PRINTING INK TECHNOLOGY - HISTORY AND FUTURE TRENDS

Very little exist on history of ink manufacture because of 2 factors:
Early progress in ink development was very slow, with several centuries passing between improvements.
Most printers keep their formulations secret.

First inks developed: writing inks 2500 B.C. by Egyptian and Chinese cultures.
1st pigment was carbon residue called also lamp black- made by burning oil.
Carbon then stirred into solution of water and gum (sticky water soluble extract from plants)
Carbon particles did not dissolve, created colloidal suspension.
Such ink – endurance through 30 centuries- attributed to carbon ‘s resistance to light and moisture.

3rd century- China- tree sap mixed with ground –up insects to create reddish dye
used for printing from wooden block.
4th or 5th century –Chinese Wei-Tang- refined lamp black, water, various gums to create ink
Tang collected lampblack by burning oil under funnel shaped cover.
Cover brushed off onto paper, mixed with gums to form a paste.
Paste applied to wooden blocks for printing.
Sometimes formed crayon like sticks for writing: paste was poured into molds.
This type of ink- widely used in the Orient next 1,000 years.
Made its way from India to Europe, called India Ink.

14th century- Europe: India Ink does not work well with metal plates being developed.
Remedy this problem: European printers used linseed oil- extracted from flax plants.
15th century Gutenberg boiled the linseed oil and natural resin prior to adding pigment.
Result: Ink insoluble in water and enhanced ink bonding to page.
Gutenberg’ s ink formula cooking resin and linseed oil- created varnish to hold the lampblack- prototype of modern inks.
Gutenberg’s ink formula was altered only modestly next 300 years.
18th century English printer John Baskerville- developed blacker and more velvety ink.
18th century English patent first granted for making colored inks.
Until 19th century printers manufactured their own inks.
19th century rapid technological advance, improvement of ink chemistry accelerated.
Agents for speeding ink drying rates.
Stiffness of varnishes became controllable.
Vegetable oils replaced varnishes on newspaper presses.

TWENTIETH CENTURY
20th century sophisticated era- synthetic pigments and resins.
Last 60 years- dramatic change of ink technology.
(Different – new drying or ink setting methods) new printing/drying equipment.
or ink invented before new necessary equipment development of new substrates.

PAST TECHNOLOGY OF 20th CENTURY
Heatset inks
Heatset Printing: Invention of heatset inks – 1930’s.
Till then- most paste ink printing-sheetfed (mechanism of drying = oxidation 6-12 hrs).
Slow drying , because of that no fast runs.
Heatset inks: drying by combination of evaporation and penetration.
Contained 50% of a blend of petroleum hydrocarbons- narrow boiling range close to volatility of kerosene.
Hard resins (phenol-formaldehyde) were used instead of drying oils as binders, producing hard film.
Invention of web presses, speed 700 ft/min. Dried with metal drums heated with steam.

Steamset Inks
In the 1940’s - new types of inks and drying systems: Superheated stem blown on the web
Operating principle of inks: setting & drying through absorption of water vapor from steam to ink. Resin, soluble in glycol precipitates with water, bind the pigment to the substrate.
These inks were widely used - low odor products (paper bread bags, waxed after printing).

**Web Offset Inks**
In the 1950’s litho presses redesigned from sheet-fed to web-fed.
Higher printing speed, different litho ink formulations.
Dried in seconds - by evaporation and penetration.
Similar solvents that were used in heatset letterpress, good water/ink balance, new synthetic resins - resisting fountain solution, maintaining good rheology of emulsified ink.
Inks- lower in tack to avoid picking.

**Flexographic Film Inks**
In the early 1960’s developed flexo ink able to adhere to new polyethylene films.
Flexo inks adhering to PE films for packaging markets.
New resin chemistry similar to NYLON- modified polyamide resins soluble in alcohol and hydrocarbons (for bread bags). Polyamide flexo inks became standard in packaging.

**Energy Curing Inks**
In the late 1960’s UV (ultraviolet) and EB (electron beam) curing inks invented.
No solvent, no resin- dried “cured” instantly upon UV or EB energy.
Stable until exposed to appropriate energy- could be left on press for extended time.
UV inks- monomers & prepolymers of unsaturated chemicals, and photoinitiator.
The EB inks- no photoinitiator – higher energy of electron beam.
New equipment needed- to safely cure these inks on press.
New elastomer materials for rollers and blankets (old would be attacked with new formulations). Safe handling- skin, eye irritation.
Slower curing of black, or metallic inks.

**High Speed Litho Inks**
In the early 1980’s litho press doubled operational speed to 2,000ft /min (10m/s).
Lower tack, changed rheology - to avoid damage of paper surface.
Attention to rate and type of emulsification.
New types of binder resins for achieving proper emulsification.
New design of dryers- longer (1 sec dwelling time).
Rate of diffusion of heatset solvent through partially dried ink films.

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**PRESENT TRENDS**
Driving force in 1990’s:
Increasing regulatory pressures
Increasing local geographic and global competition
Competition from other communication media
Demand for improved production efficiency, consistent quality of printing

**Many challenges to litho ink technology:**
Current litho press speeds are 3,000 ft/min (15m/s).
Controlled dot gain and good uniformity of printed solids are needed.
Control of misting is needed (increases with speed of presses).
Wider water tolerance is desired.
Improvement of drying rates of ink in order to minimize the increased length of drying equipment.

**Packaging:**
Flexo water based technology has grown greatly, some problems remain:
Increased use of four color process demands better rheological control of formulations, dot gain control, color reproduction.
Increased drying speed, improving wetting and adhesion.
Research needed in innovative vehicle chemistry.

**UV-EB Technology**
Reduction or elimination of monomers (source of residual odor, may be cause of skin, eye irritation).
Controlled oligomer and vehicle rheology.
Choice of proper vehicle material to change viscosity.

Development of new reactive chemicals to improve the economics.

NEW MILLENNIUM
Lithographic Inks
Conventional litho market two-fluid printing –stable- a lot of presses installed.
Trends - waterless litho - single fluid without fountain solution.
New types of ink chemistry.
Press cooling systems will appear.
Coldset ink on uncoated paper- first candidate for self dampening litho.

Publication Gravure
Solvent based with the use of toluene - dominant - solvent recovery system - a must.
Replacement of existing hydrocarbon inks:
Water based inks -slower drying rates, press modifications required.
Phase-change inks (hot melts) -actively researched, needs proper rheology.
Must be run at elevated temperature – may limit the use of inks to new equipment
Change of hot-melts rheology to achieve good print properties.

Packaging Gravure
Water based inks more than 50% market.
Gift wraps- 100% water based.
Solvent recovery and incineration as control methods.

Flexo-Publication
Water based to replace letterpress newspaper printing.
Competition with Litho coldset market.

Flexo- Packaging
Increase its market share due to increased quality of 4-color process and good economics
Penetration of UV flexo inks, UV water reducible will continue to grow - narrow web, label printing.

Screen Printing
Continue to grow –specialized nature of inks, in unique processes.
UV inks, both water reducible and 100% solids will increase.

Digital Printing
Electrographic printing – Indigo, Xeikon, Docucolor, Spontane, various color copiers,
using “toner “ type of inks, both liquid and powder type.
Ink jet printing –continue to grow strongly.
Water based jet inks both dye and pigment type.
Other types- thermal transfer, sublimation, hot melt.

INKS MANUFACTURE
Stock inks- purchased off shelf by printers- standard requirements.
Unusual formulations- unique substrate, or end-use- special formulation.
Precise formulation: color, type of the press, substrate, end -use requirements.
Manufacture of inks- simple process- producing ink dispersion efficiently, reproducibly, and very quickly.
2 categories of inks:

Oleo-resinous systems (letterpress, lithography)

Volatile solvent/resin systems (flexo, gravure, and most screen-printing inks)- subdivided further:
a- based on water-reducible vehicles
b- based on highly volatile and flammable solvents- requiring special building, flameproof electric for manufacture.
Manufacture of inks- following operations:
Varnish – vehicle manufacture.
Manufacture of additives.
Dispersion of pigments into vehicles using milling/mixing techniques.
Three basic operations for liquid inks:
Mixing
Milling
Filtration
Mixing
Mechanical agitation of pigment and vehicle/ varnish together, till no dry pigment occurs.
In stages- first stage: introduction the pigment material into the vehicle.
Distributing the solid particles throughout the liquid.
Mixing- in batches cake mixers.
Mixers-vary in shapes and sizes, tubes holding 5-1,000 gallon batches.
Mixing speed determined by the viscosity or body of the vehicle.
Heavy paste inks- slow stirring, gradually to faster speed.
Liquid gravure inks- thousands of revolutions per minute.
Key goal- pigment wetting- put it in contact with vehicle, driving out the air pockets from around or within the agglomerates, pigment clusters.
Amount of time required: Viscosity of vehicle, Amount of predispersion
Flushed pigments- dispersed in proper vehicle (oil), easy mixing, or mixing omitted.
Inadequate mixing: inconsistent in performance, drying rate, appearance (ingredients not uniformly distributed).
Milling
Process where pigment /vehicle mixture is refined and pigment particles reduced to a size suitable for intended printing process.
Breaking down and further wetting of pigment agglomerates.
Amount of milling - depends on the nature of pigment, effectiveness of milling process.
Dispersion- breaking down the pigment agglomerates into individual particles.
Agglomerates broken up- air pockets flushed out, pigment wetting is improved.
Pigment particles tent to flocculate, reassemble into groups- dispersion must proceed to a point of stable pigment – vehicle mixture.
Paste inks, inks without volatile solvents milled in 3 - roll mill.
3 steel rollers- revolve in opposite direction at different speeds, generating friction on the nip, friction causes the reduction of pigment particle size.
Ball mill
Large cylindrical canister containing thousands of steel or ceramic media (balls).
Rotation- cascading down- friction between the media disperses the pigment particles.
Factors affecting degree of pigment dispersion:
Milling time
Size and shape of media
Rotation speed
Advantages of ball mill: Cheap to run (during the nights), they act as a mixer as well as mill, low maintenance cost.
Disadvantages: Bulky, noisy, only 50-60% of volume can be used for batch to cascade efficiently, cannot be speed up, emptying can be difficult- (thixotropic product), can only handle low viscosity inks.
Pebble mills- mill wall is lined with nonmetallic material; steel balls replaced with ceramic or porcelain media.
Shot mill
Stationary cylinder standing on an end.
Rod with several evenly spaced propellers on it rotating at high speed inside the cylinder filled with steel shot.
Ink is pumped into the bottom – making its way upward- being caught up in the steel shot.
Whirlpool –like flow pattern between each set of blades- breaks down the pigment.
As the ink reaches the top of the cylinder: screen- ink pass, shot stays.
Shot mills efficient in pigment dispersion, difficult to clean, tendency to clog = limits popularity.
Coating of pigment with polymer- micro-encapsulation.
Filtration
Liquid inks- remove grit, dirt- pumping the ink through the bag, that traps contaminants.
INK INGREDIENTS- continue..
SOLVENTS
Dissolve oils, resins, additives.
"Like dissolves like" - solubility parameters.
Solubility parameter is a measure of cohesive energy density (CED), proportional to the energy required to vaporise 1cm$^3$ of a liquid. CED$^2$ = Hildebrand parameter of solubility. Includes dispersion forces, polar forces and hydrogen bonding forces involved in solvents, plasticizers and resins interactions.
Solvent must:
Dissolve the resin, does not cause pigment to bleed.
It must evaporate at acceptable rate.
Must be compatible with printing plate.
Impart the flow and adhesion properties that are desired.
Flexo, gravure- mainly alcohols, toluene, heptane, acetate (SOLVENT INKS) publication, packaging
Flexo, gravure- water (WATER-BASED INKS) no emissions of volatile organic compounds (VOC’s).
Solvents with high hydroxyl content- polar- high dielectric constants.
Hydrocarbons- non-polar- low dielectric constants.
Crucial factor- volatility (speed at which it evaporates).
Not volatile- fail to dry quickly enough- smearing.
Extremely volatile- dry in cells.
Press becomes tacky, picks, tears the sheets.

