Additives in Papermaking

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Wet end chemistry
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Paper and paper products play an important role in our life; it is obvious to everyone. The uses and applications for paper and paper products are virtually limitless.

Paper defined by a felted sheet formed on a fine screen from a water suspension of fibers of and non-fibers materials.

Paper is made by:

- Pulping and bleaching, to separate and clean the fibers
- Beating and refining the fibers
- Diluting to form a thin fiber slurry, suspended in solution
- Forming a web of fibers on a thin screen
- Pressing the web to increase the density of the material
- Drying to remove the remaining moisture
- Finishing, to provide a suitable surface for the intended end use.

Papermaking processes

Dry Cont. range %	0.1-1.5 %	15-25%	35-55%	90-98%
Stock Preparation	Head Box	Wire Sec.	Press Sec.	Dryer Sec.
Function:	Suspension slurry	slurry Distribution	Web Forming	Web Pressing

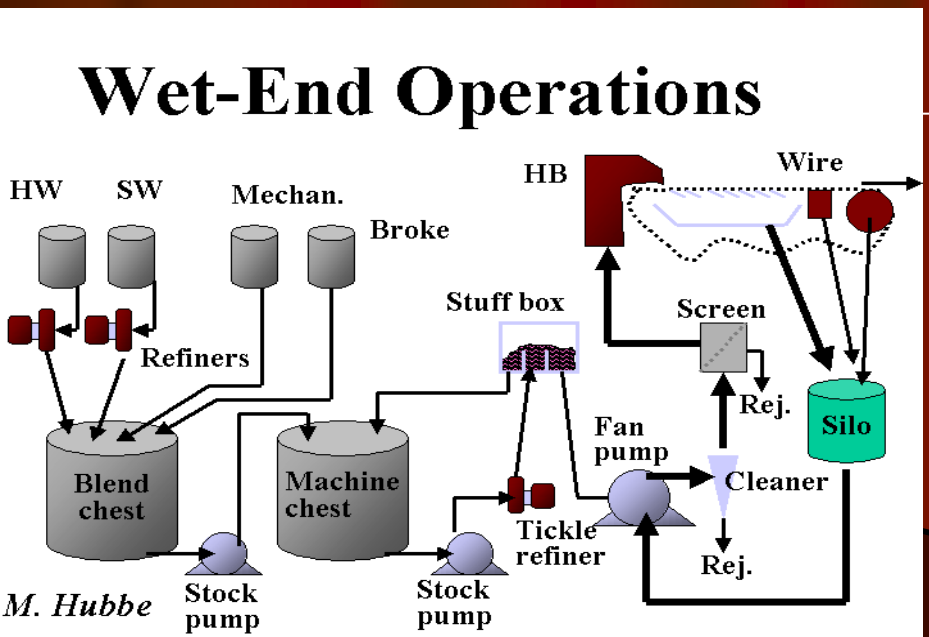
drying

Size Press → Dryer Sec. → Calender

Web sizing 60-85%

Drying 90-96%

Smoothening



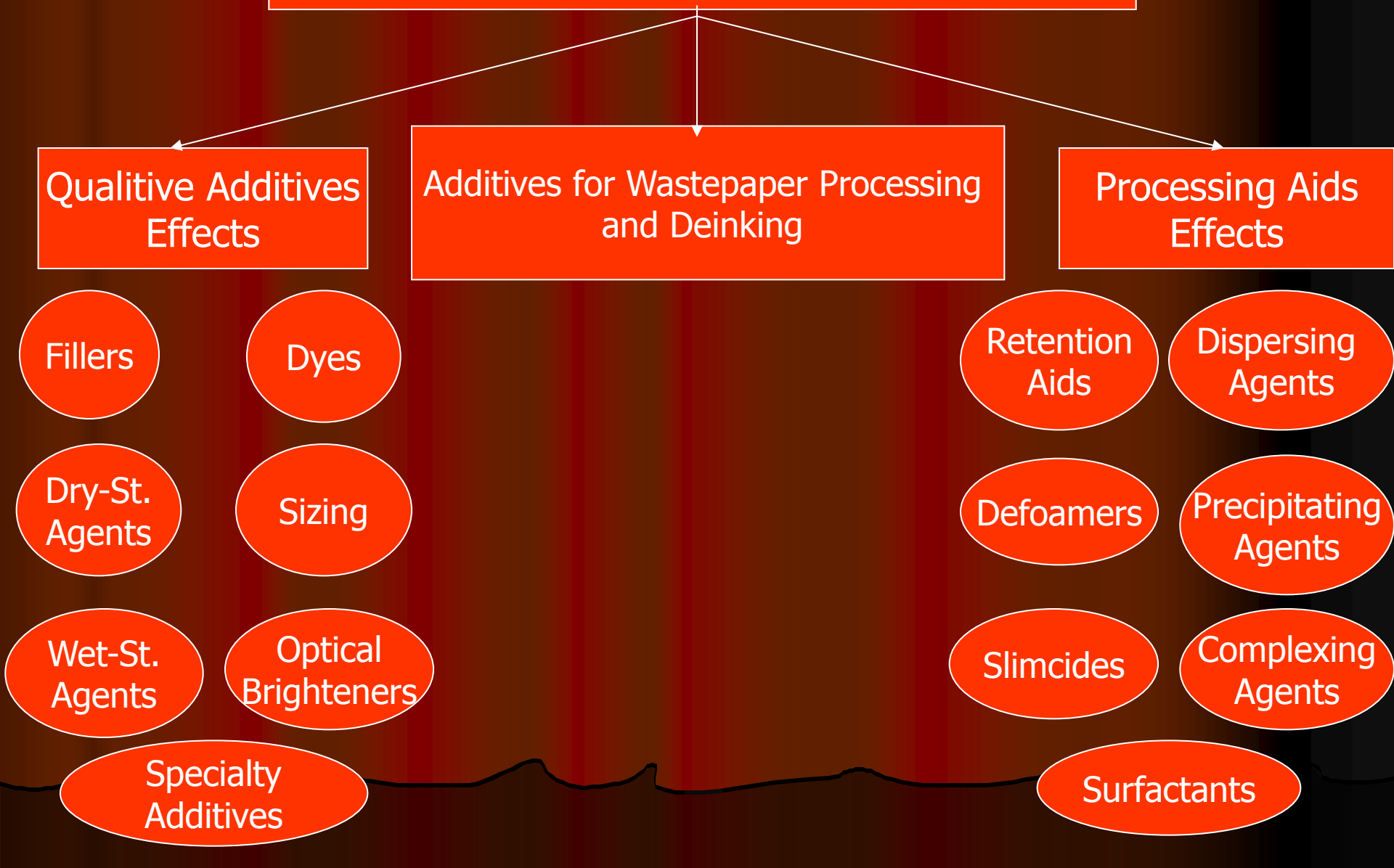
Paper = Fibrous + Non-Fibrous Additives

Non-fibrous additives are including in the pulp and paper industry for three main reasons:

- To enhance the properties of the fibers
- To introduce special properties into the paper or board product
- To improve the efficiency of the papermaking process.

The non-fibrous portion is added to the pulp furnish during papermaking operation either in the beater (Beater additives) or after beating the pulp in the stock preparation process (Wet-end additives).

