity on Durability of Sizing Protection

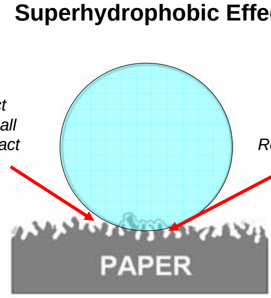


Edge penetration rate of water into PE-laminated AKD/rosin-sized paperboard. The inset in the graph shows the temperature-dependence of water vapor pressure in the same temperature range.

Superhydrophobic Effect

Projected contact area might be small while the real contact area is large

Reverse capillary effect "lifts" the drop



- Surface roughness of sized paper may affect the wetting dynamics.
- Measured contact angle may not reflect the surface energy.

Related Publications

1. J.C. Robert, Paper Chemistry, Blackie Academic, London, 1991.
2. W.F. Reynolds, The Sizing of Paper, Tappi, Atlanta, 1989.
3. D. Eklund, T. Lindström, Paper Chemistry, DT Paper Science Publ., Grankulla, 1991.
4. M. von Bahr, R. Seppänen, F. Tiberg, B. Zhmud, *J. Pulp Pap. Sci.* 30 (2004) 74.
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6. B. Zhmud, F. Tiberg, in *Surfactants in Polymers, Coatings, Inks and Adhesives*, (D.R. Karsa, Ed.) Blackwell Publ., CRC Press, 2003.
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12. B. Zhmud, 27th IARIGAI, Research Conference on Advances in Paper and Board Performance (Graz, Austria, September 10-13, 2000).
13. B. Zhmud, Pira Int. Print. Conf. "Ink on Paper" (Brussels, Belgium, Jan. 14-16, 2003).
14. B. Zhmud, Int. Conf. on Functional Materials (Kiev, Ukraine, September 24-29, 2002).