ADDITIVES
Driers
Ink makes skin across the top of ink film- drying oil reacts with air oxygen.
Oxidation accelerated when catalyst (drier) is present Cobalt, Manganese compounds.
Manganese-promotes the drying through the film – through drier.
Manganese nitrate- removes fountain solution from inks.
Cobalt- promotes oxidation- top drier (Cobalt chloride, Cobalt acetate).
Cobalt – if dries too fast- crystallization, gloss ghosting.

Plasticizers
Resins- stiff, brittle in nature.
Printed on flexible substrate- cracking, flaking off.
Flexibility– needed for some applications- toothpaste tube, bread bag.
Plasticizers- make ink softer, more flexible, adherent to substrate.
Plasticizers- react with ink resin – polymer reduce crosslinking of polymers.
Plasticizers also: enhance gloss, improve adhesion to problematic surfaces, protect from becoming too brittle at too
low temperatures – frozen food packages, prevent blocking, less discoloration at higher temperatures.
Plasticizers- have high boiling points- do not evaporate- became permanent part of ink film
Plasticizers: litho, letterpress, screen, gravure, flexo.
Phosphates, epoxy-compounds, polyesters, sulphonamides, polyglycol derivatives, phthalates,
citrates.

Waxes
Improve slip and resistance to water.
Used in form of powder, or as a dispersion in oil vehicle.
Waxes move out from emulsions with the vehicle during drying, migrate to the surface- create film which not
readily accept subsequent ink- crystallization.
3-5% wax maximum. Excessive wax reduces gloss, increases drying time.
Used in flexo, gravure, most letterpress, litho, screen, carbon copying, hot melt inks.
Animal waxes- bees, vegetable- carnauba.
Mineral-paraffin, polyethylene:
\((-\text{CH}_2-\text{CH}_2-)\_n\) 1500-4000 FW
Teflon: Polytetrafluoroethylene PTFE: 2CHClF\_2 \rightarrow CF\_2= CF\_2+2HCl
Pyrolysis of chlorodifluoromethane to tetrafluoroethylene and subsequent polymerization at high pressure. Suitable
for all types of printing inks, ideal for heatset inks- high temp. of drying – no use of polyethylene waxes.

Petroleum waxes: extracted from crude petroleum- distillation of oils at 300°C and subsequent refining: C\text{15-H}\text{38} to
C\text{32-H}\text{66}, microcrystalline wax: C\text{34}-C\text{43}.
Petroleum waxes reduce tack of letterpress inks, slip agents.

Antiskinning agents- Antioxidants
Important for sheetfed offset, letterpress inks- prevents the ink from skinning over
React with free radicals formed during autooxidation- till antioxidant molecules are exhausted
Antioxidant incorporated into ink-delay the initiation of oxidative polymerization drying
Pyrocatechol, eugenol, guaiacol, butylated hydroxytoluene

**Wetting agents**

Pigment agglomerates – clusters together – air pockets form around these clusters- pigment does not disperse uniformly through the vehicle.

W. A. - Reduce the vehicle’s surface tension and help the vehicle penetrate the microscopic air pockets in pigment agglomerates.

**Defoamers for Aqueous Inks**

Defoamers – surface active blends of hydrocarbon liquids, surfactants, metal soaps, hydrophobic silica, with/without silicone modification. Used during the preparation of aqueous inks to prevent foam buildup- added also during application.

**FLEXOGRAPHY**

Flexography is the fastest growing conventional printing process, especially in packaging such as corrugated containers and flexible films.

It has made significant advances in publication printing, particularly newspapers.

Because the quality flexo printing has improved so much, it is now used extensively for process color printing on a variety of substrates.

It is used extensively for printing tags and labels, many in full process color.

**HISTORY**

Flexography was originally called “aniline” printing because of the aniline dye inks that were originally used in the process. Banned from the food packaging because of their toxicity.

Others coloring agents were developed which were safer, but the name aniline printing persisted.

Because the name still carried bad connotations, Franklin Moses in 1951 started a campaign to change the name of the process.

Over 200 possible names were submitted by readers of “Moss” publication the “Mosstyper”.

A subcommittee of the Packaging Institute’s Printed Packaging Committee, narrowed the choice down to three names- rotopake process, permatone process and flexographic process.

Mail –in ballots from the readers of The Mosstyper overwhelmingly chose flexographic process.

Flexo plates are flexible and imaged in relief, a natural outgrowth of the letterpress printing.

The origin of these plates was in rubber stamps, which were formed in plaster molds that had been pressed with lead type.

Thus, original plates for aniline printing were made of molded rubber.

Moss’s Mosstype corporation was a pioneer in rubber platemaking for both aniline and letterpress printing.

The first aniline press was built in 1890 by Bibby, Baron and Sons in Liverpool, England.

It used water based dye inks which were not chemically bleed proof.

Because the colors smeared and ran, the device was called Bibby’s Folly”.

In 1905 C.A. Holweg built an aniline press as a tail end unit on a bag machine.

1908 he made it the first patented aniline press.

The ink metering on these presses was crude until 1938 when the anilox roll was introduced.

This roll, patented by Douglas Tuttle and Col. Joe Viner, employed a mechanically engraved copper coated roll with controlled cell sizes. The idea grew out of gravure printers laying down coating from a uniform cell- engraved roll.

The anilox uses this process to coat the raised surfaces on the plate.

As with gravure cylinders, the anilox rolls were coated with chrome to prevent wear.

The original anilox inks gave way to ones based on polyamide resins.

These stable, fast drying inks enabled web speeds to increase from 150 to 750 ft/min.

The 1980 Clean Air Act lead to more extensive use of water based inks in flexo.

Water based inks are now used extensively for printing linerboard.

In the 1950’s, cosolvent and polyamide inks were developed for flexo printing on transparent polymeric films such as cellophane, polyethylene, and polypropylene.

In 1970’s rubber plates began to make way for photopolymer plates.

The use of photopolymer with their hard UV cured raised areas has enabled the significant improvement of the quality of flexographic printing. The print quality is rapidly improving.

**Flexographic Markets and Press Characteristics**

**Wide Web**

Plastic Bags

Bakery Products
Snack food
Candy and Confectionary
Frozen Food
Dairy Products
Industrial Agricultural
Meat, Poultry and Seafood
Fresh Produce
Dry Mixes (e.g., cereal)
Beverages
Drugs, Surgical, Medical
Household and Sanitary
Toilet, Cosmetic, Cleaning
Apparel / Textile
Tobacco Products

Wide Web Press Characteristics
Press sizes 32" - 65"; (40-50 most common)
Number of color units 1 - 10; (3 - 6 most common)
Run lengths (lineal feet) 30,000 - 200,000; (30,000 - 100,000 most common)
Press speeds (feet / min) 400 - 1,000 (600-600 most common)

Narrow Web
Industrial
Primary Labels
Specialty Labels
Grocery
Pharmaceuticals and Cosmetics
Tags and Tapes
Decals

Narrow Web Press Characteristics
Press sizes 1" - 18" (7-10 most common)
Number of color units 1 - 10; (1 - 3 most common)
Run lengths (lineal feet) 5,000 - 50,000; (5,000 - 20,000 most common)
Press speeds (feet / min) 10 - 400 (100 - 250 most common)

Folding Carton
Drugs, Surgical, Medical
Candy and Confectionery
Industrial / Hardware
Toilet / Cosmetic / Cleaning
Frozen Foods
Paper Products
Bakery
Automotive
Toys
Fast Foods
Dairy Products / Liquid Packaging
Apparel / Textile
Computer Supplies
Beverage Carriers

Wide Web Press Characteristics
Press sizes 28" - 44+"; (40"+ most common)
Number of color units 1 - 10; (2 - 6 most common)
Run lengths (lineal feet) 10,000 - 1,000,000; (10,000 - 500,000 most common)
Press speeds (feet / min) 400 - 1000 (400 - 800 most common)

FLEXOGRAPHIC PROCESS
Flexo prints from a raised image surface.
Flexo plates, whether molded from rubber or imaged from photopolymer, are generally made from flexible materials.
The simplest form of flexo process consists of four components:

- **Fountain roll**
- **Anilox roll** – ink metering roll
- **Plate cylinder**
- **Impression cylinder**

**Fountain roll** (usually made of rubber) rotates in a reservoir of ink and its purpose is to deliver a relatively heavy flow of ink from the fountain. Fountain roll and anilox do not rotate at the same speed – fountain roll is driven more slowly than the ink metering roll, causing it to wipe away excess of ink from the surface of the metering roll. The pressure and speed differential between fountain and anilox roller is considerable. Must be set to wipe off excess of ink from the surface of anilox, leave the ink only in engraved cells.