Classification of Additives in Papermaking



Common Additives Widely Used in Papermaking

Additives	Application
Acids & Bases	Control pH
Alum	Control pH, fix additives onto fibers, improve retention
Sizing Agent (rosin)	Control penetration of liquids
Dry-Strength Adhesives	Improve burst, tensile and stiffness and pick resistance
Wet-Strength Resins	Add wet strength to such grades as toweling and wrapping
Fillers (clay, talc, TiO_2)	Improve optical and surface properties
Coloring Materials (Dyes & Pigments)	Impart desired color

Retention aids	Improve retention of fines & fillers
Fiber flocculants	Improve sheet formation
Defoamers	Improve drainage and sheet formation
Drainage aids	Improve water removal on wire section
Optical brighteners	Improve apparent brightness
Pitch control chemicals	Prevent deposit/accumulation of pitch
Slimicides	Control slim growths & other microorganisms
Specialty chemicals	Corrosion inhibitors, flame proofing and antitarnish chemicals.

Filling and loading Materials

Filling or loading, a traditional term means the incorporation of inorganic materials (fillers) into the fibrous web to improve the quality of papers .

Fillers are inorganic and organic mineral pigments which primarily used in printing and writing papers.

Advantages of fillers:

1-They increase the opacity and improve the surface and printability of the sheet.

2-Improving the appearances & absorbency of paper as well as increasing density.

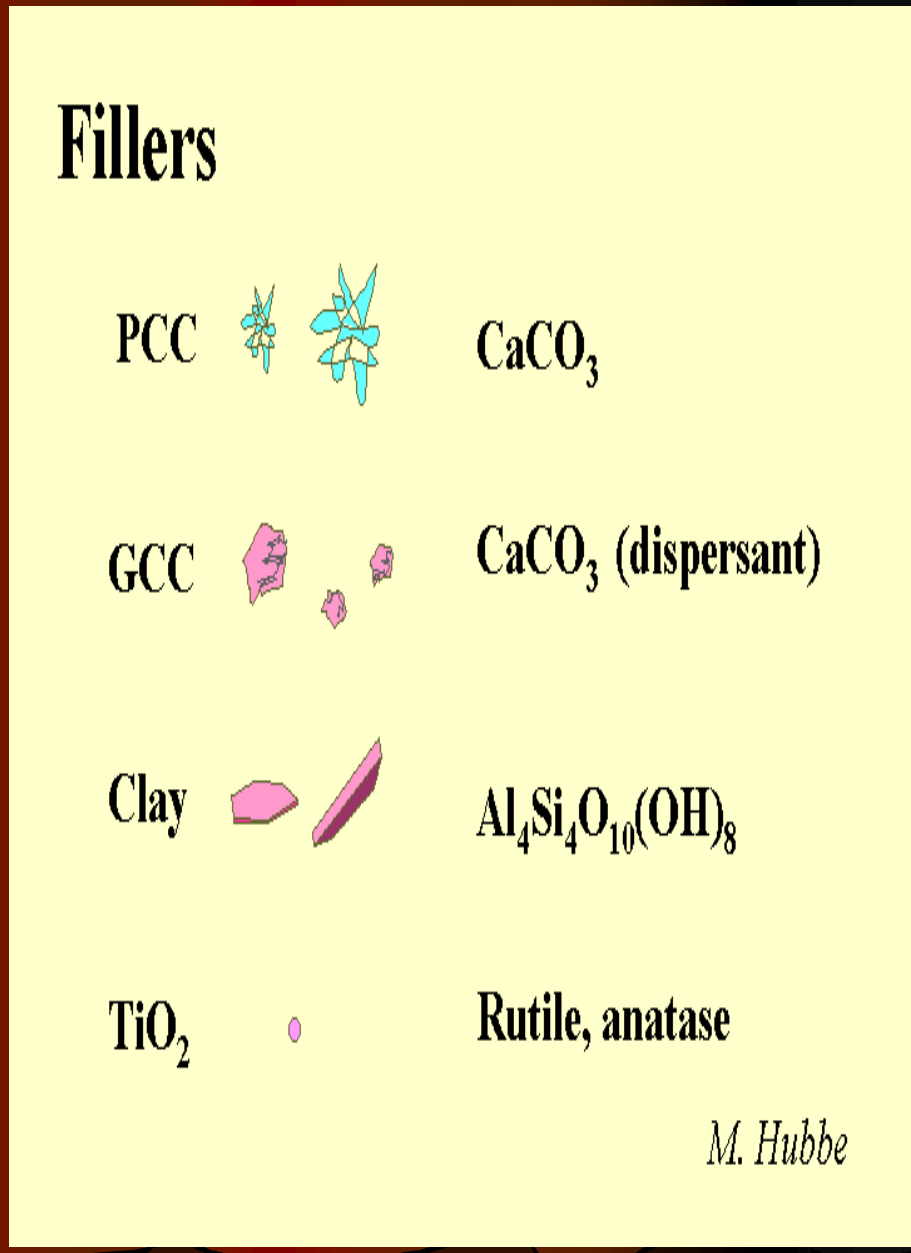
Types of fillers:

The principal fillers used are clay, calcium carbonate, talc, titanium dioxide.