**Anilox roll** – Ink metering roll, made of either steel or ceramic materials. Surface is engraved with uniform cells that carry and deposit a thin uniform ink film onto the plate.

- Number of cells: 80-170 lpi (80-70 cells per linear inch).
- Anilox supplies a fine film of ink to the printing plate.
- The anilox is often used with a reverse angle doctor blade to wipe excess of ink = two roll system.

**The plate cylinder** is usually steel and installed between the anilox roll and the impression cylinder.
- Printing plates are attached to the plate cylinder with stickyback (a special double-sided tape).
- The plates raised surface picks up ink from the anilox and transfers it to the substrate.

**The impression cylinder** is smooth, highly polished metal cylinder. Impression cylinder backs up and supports the substrate as it contacts the printing plate.
- The contact point, or nip, gives “kiss impression” – the lightest possible impression that transfers the ink to the substrate.

**DESIGN**
- The design of a printing job for flexo is similar to that of all other processes.
- The desired printed image is designed and laid out on the computer.
- Negatives are produced photomechanically or digitally. Direct to plate systems for flexo are appearing on market.
- Compensation and shape distortion is an issue, which is not of importance for other printing processes.
- Printing plate elongation takes place when the plate is curved around the plate cylinder.
- This causes the print repeat length to increase and all design elements to grow in the circumferential direction.
- To compensate for this the image must be “preshrunk” along this direction.

**FLEXOGRAPHIC PLATES**
- Rubber plates – solid rubber pieces made from a mold. Mold can be used over and over to make new plates.
- Photopolymer plates have taken an increasing share of the flexo plate market.
- Photopolymers - light sensitive polymers that crosslink when exposed to UV light.
- Steps of preparing photopolymer plates are:
  1. Back exposure of base to UV light to harden (cure) the floor
  2. Face exposure of surface to UV light through a negative to cure the image area
  3. Washout of unexposed polymer with appropriate solvent
  4. Drying to remove solvent and restore gauge thickness
  5. Post expose to final cure of floor and shoulders
  6. Finish plates with chemicals or UV light to remove residual tackiness
- Photopolymer plates - 150 lpi - produce accurate multicolor registration and hold fine halftone dots.
- Acrylates commonly used as photopolymer material. Require photoinitiator to achieve curing in a reasonable time. Photopolymer layer in an unexposed flexo plate contains a thermoplastic elastomer, a polyfunctional acrylate monomer, a photoinitiator, and additives.
- UV light activates the photoinitiator, which starts the crosslinking.
- A popular photopolymer plate is produced by crosslinking poly (2-chloro-1,3-butadiene ), commonly known as chloroprene with trimethylolpropane triacrylate.
- Upon exposure the trimethylolpropane triacrylate crosslinks the polymer rendering it insoluble.
- The photoinitiator accelerates the reaction by UV light. The photoinitiator absorbs UV light, it splits apart into free radicals.
- The unpaired electrons on the free radicals attack the -C=C- (carbon-carbon double bonds) of the elastomer or the acrylate, which open up and react with other double bonds.
- Typical photoinitiator - e.g. benzophenone.
- The photoinitiators generally become part of the polymer chains and therefore initiate very long polymer chains.
The washout solvents are frequently chlorinated solvents—such as perchloroethylene. Because of environmental hazards of chlorinated solvents, substituents are being sought. Introducing carboxyl groups into the elastomer improves the solubility of the non-cured elastomers in washout solvents.

Most photopolymers work well with alcohol and water based inks. Oil based inks tend to swell natural rubber plates. Butadiene-acrylonitrile elastomers are used for oil based inks. Overall plate thickness and relief height vary with the substrate.

Plates for printing corrugated greater relief than for printing film or paper.

**FLEXOGRAPHIC PRESS TYPES**

The three types of flexo presses are most common: Stack, central impression, and in-line.

In the stack press the different color units of the press are stacked over one another on one or both sides of press frame.

There may be one to eight stations with six being the most common.

There are three advantages of the stack press:
- The web may be reversed to allow perfecting.
- The stations are very accessible.
- Stack press can print on a wide variety of substrates.

The central impression press, sometimes called drum, common impression or CI, supports all of its color stations around a single steel impression cylinder.

The impression cylinder supports the web and helps to maintain color registration between print stations. Its greatest advantage—holding registration.

The in-line press has separate color stations (new Comco press) in separate complete units driven by a common lineshaft. They are arranged in a horizontal row, each standing on the floor. They can handle wide webs. They are used for folding carton, corrugated, and multi-wall bag presses. Used also for pressure sensitive and standard labels. In line operations can be included right after printing section.

Flexo presses print webs as narrow as 4 in. (10.1 cm) and less for labels, and wide as 100 in. (25.4 cm) for shower curtains, toilet tissue. Speeds up to 2,000 ft/min (609.6 m/min).

**ANILOX ROLL**

The anilox roll (metering roll, engraved roll, ink aplicator, ink transfer roll) is engraved mechanically or laser engraved.

The anilox roll may be either chrome plated or ceramic coated.

Laser engraved rolls are generally ceramic coated prior to engraving.

The cells in a mechanically coated anilox are in the form of an inverted pyramid. The volume of inverted pyramid is given by:

\[ V = \frac{h}{3} [At + Ab + VAt Ab] \]

Where:
- \( h \) is the depth of the pyramid
- \( At \) is the area of the opening
- \( Ab \) is the area of the cell bottom.

Anilox cell volumes are typically measured in units BCM (Billion Cubic Microns per square inch). Unit obtained by multiplying the volume of a single cell by the screen count in line per inch squared.

A more sensible unit is micron \(^3\)/micron \(^2\). As a unit of length it gives a measure of the linear size of the cells.

Since the opening is the base of the inverted pyramid, it is the part most sensitive to wear.

Since the region around the opening contains the greatest volume per change in depth, a little wear can cause a significant change in the amount of ink transferred.

Anilox screen count should be at least three to four times the value of the plate screen. E.g. printing plate has screen of 133 lines per inch, it would require an anilox roll with a minimum screen count of 400 to 530 lpi.

Typically, a converter would choose a 550 lpi or 600 lpi anilox when using a 133 line plate, depending on ink volume required.

**Pattern of engraving:**

The cell structures may be of one of five types:

- **Trihelical, Pyramid, Quatrangular, Hexagonal, Hexagonal Channeled screen.**

  **A.** A trihelical screen is an unbroken line inscribed at 45° angle to the roll axis. These are used in coating applications of viscous fluids.

  **B.** A pyramid cell is a full inverted pyramid. These are primarily used in wipe roll metering systems.
C. A Quadrangular or Quad cell is truncated inverted pyramid. These are very versatile when used with wipe roll and doctor blade systems.

D. A Hexagonal cell is a truncated inverted hexagonal pyramid. These can be packed very efficiently in two dimensions and have very good release characteristics.

E. The Hexagonal channel screen is a deep hexagonal cell with a shallow vertical channel that links the cell. This releases heavy body inks. Gives the most even laydown of the ink.

The anilox is changing more rapidly than any other single component of a flexo press. They are made from a special grade of seamless steel tubing treated for engraving.

Anilox wear - profound effect on the volume of ink transferred.

20% reduction in depth of a pyramid cell can lead to 40-50% reduction in volume depending on the screen count and cutting angle.

It has been estimated that the approximately bottom third of the cell does not release ink.

So when the cell is worn down, the actual ink deposited may be only 40% of the designed amount.

The wear of anilox surface is caused by the use of doctor blades (DB).

The doctor blade removes the excess ink from the surface of the anilox and provides better control of ink transfer to the plate cylinder. This is particularly important in printing process colors and halftones.

There are several varieties of anilox rolls to choose from.

Smooth Ceramic- Long wearing, the least expensive anilox roll. Do not allow controlled metering of ink because of smooth finish.

Usually employs flame sprayed Aluminum or Chrome oxide.

Textured ceramic- Long wearing like smooth ceramic, but uses a coarser ceramic powder.

The surface roughness provides the mechanism of ink transfer.

Ceramic, Laser engraved - Longest wearing engraved metering rolls.

Available in screen counts 500 lpi. Cells are burned into the ceramic using a CO2 laser.

A wide variety of cell patterns is available, cells deliver repeatable metered volume of ink.

Stainless Steel or Nickel/Copper- Flame sprayed to a smooth finish similar to ceramic.

Engraved and chromed- most common engraved anilox roll for high quality print result.

Chrome plated for surface protection. Can be reengraved when worn.

Electronic engraving has come to flexo from the gravure industry.

The reverse angle DB used with anilox is very efficient. The theoretical ideal angle is 30 deg.

Newer chambered blade systems employ double doctor blades, one on the up side and one on the down side of doctor blade holder.

FLEXOGRAPHIC INKS

Water- based

Solvent- based

UV- curable

Water Based vs. Solvent Based:


Flexo inks- evaporate on the press- change viscosity- change color value.

Continuous viscosity control- adding solvent.

Variation in viscosity - major cause of color variation in flexo printing

Low viscosity needed to transfer properly. Too low viscosity - ink will not remain on the surface of the plate or have adequate density. Runs down the sides of image, builds halo around the printed image, fills in halftones.