Clay & calcium carbonate are the most widely used.

The filler should have:

High degree of whiteness
High index of refraction
Small particle size
Low solubility in water
Low specific gravity
Should be chemically inert
It must be cheap



Types of Fillers

General Purpose Fillers

Those used at loading levels greater than 10% wt.in sheet, such as **Clay,CaCo3(GCC&PCC), Talc(Mg3Si4O11.H2O)**

Other Types of Fillers

Used only for specialty paper because they are expensive and have special properties like:

Barite (Barium sulphate) ,

Magnesite (Magnesium carbonate),

Synthetic organic fillers.

Specialty Fillers

Those used at loading level less than 10% wt. in the sheet, such as **Tio2, calcined clay, UF, synthetic alumino-silicate and ppt.silica**

The effect of filler on paper properties :

In general, paper strength particularly burst and tensile strength is reduced by the fillers while the bulk per unit mass of fiber increases as well as optical properties.

The effect of filler on paper strength :

The addition of filler results in a significant loss in the strength this is due to, the pigment particles occupy the space between the fibers and, thus, interfere with the fiber bonding & decrease the number of bonds.

This leads to an increased number of fiber- air and pigment-air interfaces , which is the main reason why the opacity is increased.

Effect of filler on the optical properties:

1-The specific absorption coefficient (K) and the specific scattering coefficient (S), can be used to explain both brightness and opacity.

2-The increase in sheet brightness obtained by filling depends partially on the original brightness of pigment & partial on its particle size.

3-The opacity depends on the number of individual particles within the sheet, and on the refractive index of these particles .

4-Filler generally improve the smoothness of paper especially, after calendaring process.

Internal Strength Additives

- Natural Polymers

Starches
- **Unmodified**
- **Chemically modified**
- **Cationic starch**
- **Anionic starch**
- **Oxidized starch**
- **Dextrin**

Guar Gums
(natural & ch.modified)

Cellulose Derivatives
(Hemicellulose, Cellulose hydrazone, methyl cellulose & CMC)

- Synthetic Polymers

-Phenolics
-Lattices (Latexes)
-Polyamines
-Polyacrylamides
-UF
-MF
-Polyamides

Strength Additives

Wet-Strength Additives

It used for wetted paper sheets to protect the natural hydrogen bonds from attack by moisture.

These additives form additional water-resistance bonds.

Wet-strength agents included: Polyethylene imines (PEI), polyamides, UF & MF condensate, Polyamidoamine-epichlorohydrine (PAAE).

Dry-Strength Additives

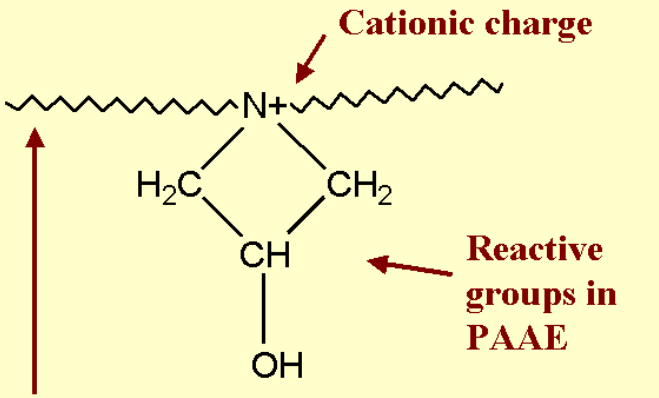
It used after sheet formed to increase fiber-fiber bonding and form additional hydrogen bonding.

These additives are water soluble hydrophilic natural and synthetic polymers.

Dry-strength agents also included: Cationic polyamideamine-epichlorohydrin condensate (PAE), anionic polyacrylamid, and anionic CMC.

New Wet & Dry strength additives

PAAE Wet Strength Resin



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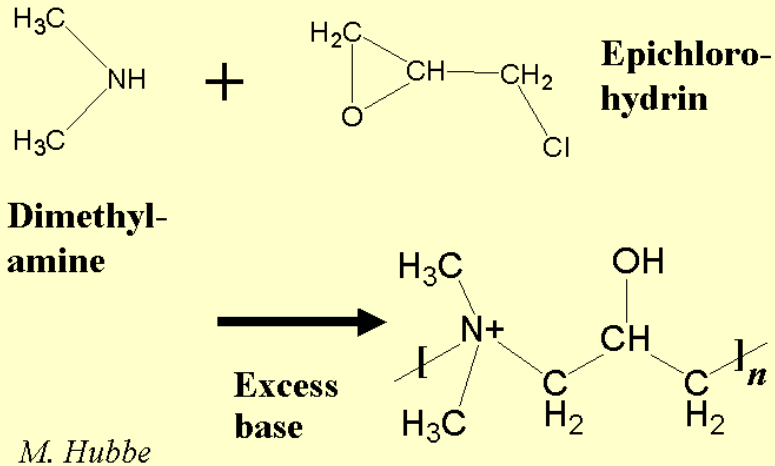
Synthesis of Polyamine



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Sizing Additives

- The purpose of sizing process is to enable paper products to resist penetration by fluids.
- Sizing makes paper hydrophobic and prevents the spreading of ink or color.
- This process is achieved either before sheet formation or after finishing by surface coating (size press).
- **Wet- end sizing agents included:**

1- Rosin & Alum

2- Alkyl ketene Dimer (AKD)