Ink formulated with the correct balance of solvents- prints at lower viscosity than improperly formulated ink.

Solvent evaporates from ink fountain and rollers- change of solvents balance- more volatile solvent evaporates more readily- proper solvent mixture to replace evaporating solvent.

Aqueous inks- ammonia, morpholine base- volatile. They can evaporate on the press. Insufficient base is present- resin will precipitate- pH decreases, resin separates from the solution before ink is printed. WB- flexo- pH should be monitored while printing, additional base can be added.

Drying of ink can be regulated by adding faster, or slower solvent to change drying rate of ink.

Multicolor printing- several colors are printed in sequence. Building ink layers, influencing drying rates.

Drying rates- must be graduated- selecting right solvents- to ensure proper trap.

First down- fastest solvent, last down- the slowest solvent.

Formulating Principles

3 main components: colorant, binder, solvent, and additives.
Water-based Inks
Styrene-maleic, rosin-maleic resins (base: ammonia, morpholine)- low gloss, poor rub

Problem: Organic pigments are not compatible with the resins for WB - coagulate
Solution 1: Pigment chips- use of acrylic carrier to produce acrylic color concentrate
New pigment application must be utilized to produce pigments that have water stability
Stabilize pigment not to gel, flocculate, or separate over time.
60% organic pigment 40% water soluble acrylic resin (compatible with other w-b resins
Pigments: Azo, Naphtol Red, Diaryllide Yellow, Phthalocyanine Blue and Green, Methyl and Carbazole Violet. No additives, dispersants, defoamers
Pigment and acrylic resin combined via pre-mixing. Dry mix is dispersed on high horse power heavy duty two-roll mill with power knives. Two roll mill sheets are cooled and chipped via a mechanical chipper to uniform non-dusting particle size.
Dry mix: no settling, bodying, dusting.
Color chip: pigment locked into a vehicle system. Dry color concentrate cut at customer site. pH of cutting solution must be above 8.5 (morpholine, ammonium derivatives)
Solution 2: Addition of surfactant to disperse the pigment

News Inks
Flexo newspapers- acrylic polymers ammonium salts, amonia evaporates - free acid groups- precipitate. Good rub resistance.
According to Research Institute of the American Newspaper Publishers Association (ANPA/RI) – evaluated most suitable processes to print newsprint: Flexo was the most suitable. Flexography meets the requirements of: Low cost press, high quality reproduction, minimum printed waste, a low cost plate, minimum personnel needed for operation and maintenance, adaptability to different types of inks.
Newspapers printed flexo: Pittsburgh press, the Easton Express, the Providence Journal Bulletin, the Greater Buffalo Press (four color comics), the Washington Post.

Flexographic Inks for Various Substrates
Solvent inks- coated papers, lightweight stock.
Polyethylene – coated paper and boards – need corona treatment to increase surface tension – to print with alcohol-based polyamide inks.
Polyolefin films, nitrocellulose, polymer coated nitrocellulose- printed with polyamide inks (excellent adhesion, gloss, flexibility). Nitrocellulose increases grease and heat resistance.
Polyamide co-solvent (alcohol and aliphatic hydrocarbon) gives good resistance to water, acid and alkali.
Polyvinylchloride films contain plasticizers- may bleed back to ink, soften it, create blocking problem.
Alcohol reducible nitrocellulose and polyamide inks- useful for printing aluminum foil.

Surface printing, Reverse printing, and Laminating
Surface printing- to any substrate.
Reverse printing- to underside (corrugated, laminated films).
Combination of film or foil on paper or other foil- protection from oxygen, moisture
Ink reverse-printed before other material is laminated to it. Ink must adhere well to both materials used. Ink must have low solvent retention- solvent must not be trapped in between the layers.

UV Inks for Flexography
Recent years-development of UV inks.
First- modified letterpress UV inks with lowered viscosity, now different formulations.
Difficult- high pigmentation and good flow characteristics- heating up to 40oC (ink must be stable at this T).
Label Flexo UV Inks
Main flexo market- flexo labels : Self-adhesive label printing , flexo is cheaper and simpler than letterpress.
Formulations- almost like at letterpress, but more reactive diluent, less prepolymer and filler.

Example of UV ink for printing labels:
Constituent Parts by weight
Epoxy acrylate 15
GPTA (glycerol propylated triacrylate 30
TPGDA (triproplyleneglycol diacrylate) 31
Triethanolamine 3
Benzophenone 6
Polyethylene wax 1
Pigment 14
TOTAL 100
Carton UV Packaging Inks
Cost of UV flexo = ½ of offset litho
Good cure and rub resistance, low odor for food applications.
Example of Low Odor Flexo UV Ink for Carton Packaging
Constituent Parts by weight
Polyester acrylate 10
Epoxy acrylate 5
GPTA ((glycerol propylated triacrylate) 30
TPGDA (tripropylene glycol diacrylate) 31
IXT 2
Amine acrylate 3
Stabiliser 1
Polyethylene wax 1
Pigment 14
TOTAL 100
NEEDS:
Flexible packaging inks- need for solvents emission reduction- especially in food packaging- low odor, need for
good adhesion (frozen food), combined with low viscosity, good flow and substrate wetting characteristics.

GRAVURE PRINTING
History
The originals of gravure printing were with the creative arts of the Italian Renaissance in the 1300s.
1446- First intaglio plate engraved in metal used for printing.
Fine engravings were cut by hand into soft copper.
The engraved surface consisted of channels of sunken areas.
1505- Invention of Chemical etching.
Etching- fixing image on a metal surface by mordant (acid).
Inventors credited with the invention of etching: Daniel Hopfer- Augsburg (1505), Franco Mazuolli (c.1504-1540).
Chemical etching:
*Draw on soft “resist” coating over the plate
*Scrape away the resist layer.
*Acid would penetrate the exposed copper – dissolve it.
Another metals: zinc, steel (later).
Cylinder vs. flat plate
Pressure- considerable force needed to press entire surface of paper against an image carrier evenly- intaglio.
Early presses- made entirely of wood- possible to print only small images without cracking.
Limit- how much force to apply through a screw (hand- foot lever)
First metal printing press- 1550- larger sheets, but still difficult to operate.
Putting paper or image (or both) on cylinder- less pressure- image carrier touch only a small “print zone”.
The Italian word INTAGLIO (in-tal-yo) means engraved or cut in.
Intaglio refers to a method of printing whose image carrier consists of lines or dots recessed below the surface.
Intaglio reproduces original design by pressing paper into the recesses.
The first intaglio plate was used for printing in Germany in 1446 about the same time as Gutenberg.
Unfortunately, intaglio was not compatible with Guttenberg’s letterpress, so it was not adopted by early printers.
The modern gravure printing press resulted from the invention of photography and the adoption of rotary printing
from cylinders.
1818- first perfector- sheetfed press- took the sheet from the first form an printed the other side. Quadrupled the
output- from 250 to more than 1,000 sheets /hour.
Invention of Photography
1826- Joseph Nicefore Niepce- while searching for way to transfer images from litho stone to intaglio plates-
invented light sensitivity of some chemicals
1838- principles of photography tested and proven.
Dichromated gelatin as the sensitive coating on copper or steel plate – Fox Talbot placed leaves, laces on the coating and exposed it to daylight. Gelatin hardened where exposed to light. Washed with cold water, dried. Gelatin served as resist for etching solution. Etching solution penetrated the soft unexposed gelatin and etched underlying metal. All printing processes benefited. The use of photosensitivity to create new kinds of image carriers (faster to produce, easy to duplicate). Printers learn how to reproduce the fine grain and tonal variations of photographic print.

The Halftone Screen
1860-Fox Talbot – principle of the halftone screen. Black cloth between a light source and a photosensitive steel plate. He had imaged the plate with fine dots of varying size. Placing screens between a projecting lens and a photosensitive material- broke up continuous tone into discrete dots of varying size- it reproduced tonal gradation. This method is used to reproduce photographic images in all printing processes. Auguste Godchaux received a patent for a reel-fed rotary gravure perfector press in 1860, press still in use in 1940. 1890 -Development of photoengraving (Samuel Fawcet). 1892 -Karel Klic- number of patents- father of rotary gravure. Klic and Fawcet didn’t have patents of their process, so they tried to keep the process secret. They sold prints from their press as “heliogravure” prints, even though they were really rotogravure as we know it today. Their process remained a trade secret until an employee emigrated to the United States and made it public. Gravure presses were used to print Jell-O cartons starting in 1938. The process continued to improve with electromechanical engravers being introduced in 1968 with digital controls added in 1983. Rotogravure printing has a significant advantage relative to other printing processes for medium to long runs. Gravure can produce very high quality multicolor printing on a variety of substrates. Its success results from the simplicity of the process. Having fewer variables to control ensures consistent print quality throughout the run. Each print unit has 4 basic components: an ink fountain, engraved cylinder, doctor blade and impression roller.

The Gravure Industry
Gravure is the process of choice for long-run high quality publication printing. About 3 billion copies of gravure printed magazines are produced in a year. Sunday supplement magazines such as Parade are printed with gravure (National Geographic, Better Homes, Cosmopolitan) Reader Digest Newspaper inserts, catalogs, are printed gravure. Gravure printing is used extensively in the packaging industry. Gravure- folding cartons, flexible packaging made from paper, film, foils, laminated wrappers- Al foil. Labels are printed gravure. Gravure is used to print gift wraps, vinyl plastics- including wall coverings, shower curtains, tablecloth, ceiling tiles, decorative laminates, wood grains, floor coverings, paper towels. Sheedfeed gravure with plates rather than cylinders is used to print postage stamps, securities, currency, bank notes. It uses extremely high impression pressures, intaglio plate has continuous engraving, (not engraved discrete dots), ink is very pasty, heavy.