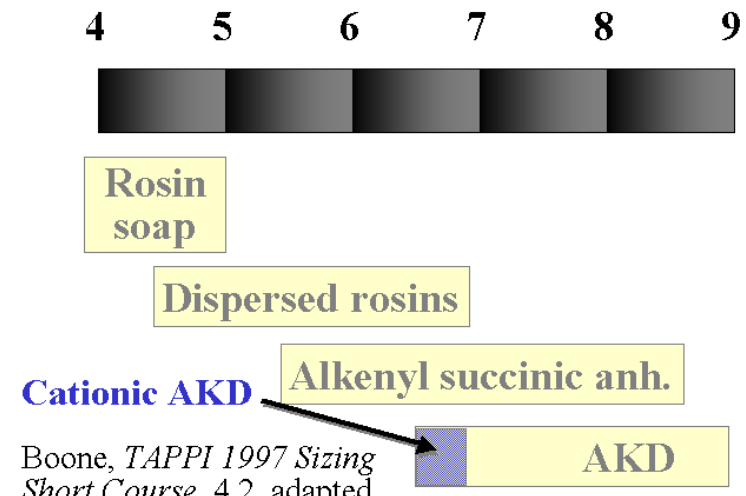
3- Alkenyl Succinic Anhydride (ASA)

Sizing Process

Sizing of Paper

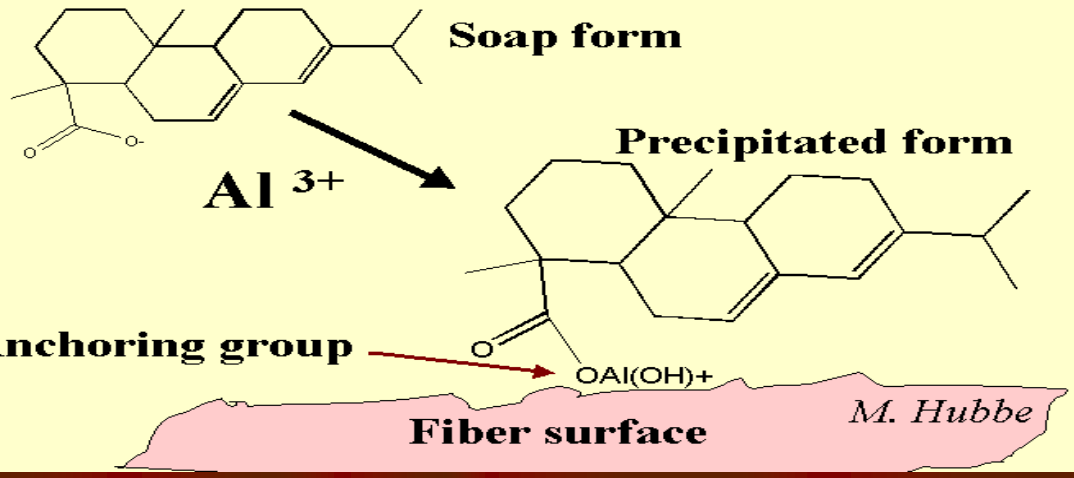
Type of sizing	Internal sizing	Surface sizing
Where added?	To the furnish	At the size press
What for?	Fluid resistance	Surface strength +...

pH Ranges of Sizing Agents

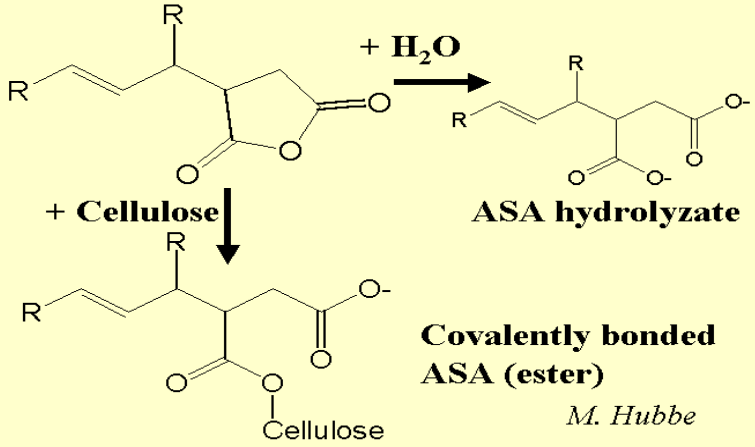


Boone, *TAPPI 1997 Sizing Short Course,* 4.2, adapted.

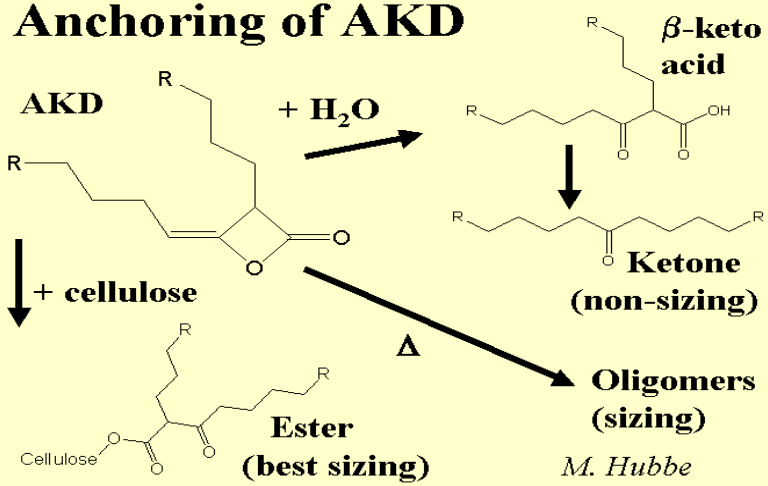
"Setting" of Rosin Soap



Anchoring of ASA



Anchoring of AKD



New Wet-End Sizing Agents

- Carbamoyl chloride (CC)
- Stearic Acid Anhydride (SA)
- Styrene- Maleic Anhydride (SMA)
- Styrene Acrylate (SA)
- Alkylated Urethane Copolymers

All of them more reactive sizes to react chemically with cellulosic fibers to render their surface more water repellent.

Dyes & Pigments

Dye: A chemical compound having the ability to absorb visible light over a certain range of wavelengths so that the diffusely reflected light appears colored.