GRAVURE PROCESS
Gravure transfers ink from small wells or cells that are engraved into the surface of the cylinder. The cylinder rotates through a fountain of ink. The ink is wiped out from the surface – non-image areas by a doctor blade. The inverted pyramid- shape or cup-like shape of each cell holds the ink in place as the cylinder turns past the doctor blade. Laser engraved cells. Cells can be chemically etched or electro-mechanically engraved. The latest technology- electron beam engraving 150,000 cells/sec. (Electromechanical- up to 5,000 cells/sec.). The formation of perfect cells is accomplished by the gravure engraver. The gravure cell is characterized by 4 variables, depth, bottom, opening, cell wall. The depth of the cell is measured from the bottom to the cylinder surface.
The opening is described by the shape and cross sectional area. Bottom can be flat- or nearly flat – chemically etched, laser engraved or inverted pyramid shaped- electromechanical engraver with diamond stylus- 90-130 deg diamond. Cell wall- bridge is the surface of the cylinder between cells.

**GRAVURE CYLINDER ENGRAVING**

Chemical etching- historically three types of chemically etched cells- 
Conventional- same area, different depth, 
Lateral hard dot-variable size, variable depth and 
Direct transfer- variable area, same depth. 

The chemical etching of lines and dots through photo resist was the beginning of roto gravure. The carbon tissue method of image photo-transfer to a gelatin resist was discovered and perfected in the later quarter of 19th century.

**Traditional Chemical Etching** - The same cell area, variable depth. 
1940-1960-conventional gravure etching –combination of 2 glass photo positives exposed to carbon tissue. Carbon tissue is a water sensitive fibrous paper coated with smooth gelatin resist. Tissue was etched by FeCl$_3$ ferric chloride- depth 45 micron, various screen counts. The resist is sensitized to light by submerging it into a potassium bichromate solution. The sensitized carbon tissue can be dried, and refrigerated until used in the photo-transfer process. Tissue is formed into a sheet sizes and wrapped around copper plated cylinder. A glass positive was used to expose the light sensitive gelatin. One positive is a continuous tone variable density image. The second positive is a gravure screen of specified count 100-200 lpi (lines per inch). The two positives are exposed consecutively to UV light on the same sensitized surface. After double exposure, the carbon tissue is wrapped around the cylinder and all the backing is removed. The exposed areas are hardened with alcohol and forced air dried. (This is done in amber light to prevent UV exposure). Variable thickness membrane is formed- depending upon the amount of light passed through the two positives. The membrane is thick in the highlights and thin in the solids. This controls how quickly the etchant will break through the membrane and begin to etch the metal. This process forms cells of variable depth, but uniform cross sectional area. Ferric chloride-reliable for copper removal at a controlled rate 

2 FeCl$_3$ + Cu -->2 FeCl$_2$ + CuCl$_2$

Ferric chloride +copper -->ferrous chloride +cupric chloride

Supplied at spec. gravity 48 deg Baume, carefully diluted for use (42 deg Baume), tested with hydrometers sensitive to .05 deg change. Lower concentrations tend to break down the gelatin and speed the process, while high concentrations pass more slowly through the gelatin. Temperature- constant, etching at constant conditions ? micron/minute. Impurities in HCl, Fe$_3$(SO$_4$)$_3$ - would cause problems.

**DIRECT TRANSFER (SINGLE POSITIVE)**

Produces cells of uniform depth, but variable area. 
1950s- photographic polymer films introduced to industry 
New transfer method- image transfer from film directly to metal, single positive or direct transfer system. Exposure through film to a resist coated cylinder. Wrap-around photographic film and light sensitive photographic emulsion Single film with combination of halftone and screened solids. 150 line screen engraved to a depth 42-44 microns. Finished etched wall is about 12 microns wide. Also other screens used: 175, 20, and 250 line hex-shaped screens. Normal etching time-3-4 minutes. Photopolymer emulsion- high contrast, high resolution emulsion, forming tough rigid resist layer when properly exposed and developed. Emulsion sprayed on cylinder surface with precise control – volume/inch square. Emulsion- light sensitive photopolymer – chemically altered after exposure. Exposure – UV light through photographic film as the film emulsion and polymer emulsion are in direct contact and rotated around circumference of gravure cylinder.
Several techniques to bring the positive emulsion in contact with polymer emulsion.
MYLAR drive film- continuous belt around 3 rollers,
One- drive roller, above it idler roll. Third- movable back and forth- Tensioning roll.
Film belt acts as a drive and overall contact impression device to hold the positive firmly in alignment and contact.
Positive film is aligned around the cylinder, the cylinder rotates against the drive film, in front of mercury vapor exposure light.

**DIRECT TRANSFER PROCEDURES**

Photo resist direct transfer methods and developing of exposed resist- similar in most processes. Photo resist-colorless when applied.
During developing process dark blue, green or black dye applied to softened resist.
Developer- water, rinsed from surface-carry away unexposed material, leaving rigid resist.
Cells develop cleanly leave exposed copper metal when resist developed away.
Etchant application- roller applied, rotated in bath, paddle splashed and sprayed. Time to etch 2-4 minutes.
Direct system- very accurate in color to color register, cell specifications. Not affected by humidity. Engraving can be interrupted, adjusted again and again.
Chemical etching- are quick, provide wider variety of cell configurations.

**ELECTROMECHANICAL ENGRAVING**

Electromechanical engraving is recognized as the most common method of cylinder imaging today. There are, however, many applications that still require chemically etched cylinders. Some of these uses include unique packaging products and specialty products such as wall coverings and flooring patterns. The ratio of electromechanical to chemical cylinder making is about five to one.

**Cylinder Cell Geometry**
The cylinder cells are the most important part of the gravure printing process. The quality of the printed image is dependent on the size, shape and depth of the cell.
The width of the cell refers to how wide the cell is in the cross direction. The depth is how far below the surface the cell extends. The wall is the barrier between the cells and is used to support the doctor blade. The top of the cell wall and the unengraved areas of the cylinder are sometimes referred to as the land.

The electromechanical method of engraving is a direct result of advances in electronic technology. There are two common types of mechanical engravers. One is a Helio-Klischograph and the other is an Ohio engraver. The Helio and Ohio are the industry leaders.

**Image Processing.** There are two methods for image processing on these machines. One method is from a direct positive photographic film image. This film image is mounted on a synchronized rotating drum and the varying density information is read by an electronic scanner. The scanned information is digitized and processed for the engraving section.
The other method of image input is through direct electronic transfer. The image information is scanned at another site and transmitted to the engraving machine by disks, tapes, phone lines or satellite.

Engraving. Once the image information has been scanned and digitized it is processed for the engraving section of the machine. The objective of the engraving process is to produce cells which, when printed, will duplicate the density of the desired image. The very small volume of ink must be controlled within the engraved cell volume. A typical cell volume is less than the size of a single grain of sand. All of these tiny cells, when printed together, produce a solid area of color.
The tool used for engraving these cells is a diamond stylus of triangular cross section that engraves an inverted pyramid. The digital processed image information is converted to an electronic vibration that produces a mechanical motion in the diamond stylus. The darker the desired image the deeper the diamond penetrates into the copper. The large cell will carry more ink and produce more density. Conversely, if a light tone is desired, the diamond makes only a slight cut into the copper.
The cells are cut at a rate of 4000 per second. The average processing time for a packaging cylinder is 30 to 40 minutes depending on how much copy needs to be engraved. The copper chips or debris from the engraving operation are collected through a vacuum system and recycled.

Electromechanical Cell Configuration. There are four basic cell structures formed during electro-mechanical engraving. They are compressed, elongated, normal and fine. By using these alternately shaped cells, color process printing becomes possible. The size and position of the cells begin to form a line screen image. This screening effect allows for the successful combination of the four process colors.
Corrections. The electromechanical process should begin with accurate film positives. Any color correction (or adjustment) should be made during the color separation (pre-press) stage.

Cost. A diamond stylus may cost between $500 and $800 and can engrave 600 to 800 hours. The diamond stylus can be resharpened at a cost of about $90. The cost of the cylinder base can range between $800 and $1,200. The engraving, depending on type and difficulty, can cost between $1,000 to $10,000. As you can see, the finished cylinder is a very expensive and significant part of the gravure process.

**PACKAGING PAPER SUBSTRATES**

**Paper-25-60 lb./ream**
- Packaging- specialty papers specially designed for given end use
- Several categories
  - **Uncoated Stock**
    - Papers made without any surface treatment – (only light surface sizing)
    - Uncoated –not sufficient smoothness, ink holdout
  - **Supercalendered Paper**
    - Smoother, denser than uncoated- fine halftone reproduction
    - Supercalendered- loss of strength, opacity, bulk
  - **Coated Papers**
    - Most widely used in gravure packaging
    - C1S, C2S, multiple coated
    - Mostly- blade coated – on paper machine, off paper machine, or combination of the two
    - Sometimes- coating + supercalendering
    - Gravure packaging- printed one side
    - Reverse side- required various properties on reverse side. Special quality-multiple blade coating.
  - **Label Stock**
    - Chemical wood pulp
    - Smooth machine or supercalendered finish- good printing, gumming characteristics
    - Clay coated on 1 side- C1S
    - Basis weight 40-80 lb./ream (25x38 in.)
    - C1S- variety applications
    - Usually supercalendered or multiple coated-high gloss smooth finish
    - Base sheet - needs sizing (or backside coating) to control curl
    - Curl- problem during sheeting, cutting, dye cutting, customer application process
    - Specific coating formulations: using delaminated clay, soft latex, blade coating
    - Uncoated- machine glazed, machine finish- to avoid blistering
    - Coated >uncoated in print quality
    - Uncoated- laminated structures
  - **Specialty Label Papers**
    - Citrus paper- withstand citrus juice packaging- free of pin holes
    - Can wraps- withstand high speed can wrapping operations
    - 35-55 lb./ream (24x36 in)
    - Beer label paper- white, good wet and dry opacity
    - Highly sized- wet storage
    - 40-55 lb./ream (neck-body of the bottle- differs)
    - Oil and grease resistant paper- OGR- treated with fluorochemicals- prevent penetration of oil, grease
    - Products: corn, cooking oils, salad dressings, cosmetic bottles
  - **Paperboard**
    - Heavier in basis weight, thicker, more rigid than paper- 0.012 in caliper
    - (Exceptions)
  - **SBS**
    - Solid Bleached Sulfate- 100 % bleached, virgin pulp
    - White sheet clay coated one side- improved printability
    - High quality performance, appearance – cosmetics, toiletries, pharmaceuticals
    - SBS- range of thickness, caliper, more smooth consistent in quality than other grades
  - **Coated Unbleached Board**
    - (or Natural kraft) variety of characteristics for specialty product needs
    - Made for variety of printing processes
Smoothness = f (n physical properties)
Increase of smoothness negatively affects: tear, basis weight, bulk, long fiber content
These properties required for high speed folding, glueability, tear, stiffness

**Recycled Paperboard**
Clay coated recycled paperboard- from recycled fibers
Detergent cartons, cereal boxes, diaper cartons, tissue boxes
Manufactured in layers top liner, filler, back (bottom) liner, chemical additives according to required properties
(grease, water-resistant grades)
Appearance- vary from manufacturer to manufacturer
Recycled Paperboards- vary in smoothness
Recycled Paperboards- compressible- printability- impression pressure (maybe increased)
- reduction of missing dots, snowflaking
Impression pressure- monitored (deforming the board)

**Outside Wax Laminated Paperboard (OWL)**
Packaging the products that require high degree of moisture vapor protection
(powdered, granulated dry bleach)
OWL -made by wax laminating a coated two side litho grade paper to an uncoated recycled paper board
Caliper- customer specification
Printing surface depending on paper surface, amount of the wax adhesive, surface of recycled board
High quality graphic reproduction
Temperature of gravure press dryers- excess T- delamination (wax melts)

**RUNNABILITY TESTS**
Physical properties - strength, durability- made according to standard test procedures
TAPPI- Technical Association for Pulp and Paper Industry
CPPA- Canadian Pulp and Paper Association
GATF- Graphic Arts Technical Foundation
ASTM- American Society for Testing Materials

**Burst**
Resistance of paper to puncture
Perkins Mullen instrument
Bursting pressure- applied by rubber diaphragm at controlled increasing rate
30.5 mm diameter
Bursting strength [kPa]
TAPPI T 403 OM-85

**CALIPER**
Thickness of the paper- perpendicular distance between top and bottom surfaces
Value given in micrometers, or thousands of inch
Pressure 50 ±2 kPa during 3 sec- determination of caliper
TAPPI T411 OM – 84

**HUCK-GRI PRINTABILITY TESTER**
Simulate gravure printing- evaluate smoothness- skipped dots, ink holdout, print through, print gloss
TAPPI Useful Method 561

**MOISTURE**
Loss of weight measured after being dried to a constant weight at 105 ± 2 oC

**BASIS WEIGHT**
Mass in pounds of ream of paper ream can be 480-500 sheets
Sheet can have 13 different sizes (traditionally from 19th century)
Grammage- ISO - air-dry basis: 23 ± 1 oC, 50% relative humidity

**PRINT QUALITY TESTS (PRINTABILITY)**

**BRIGHTNESS**
Amount of light reflected by a substrate [% standard]
Spectrophotometer- 457 nm diffuse illumination and normal viewing- ISO brightness (diffuse brightness)
TAPPI T452 OM-87

**OPACITY**
Show-through- of print from back side
Measure of hiding power (light scattered and absorbed) of the sheet
Amount of light reflected from a single sheet placed over a black backing, expressed as a % of reflection from the
same sheet backed by effectively opaque pile of the same paper
TAPPI T452 OM-87
COLOR
Can be measured with 3 well-known systems: Dominant wave length and purity, Hunter l,a,b and CIE L*a*b*
values- spectrophotometer
L* Lightness [%] ranging: 100% - perfect white 0%-perfect black
a* redness (+a) or greenness (-a)
b* yellowness (+b) or blueness (-b)
Standard TAPPI T 524 OM-86
GLOSS
Paper surface reflectance- smooth papers will give shiny, lustrous appearance
Specular gloss- the angle of incident light is equal to angle of reflected light
20, 45, 60, 75-degree specular gloss, 75 deg – paper specially
TAPPI T 480 OM-85
POROSITY AND INK HOLDOUT
Porous material- gaps- pores- passage of fluids (inks)
Porosity- measured as air permeability
Gurley Densometer TAPPI T460
Sheffield Porosity tester
Porosity by forcing air through paper, measuring the rate of the flow
Gurley- the time it takes for 100 cubic centimeters of air to pass through the sheet
Higher value- denser sheet
Sheffield- the rate of flow at continuous flow of air.
Parker Print Surf- the same principle
Here- the higher the number- the lower paper density
Porosity- high enough to allow vehicle to penetrate, pores small enough not to allow pigment to soak in. Ink
holdout- indirectly- gloss, density
SMOOTHNESS/ ROUGHNESS
Smoothness-top priority for gravure, offset
Smooth- free of irregularities
Measure smoothness- measure the extent of irregularities
Roughness- deviation of the surface from the ideal plane
Tests: smoothness of “free” surface vs. smoothness under pressure (mimic printing nip)
Air leak tests: paper pressed against annulus (ring) with flat surface
Flow of air between paper and annulus –measure of roughness
Sheffield Roughness – most widely used in USA
Clamps paper using 2 concentric annular lands (rings with indentations permitting air flow) against glass surface
Air-constant pressure, fills space between lands and paper surface
The air flow across the paper surface is determined
TAPPI OM-518
Parker-Print-Surf Roughness- widely accepted in last years
PPS- roughness under pressure

PUBLICATION PAPER SUBSTRATES
Substrates- play role in process color printing.
Provide the foundation and background for the ink film.
Substrate absorption- influence the resulting process color.
Substrate that absorbs more ink –results in reduction of gloss.
Less absorption- increased ink holdout- increased gloss.
ROTO NEWS
Variety of uncoated groundwood papers
Paper Committee GAA-classification system 1982
Classification based on: brightness, color, roughness
Brightness- measure of ability to reflect light ( reflectivity at different wavelengths
Color- perceived shade, hue. Color cast- yellow, blue, red
Smoothness- levelness of paper surface
Basis weight: Newsprint – ream 24x36 in (500 sheets)
Other paper grades – ream 25x38 in (500 sheets)
Basis weight : terminology based on paper sizes standard for sheetfed presses
Grammage : g/m² ISO (International Standards Organization)

5 categories of Roto News
Empiric measurements of paper samples, not intended to be recommended specifications for buying

**Group E: Newsprint**
The lowest price grade, used in gravure
Lowest brightness, greatest roughness, high color saturation

**Group D: Standard Roto News**
D- most economical grade of groundwood paper for gravure
Slightly brighter and smoother than newsprint, color saturation the same

**Group C: Premium Machine Finished (MF) Roto**
Originally: Tappi Brightness 58-62, PPS smoothness 2.5 - 3.6
Recent years: Brightness 60-66, PPS 1.8 - 2.8
New development: Soft nip calendering- improved smoothness
Soft-nip= running paper web through series of paired cylinders, one is made of heatable hard metal and the other
cylinder has soft covering
Varying temperatures and nip pressures, number of sequences
Most common: 33 and 35 lb. / ream (25x38 in); lighter, heavier- less frequent
Quality of MF- between newsprint and supercalendered grades
Price: based on brightness, smoothness
Before 1989- Major use- Sunday magazines, now- newsprint
High quality MF- inserts, flyers, also heatset offset
Producers: Boise-Cascade, Canadian Pacific Forest Products, Champion, Kimberley-Clark, Macmillan Bloedel,
Stone Container Corp.

**Group B: Hibrite Roto News**
B grades- better in brightness, smoothness- superior brightness
SC-B 64-65 TAPPI brightness
PPS smoothness below 2.0 micron
Brightness and smoothness- improved with fillers addition

**Group A: Supercalendered Roto News**
Supercalendering- method of sheet smoothing and polishing its surface to higher gloss through friction and
pressure
Stack of alternating fiber-filled rolls and chilled iron rolls
Supercalendering- polishes paper through pressure of iron and cotton rolls-“ironing” both sides of sheet- smooth
finish, high gloss
Steam showers-moisten the sheet
SCA Roto News- superior quality –70 TAPPI Brightness, bellow 2.0 micron PPS smoothness
SC-A+ grade current high-tech newest SC grade
New gap-former technology – distributing filler material close to paper surface- ink holdout and printability better
than SC-A
1994- USA consumption of SC papers- 1.9 million tons.

**Uncoated Groundwood**
Uncoated supercalendered- resemble Roto News, but contain high content of bleached chemical pulp, and fillers
Basis weight- 30-50 lb./ream (25x38in)
Gravure printed catalogues, newspaper inserts, magazines

**Coated Papers**
2 major categories- groundwoods and freesheets.
Coated- more expensive than uncoated- higher quality, richer image
Publication papers for magazine, catalog- coated to improve printability: increased ink holdout, smoother surface,
color, gloss, brightness, compressibility, enhances color fidelity
Coating: pigment: calcium carbonate, clay, Titanium dioxide
Binder: starch, latex- anchor the pigment to base stock
Coating: improves brightness, gives more pleasing shade, more even reflectivity, higher opacity
On-machine coating, off-machine coating, combination of the two
Off- machine- better quality
Coated papers: dull, mate, glossy
C1S, C2S
Multiple layers of coating (double coated sheet)

**Coated Groundwood**
1994 –U.S. consumption of all coated groundwood grades- 5.2 million tons
Principal papers – magazine printing
Coated Groundwood: 30-60% chemical pulp, reminder mechanical pulp, groundwood or TMP
Recycled, deinked pulp- in varying amount
Low to moderate pigment filler
Coating- 25-35% total weight
Basis weight: 28-70 lb./ream ((25x38in)
Light weight coated 40 lb./ream- majority
Brightness: 67-71 #4
Hunter Gloss: 45-60
Opacity : 87-92 (basis weight, mechanical fiber content) (MF-superior opacifying properties)
Blade-coated-coating similar to latex house paint,
White kaolin clay from Georgia.
Latex binders hold kaolin particles
Coated groundwood- #4 or #5 increasing brightness
Coated groundwood grades:
ULWC Ultra Light Weight Coated 32 lb.
LWC- Light Weight Coated up to 40 lb.
MWC- Medium Weight Coated over 40 lb.
Heavy Weight Coated HWC

**Coated Freesheet**
No groundwood, (freesheet, wood-free). Less than 10% mechanical pulp.
Higher brightness, gloss, grades 1-4 according to brightness
The highest quality (price) magazine papers ,
The heaviest basis weight- 35-100 lb./ream (25x38in)
Brightness 76-90
#1 and #2 76-82 , and over brightness, 60-110 lb./ream-annual reports, high-end commercial printing
#3 and #4 76-82 brightness, 45-80 lb./ream – catalogs, magazines, commercial printing
Coated freesheet- high basis weight, superior brightness, printed gloss
Mixture of hardwood , softwood kraft pulps, low to moderate filler pigments, some recycled fiber
Blade coated predominantly, roll coating, kaolin clay, calcium carbonate, latex resin.