Pigment: Finely divided particulate matter that is mainly intended to affect optical properties of a product.

synthetic inorganic (iron oxide, cadmium, chromium oxide); the organic (azo and polycyclic); and the metal complex pigments are used for paper dying.

Dye Classification

Class	Charge	Substantivity
Direct	Negative	High, all grades
Cationic direct	Positive	Very high, all pulps
Acid	Negative	Low, seldom used
Basic	Positive	High-yield fibers

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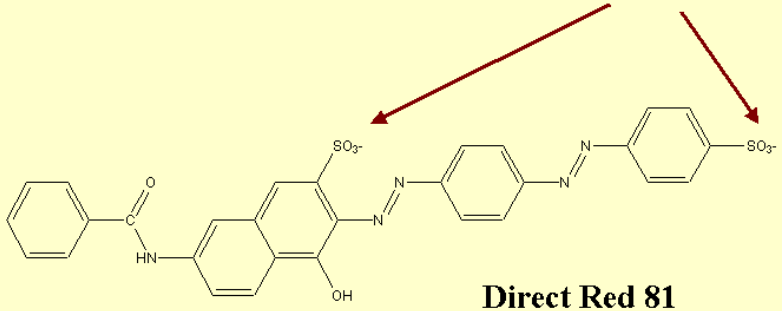
Direct Dye Example



Direct Red 81

$C_{29}H_{19}N_5O_8S_2^{2-}$

Exact Mass: 629.07

Mol. Wt.: 629.62

C, 55.32; H, 3.04; N, 11.12; O, 20.33; S, 10.19

Planar, conjugated structure

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Coloring Agents

The coloring of paper can be achieved by pulp dyeing, dip dyeing, or surface dyeing.

The most important processes are:

1- Penetration of the dye molecules into the capillaries and cavities of the pulp fibers

2- Adsorption of the dye molecules onto the inner and outer fiber surface

3- Formation of a sparingly soluble complex in the presence of salts or fixing agents.

Types of Dyes

Acid Dyes: Colorant molecules that have a negative charge as alkali-metal salts of dye sulfonic acids. They have no affinity for plant fibers and must be precipitated as colored lakes in the paper stock.

Basic Dyes: Colorant molecules that have a positive charge due to amine groups and have a strong affinity for the surfaces of high-yield fibers.

Direct Dyes: Dye molecules that are sufficiently large and planar that they tend to remain on a fiber surface without need of **a fixing agent.**

Direct dyes are usually the sodium salts of azo dyes containing sulfo groups.

Optical brighteners

- Optical brighteners are substances which transform ultraviolet light into visible blue light.
- Optical brighteners increase the luminosity as well.
- These substances are mainly derivatives of diaminostilbenedisulfonic acid and can form hydrogen bonds, allowing them to absorb onto cellulose fibers in the same way as direct dyes

Optical Brighteners

- Fluorescent: A property of some materials to absorb light of a lower wavelength, convert some of the energy to heat, and emit light of a longer wavelength
- Fluorescent whitening agent: A dye material that absorbs ultraviolet light and re-emits light in the blue region

Specialty Additives

- Fire-resistant papers are used for wallpaper base materials, Chinese lanterns and paper streamers.
- These papers are produced by the addition of flame-retardants to the pulp or to the coating.
- Examples include calcium chloride, magnesium chloride, diammonium ethyl phosphate and mixtures of zinc borates, antimony oxides and organic halides salts, as well as inorganic bromides and oxybromides.

Specialty additives

- Anticorrosion paper is impregnated or coated with chemicals that inhibit corrosion, e.g. sodium nitrite or sodium benzoate.
- Anti-rusting paper is coated by deposition of the chemicals from the vapor phase. These papers prevent the rusting of iron parts and the tarnishing of silver, aluminum, and copper.

Retention Aids

Retention aids are used in papermaking to retain fiber fragments and mineral fillers when the fiber suspension is filtered through the wire on the paper machine.

Flocculation: Another process used to collect fibers together in bunches especially in the presence of retention aids.

The retention-aids can cause the colloidal filler particles to deposit onto cellulosic fibers or to retain in the paper via chemical forces.