**HYBRID GRADES**
In-between grades SC-LWC in brightness and gloss
New manufacturing technologies- new properties
FCO- Film coated offset- mechanical pulp, very thin film of starch with clay pigment. Film metered by blades onto a rubber roll, transferred onto paper.
Subsequently supercalendered.
Improved ink holdout
MFC- machine finished coated- coated with rolls or blades
Soft-nip calendering, all on paper machine.

**INK VEHICLES**
Vehicle- liquid portion of ink.
Vehicle composition determines: stiffness, drying rate, gloss, rub resistance,
appropriateness to printing processes
Vehicle: carries pigment, controls flow, binds the pigment to substrate
To bond pigment particles to one another, to substrate- resin (binder).
All of ink characteristics (except color) determined by vehicle.
Vehicle: Resin + Polymer and/or Drying oil + Solvent
Often, two or more components (resin + polymer, polymer + polymer, polymer +
drying oil) will be combined to capture desired characteristics of each.

RESINS
Natural:
- Rosin Based (lithography, letterpress, gravure, flexo)
- Cellulosic : Nitrocellulose, CMC, EHEC (flexo, gravure)
- Cyclized rubber (screen printing, offset duplicator)
Synthetic:
- Acrylic (flexo, gravure, screen printing)
- Vinlys (Screen inks)
- Maleics (Litho, flexo)
- Polyamides (Flexo)
- Epoxies (Metal decorating)
Synthetic- polymerization (condensation, addition of monomers). Controlled
reaction- product with closely controlled properties.

NATURAL RESINS
Rosin
Pine trees- wood rosin- crushing stumps of pine trees, extracting rosin and rosin oil
with petroleum solvent.
Gum rosin- tapping live trees, sometimes with adding aid to artificial simulation to
accelerate the flow of extruded sap.
Tall oil - kraft pulping by-product
Wood rosin, gum rosin- similar, gum rosin- higher melting point.
Rosin- amber in color, melting point about 60°C,saponification # 172, acid # 168.
Saponification #: total amount of -COOH groups (free –COOH and esterified with
triglycerides).
Acid #: amount of free –COOH groups in molecule. Titration of –COOH with
KOH, Acid# is number of milligrams of KOH required to neutralize 1g of resin.
Rosin- inexpensive, ecologically sound.
90% acids, 10% neutral material.
Abietic acid- main component of rosin, converts to levopimmaric when heated.

Rosin: Used in alcohol base lacquers, in combination with mineral oils- newspaper
inks. Raw material for chemically modified rosin- rosin soap, metallic rosinate,
ester gum, rosin maleic adduct, rosin-fumaric adduct, modified with phenolic, and
alkyd resins
Ester Gum and Ester of Rosin
Triglyceride derived from rosin. Reaction of rosin and glycerol.
Varnishes- good pigment wetting properties.

R.COO-CH2
I
R.COO-CH2 R- rosin acid residue
I
R.COO-CH2
Pentaerythritol ester rosin – higher softening point 112°C, quicker solvent release,
better alkali and water resistance- more popular
CH2-OOC.R
I
R.COO-CH2-C-CH2-OOCR R- rosin acid residue
I
CH2-OOC.R
Maleic resin and ester- wide use in inks, steam set, letterpress inks, water reducible
letterpress inks, water based flexo inks.
Dimerised or polymerised rosin- by heating with suitable catalyst.
Cheap gloss overlacquers, letterpress black inks.
Rosin modified fumaric resin – flexo and gravure inks, in combination with other
resins- high gloss.
Fumaric- isomer of maleic.

Nitrocellulose
Wide application in flexo and gravure inks (Paper, film, foil, board), in
combination with maleic, polyamide, acrylic resins .
Cellulosic- excellent scratch, and rub resistance. Heat resistant, withstand heat-seal
temperatures. Used for overprint lacquers.
Cellulose nitrate- made by treatment of purified cellulose \( (C_6H_{10}O_5)_n \) with excess of
nitric and sulfuric acid at O°C.
Nitration complete, product is centrifuged and washed with water.
2.25 -OH groups are nitrated- it corresponds to 12.2 % N in solid cellulose nitrate.
Dry nitrocellulose- explosive- dangerous to handle. Legal minimum is 25 %
alcohol- dampened nitrocellulose.
Grades of nitrocellulose – characterized by their N content.
For each N content several viscosities available.
White fibrous material, excellent thermal stability at room temperature.
Elevated T- decomposes violently.
Compatible with shellac, rosin derivatives, epoxies, short oil alkyd resins.
Outstanding film former.
Ethyl Cellulose
R-O-Na + C₂H₅Cl ---→ R-O-C₂H₅ +NaCl
Reaction of alkali cellulose with ethyl chloride under controlled conditions. 2.2-2.6 ethoxyl groups per anhydroglucopyranose unit.
Solubility varies according to degree of ethoxylation.
Lower content ethoxy- groups: plastic films. Compatible with rosin, esters, alkyds, methacrylates, styrenated alkyds, polyvinylchloride, nitrocellulose.
Lacquers, toughness, flexibility. Flexo and gravure formulations.
Cyclized rubber- rubber treated with acid, lost elasticity. Readily soluble in aliphatic or aromatic hydrocarbons, and esters. Compatible with drying oils, resinites, cellulose derivatives, hydrocarbon resins, maleics, modified phenolics. Excellent adhesion and rub resistance (offset duplicators- prevents ink from oxidation “stay open”). Litho inks, in combination with isophtalic alkyd. Softening point 110-140°C.
SYNTHETIC POLYMERS
Acrylic: The range of acrylic and methacrylic polymers are based upon monomers of acrylic acid CH₂=CH-COOH and methacrylic acid:
CH₃
I
CH₂=C-COOH
Easily polymerized and co-polymerized – because of highly reactive double bonds and miscibility with oil soluble and water-soluble monomers.
Polymerization in bulk, in solutions, suspension, emulsion using variety of catalysts.
Polyacrylic acid:
COOH
I
n CH₂=CH-COOH --→ -(H₂C-CH--)ₙ
Polymethacrylic acid:
CH₃CH₃
I I
n CH₂=C-CH₂-COOH ---→ (-H₂C-C--)ₙ
I
COOH
Acrylic: clarity, chemical inertness, very good light fastness.
Softening points vary depending on chemical formula, molecular weight.
Range of acrylic resins so wide- soluble in almost any solvent system used in modern printing inks. Ability to co-polymerize, cross-link with epoxy resins, amines, urea, melamine resins. Adhere to most foils, fade-resistant (flexo, gravure, screen inks, high gloss lacquers)- packaging inks.
**Vinyls:**
Polyvinylacetate
Acetylene with acetic acid
\[ \text{CH}=\text{CH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_2=\text{CH-O-CO-CH}_3 \]
(Triple bond, I couldn't find it)
Frequently copolymerised with other monomers. Many viscosity grades commercially available. High molecular weights- tough films. Soluble in many solvents, except aliphatic hydrocarbons. Compatibility with other resins not good, partially compatible with nitrocellulose, phenolic resins, chlorinated rubber.
Vinyls: Screen inks, flexographic transparent lacquers for foil, heat sealing lacquers. Poor pigment wetting – not pigmented.

**Polyvinylbutyral**
Reaction of polyvinylalcohol and butyraldehyde under controlled conditions. White powders-characteristic rancid odor.
Soluble in alcohols, esters, ketones, glycols, glycol esters.
Non-solvents such as aromatic hydrocarbons – diluents.
Compatible with epoxy resins, maleic and acrylic resins, ethylcellulose and nitrocellulose.
Flexible films. Adhesion to metals, glass, plastics, paper, textiles.

**Phenolic resins**
Used in conjunction with tung oil –varnishes for letterpress and litho inks. Pigment wetting – good. Low softening point80-130°C, soluble in aromatic hydrocarbons, partially soluble in aliphatic solvents.
Tung oil phenolic varnishes excellent drying speeds, very tough glossy films. Tendency to yellow on UV exposure.
Made by heating a para substituted phenol with aqueous formaldehyde solution under reflux with alkaline catalyst.
\[ \text{OH OH} \]
\[ n \text{R-Ø-OH} + (n+1)\text{HCHO} \rightarrow -\text{Ø-CH2- Ø-} \]
\[ \text{R R} \]
Ø- benzene ring
Acid catalyst- phenolic resin can be dissolved in drying oils (tung oil) without reaction (heating 200-250°C).

**Polyamides:**
Large family of polymers- amide grouping (-CO-NH-) in the main polymer chain. Nylon group- largest group- large molecular weight and poor solubility. Extrusion, molding.
Lower molecular weight- reactive polyamides- used in combination with other polymers. Used in coatings and solventless inks.
Thermoplastic polymers- non-reactive- soluble in solvents, used in liquid inks. In conjunction with other polymers to improve film- forming properties. Molecular weights 4000-7000 alcohol/hydrocarbon solvent, soluble in hydrocarbons, higher alcohols.
Flexo and gravure inks- excellent adhesion to PE, OPP, polystyrene and films coated with PVDC (polyvinylidene chloride).
High gloss, resistance to fats, grease, fast solvent release, clean printing.
Aqueous polyamide dispersions-used in adhesives, heat seal and barrier coatings, acrylic or vinyl emulsions.