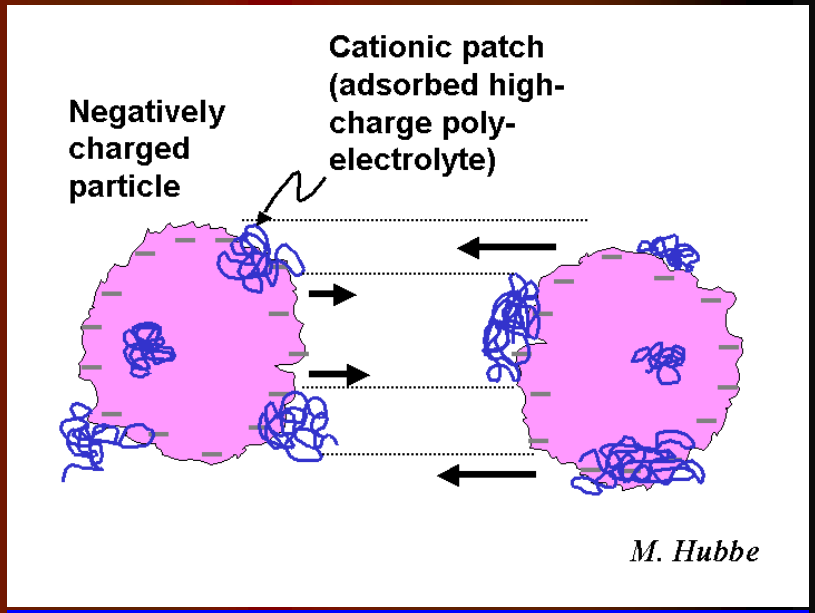
Types of Retention aids

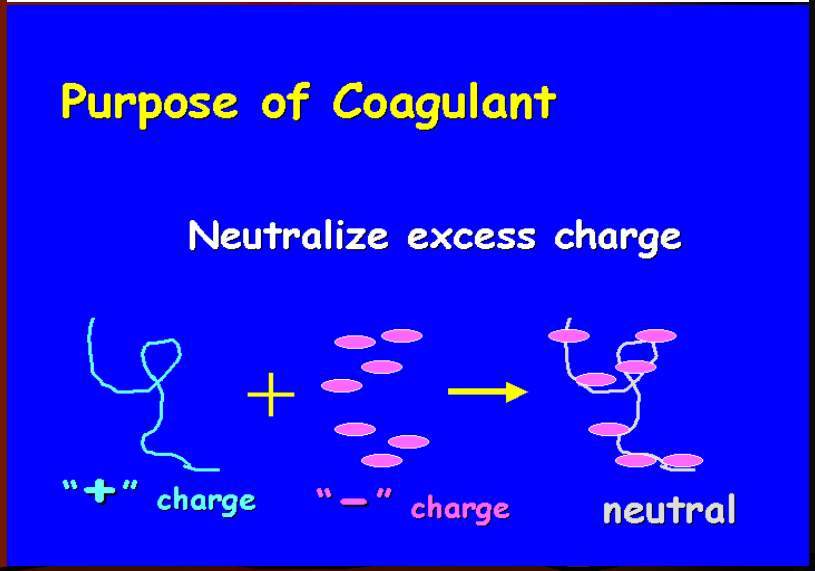
- Retention aids can be grouped together as follows:

1- **Inorganic retention aids** (Alum and silicic acid and cationic starch as dual retention aid system)

2- **Retention aids based on natural organic raw materials** such as cationic starch, gaur gum, CMC, Chitosan and dextrin

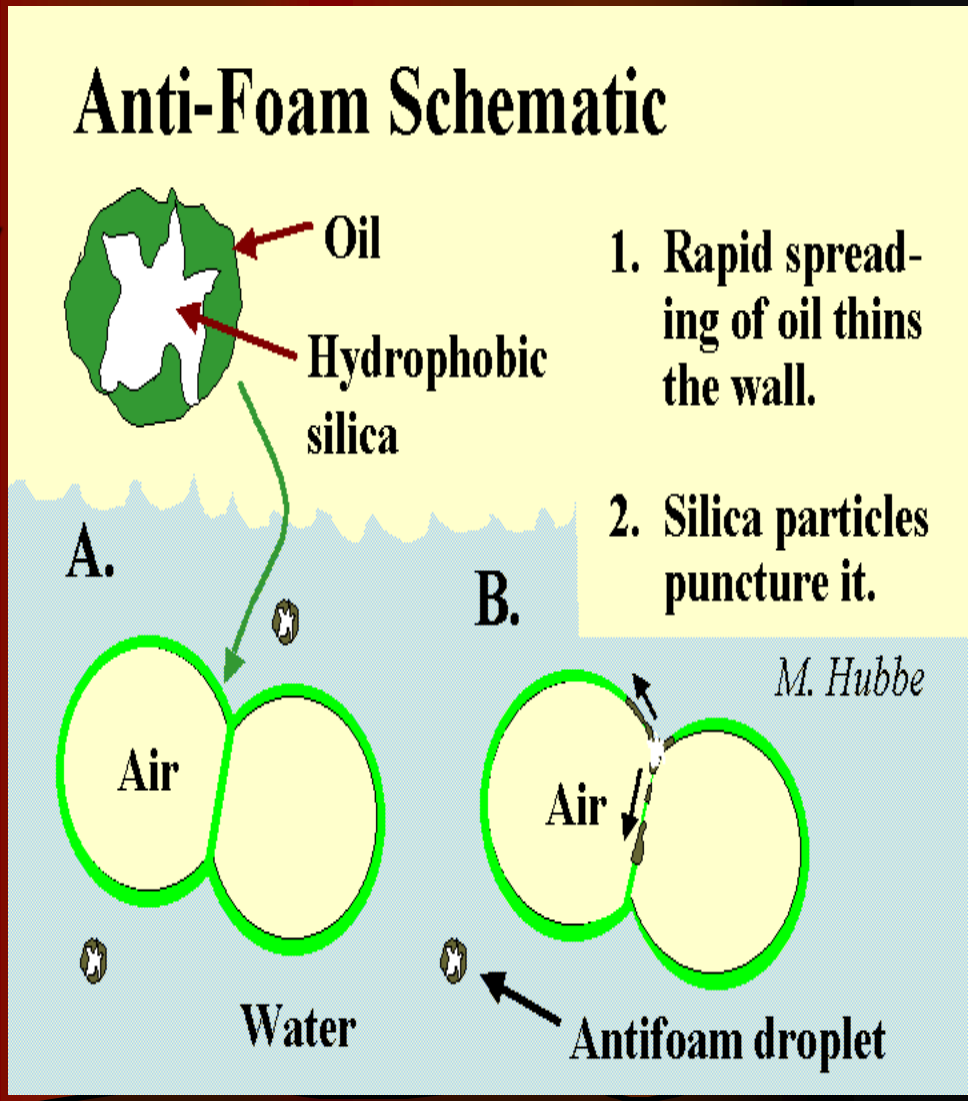
3- **Synthetic, water-soluble organic polymers** such as: polyacrylamides, polyamines, polyethylenimines, polyamido-amines and polyethylene oxides





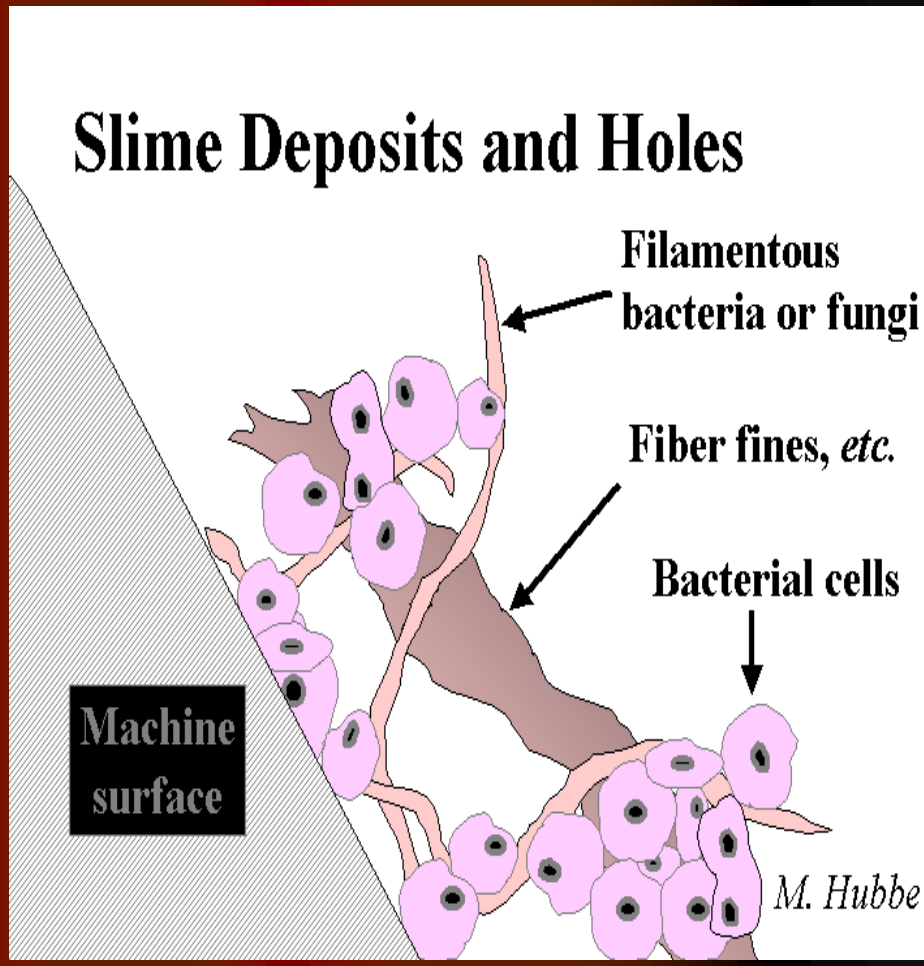
Defoamers

- Foam is a dispersion of air in water and lias physical and chemical causes.
- Defoamer: An additive mixture, usually containing a water-insoluble surfactant and often containing hydrophobic particles, that destabilizes foam bubbles.
- Antifoam: A defoamer product that has been formulated with the aim of preventing the formation of visible foam, not killing existing visible foam
- Defoamers include mixtures of higher alcohols, salts of fatty acids, and water-emulsible phosphate esters.



Slimicides and Biocides

- Slime: A slippery deposit composed of bacteria or fungal cells.
- Biocides: Chemical additives designed to kill slime-forming bacteria or fungi.
- Slime control agents include bromine, sulfur, nitrogen, or chlorine compounds. thiocyanates and acetic acid derivatives.
- Enzymes are very good at self-destruction
- Enzymes such as amylases are already used for cleaning up deposits on paper machine wet-ends.
- Biodispersants Another way to minimize the slime deposited.



Dispersing Agents

- Dispersing agents are required for both fibers and fillers.
- They increase the toxicity of slime control agents.
- They disperse resins and other sticky impurities originating from the pulp or wastepaper.
- Dispersants are either added during finishing or after the drying process.
- Dispersing agents are used in the transportation and storage of fillers and coating pigments to maintain them in pumpable slurry form.
- Dispersants substances included phosphates and acrylates compounds.

Complexing Agents

- The presence of heavy metals negatively influences many production processes and paper properties.
- Complexing agents that contain amino and carboxyl groups mask metal ions effectively.
- The most common complexing agents are: nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA). Diethylenetriaminepentaacetic acid (DTPA), and hydroxyethylethylenediaminetriacetic acid (HEEDTA), which mask metal ions by chelation.
- Other complexing agents include the soluble salts of oxalic acid, citric acid, tartaric acid, gluconic acid, amines, and ammonia.

Precipitating and Fixing Agents

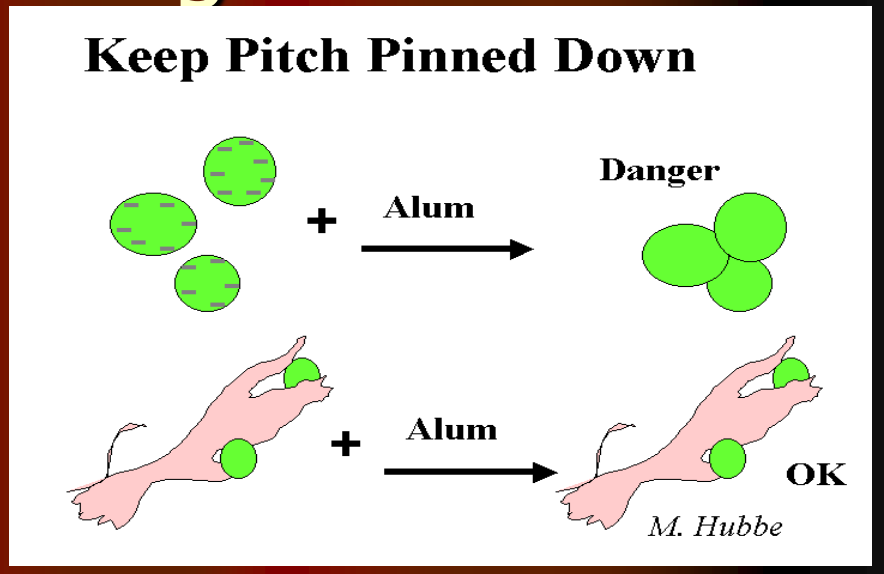
- **Precipitating and fixing agents** are used primarily for the precipitation of soluble substances onto the fibers.
- **Fixing agent**: An additive having the tendency to help retain dye material on fiber surfaces, usually because of a strong positive charge
- **Aluminum sulfate** is the most commonly used as precipitating agent.
- Other agents include condensation products of formaldehyde, urea, dicyandiamide, melamine, and condensation products of aromatic sulfonic acids with formaldehyde.

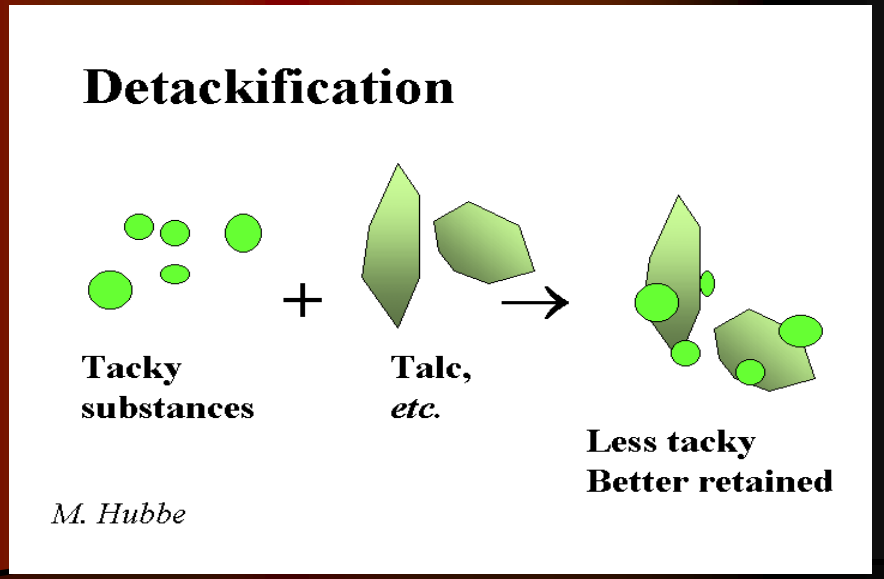
Drainage Aids

- Drainage: The ease with which water is released from among fibers during the formation of paper
- Drainage aids are usually inorganic polymers similar to those used as retention aids.
- Drainage aids function by binding the fines to the fibers. This prevents their forming flocks which would block the pores between the fibers during formation of the paper web, thus hindering drainage.
- Coagulants agents used in papermaking are generally multivalent or polymeric compounds of high positive charge density, such as, aluminum sulfate , polyamines, and polyethyleneimine (PEI).

Pitch Control Agents

- Pitch: Wood extractives, in the context of tacky deposits onto papermaking equipment or spots in the product. Talc, and highly charged cationic materials such as polyethylene-imine (PEI), polyamines, or poly-diallyldimethyl-ammonium chloride (poly-DADMAC) is the most commonly used as pitch control.





Additives for Wastepaper Processing and Deinking

Poly-aluminum chloride (PAC) is the commonly coagulate additives used in recycling process to improve the paper formation.

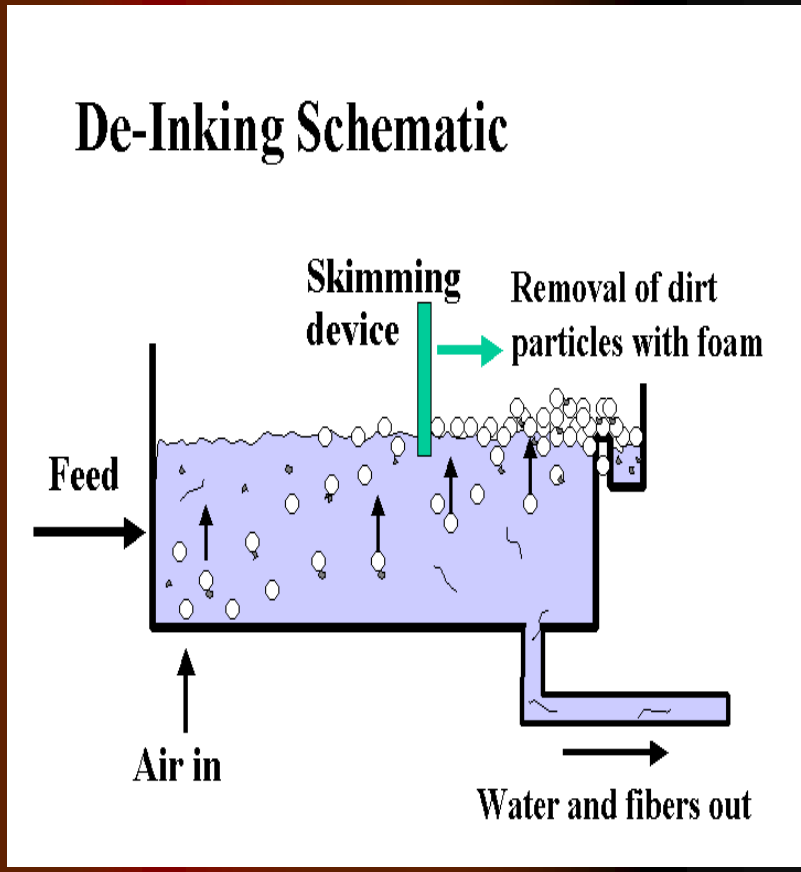
There are two main process for deinking “flotation and washing”.

The most commonly additives used in this process are, sodium hydroxide, hydrogen peroxide, sodium dithionite and calcium chloride added if the water is not sufficiently hard.

Water-glass is also added to stabilize the H2O2.

Soaps and fatty acids are used as dirt collectors and flotation agents.

Deinked stocks can be used only for newsprint up to approx. 60%, hygienic papers and improved recycling writing paper and in board production.



Conclusions

"High-Tech"

- It seems that no vision of the future ought to be complete without the words "high tech." In terms of papermaking chemicals, the key "high tech" trends to look out for will include automation, new sensors, bio-engineered processes or additives, and nano-technology. Recently it seems that nano-technology is a growth area for research.
- Bio-tech solutions are recently becoming important in the use of enzymes for deposit control and slime control. Enzymes also can be used to reduce the cationic demand of process water, especially in cases involving thermomechanical fiber. In the future we can expect to see more progress in the use of enzymes to assist with strength development and to promote more rapid drainage.