Alkyd resins
Tailor made resins for different purposes. Primary resins in formulation of paste inks- workable viscosities without the addition of solvent.
Soluble in variety of solvents. Used in screen, letterpress and litho inks. Excellent compatibility with other resins.
Manufactured by esterification of polyhydric alcohol with polyacids- polyesters. Combination of drying oil and fatty acids that modify the polyesters to allow them cross-link – make tough film.
Drying and non-drying – depending on amount of drying oil incorporated.
Linseed, tung, dehydrated castor, soya, tall oil.
Also classified as short, medium and long oil alkyds. The higher the oil length, the more soluble is in aliphatic hydrocarbons.
Most alkyds used in printing inks- long oil alkyds- more than 65% or the oil or fatty acid component.

COMPOSITION
Linseed oil 70 Pentaerythritol Isophtalic acid 20
Linseed oil 67 Glycerol Phthalic anhydride 22
Dehydrated castor 65 Glycerol Phtalic anhydride 25

Water - based inks:
2 types: Solution resins
Emulsion resins
Solution resins - dissolved by water- true solution
Emulsion resins - do form an emulsion- cannot be dissolved.
Solution resins - enhance ability of water to wet the pigment particles - glossy films - bad drying.
Emulsion resins - excellent drying properties, do not wet pigments.
Both types must be present in the formula.
Vehicle for paste ink:
Based on oils or UV curable ink system
Improve properties of oils- resins may be added (improve printing and drying properties, rub resistance).

Vehicle for liquid ink system:
Resins soluble in given solvent
Gravure: solvency, evaporation, toxicity.
Flexo: no ketones, aromatic solvents dissolving plates.
Epoxies: Offset, metal decoration
Two or more resins combined to capture desired characteristics of each.

OILS
Oldest raw material in printing ink industry, still important role in the formulation of printing inks.
Classification: drying, semidrying, non-drying depending on degree of unsaturation (iodine value).
Chemical structures of drying oils are triglycerides of fatty acids varying from those completely saturated- no double bonds, to those C18 acids - molecules with 2-3 double bonds- (or Unsaturated bonds).
Organic acid structure is –COOH.
The chemical structures responsible for drying are
-HC=CH-CH=CH- Conjugated system of double bonds- very reactive
-HC=CH-CH2-HC=CH- Isolated system of double bonds- less reactive
The more double bonds or conjugated double bonds the molecule has, more rapid will be the drying (Heat bodying) process

**Castor oil** has –OH group in molecule. Dehydration of castor (DCO) oil yields into system of conjugated double bonds – very reactive- dehydrated castor oil;
dries very rapidly (7min).

OH
I Heat, dehydration
-CH- CH2-CH2-CH=CH- + H2SO4 -------> -CH=CH-CH=CH-
- H2O
The mechanism of viscosity increase is cross-linking of unsaturated molecules in the sites of double bonds:
-HC=CH-CH2-HC=CH- + O2, energy -HC-CH=CH2-HC-CH-
-HC=CH-CH2-HC=CH- --------> -HC=CH-CH2-HC-CH-
(crosslinked)

**Linseed oil** – from flax, mechanical (pressing) or solvent extraction (petroleum ether or triclorehylene).
Crushing seeds, cooked, extracted by hydraulic pressure at 110oC. Oil drained to the tanks.
Linolenic acid- $C_{18}$ acid with 3 isolated -C=C-, linoleic $C_{18}$ acid with 2 isolated -C=C- bonds.

Heat bodied linseed oil- heat, air is blown Co, Mn added to dry it.

**Tung oil-** China wood oil from nuts elaeostearic acid with 3 conjugated -C=C-, very reactive. Heated 290-310°C, during 7 min. Litho inks, tough, glossy finish, water and alkali resistant.

**WHAT IS AN INK ?**

An ink is sticky stuff with a bunch of colored rocks in it.

An ink contains colorant, which is carried to the substrate by means of a resinous vehicle system.

**BASIC COMPOSITION:***

- RESIN OR VARNISH
- PIGMENT, DYE OR FLUSH
- SOLVENT
- ADDITIVES

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**PRINTING INK**

**COLORANT**------------------------**VEHICLE**

Purpose: Purpose:

To provide color To carry the pigment to substrate,
hold it there, provide any desirable properties:
e.g. light resistance, soap resistance,
Gloss, drying mechanism, transfer properties,
rub, setting.

**COLORANTS**

**DYES** - colored substances that are soluble in the media which they have been dissolved.

**PIGMENTS** – colored particulate organic and inorganic solids, which usually are insoluble, and chemically and physically unaffected by the vehicle or substrate in which they are incorporated.

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**PIGMENTS**

**INORGANIC**: Chrome Yellow, Zinc Yellow, Iron Oxides, Iron Blue, Ultramarine Blue, Titanium Dioxide.

**ORGANIC**: Lithol Red, Lithol Rubine, Naphtol Reds, Diarylide Yellows, Phtalocyanine Blue.

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**PROCESS COLOR USAGE OF ORGANIC PIGMENTS**

(PROCESS PRINTING: Yellow, Magenta, Cyan, Black).

75% of all Yellow organic pigments are DIARYLIDE YELLOW (PY 12).

75% of all Magenta organic pigments are LITHOL RUBINE (PR 57).

75% of all Cyan organic pigments are PHTALO BLUE (PB 15).

CARBON BLACK – Pigment Black 6 - Lampblack,
Pigment Black 7 – Carbon Black, Furnace Black, Gas Black.

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**EFFECT OF PARTICLE SIZE**

Small: Excellent color strength, saturation, gloss, hiding power, dispersion, flow.

Large: Poor dispersion (plate or cylinder wear, poor ink/water balance, hickeys, printability problems), poor flow, hiding power, color strength (color fluctuation), gloss.

**PIGMENTS**

Pigment do not dissolve in vehicle: container of fruit gelatin with the pieces of fruit.

Dyes- do dissolve in their vehicles.
Dyes converted to pigments through several different chemical reactions.
Chemistry of pigments-complicated- derivatives of benzene, naphthalene, anthracene
Some pigments have 4-5 aromatic rings in molecule.
Chromophores - responsible for color in organic pigments:
=\text{C} = \text{NH}, -\text{CH} = \text{N}_2, -\text{N}=\text{O}, -\text{C}=\text{C}-, \text{ or } -\text{N} = \text{N} -
Chromophores must be in such position in molecule - that electrons can change the energy levels when illuminated.
Molecule absorbs light energy, which promotes an electron from molecular orbital of lower energy to an orbital of higher energy content.
Pi electrons, conjugated systems.
Electrons in chromophores change energy level absorbing specific part of white light- reflecting the rest of the light - create the color.
Auxochromes- help fix the dye to substrate.
Batochromes - Shifts to longer wavelengths (-\text{NH}_2, -\text{OH}, -\text{OR}). Electron delocalization inceraseed in the presence of these groups. Donate electron pair to extended conjugated system.
Hypsochromes- Shifts to shorter wavelengths (-\text{NO}_2, -\text{CN}, -\text{SO}_3, -\text{NO})
Azo pigments- large, most important group of organic pigments.
DIAZOTIZATION:
\text{AR-NH}_2 + 2 \text{HCl} + \text{NaNO}_2 \rightarrow \text{AR-N} = \text{NCl} + \text{NaCl} + 2 \text{H}_2\text{O}
COUPLING:
\text{AR-N} = \text{N}^+ + \text{Coupler} + \text{NaOH} \rightarrow \text{Ar-N= N-Coupler} + \text{NaCl} + \text{H}_2\text{O} \text{ PIGMENT}

\text{Ar} = \text{e.g. Tobias Acid}
\text{Coupler} = \text{e.g. B-naphtol}

Pigment properties
Tinctorial strength, opacity, shade, gloss, refractive index,
Durability, particle size, specific gravity,
Hardness or texture, wettability, dispersibility,
Light, heat and chemical resistance.
Particle size
0.01- 0.005 microns = 4. \text{10}^{-7} – 2.10^{-7} in., Carbon blacks- smallest particle size, coarsest pigments -\text{TiO}_2 - poor flow characteristics.
Specific Gravity
Inoganic > Organic
Opacity
How object scatters the light 0.2- 0.4 nm particle size maximum opacity.
Refractive index n
Measure of bending of light rays entering the pigment.
\text{Pigment} = \text{Vehicle}, light pass through ink without bending- transparent ink film.
Inorganic - TiO_2 , chrome yellows have high refractive index.
Wettability
How easy will be pigment wetted by vehicle.
Dispersibility
How easy will be pigment dispersible – separate the pigment particles, surround them by vehicle.
Texture
Hardness or softness of pigment in dry form.
Lightfastness
Chemical nature of pigment.
Protective properties of vehicle.
Time of exposure and other conditions - humidity.
Fading, darkening.
Manufacture
Petroleum chemistry.
Organic pigments 65-70 % volume of all pigments consumed in U.S.
Pigment flush
Wet filter cake “press cake” put into mixer with selected varnish and processed. Then will be wettable with the varnish.

Dried pigment
Press cake put into oven, dried, then grinding into powder.

Chips
Pigment milled and dispersed into suitable resin (nitrocellulose, polyamide).

Carbon Blacks
Black- important-used more than others.
Stable- unaffected with light, heat, acid, solvents.
Several carbon blacks: channel black, furnace black, thermal black, lampblack.

Furnace black - the only important black pigment.
Elemental C, small % of ash, some volatile matter CO, CO₂, H₂O, H₂.
Carbon blacks- different particle size, oil absorption, pH, volatiles content.
Structure, particle size, surface chemistry- determine their behavior.
Finer particle size, better opacity, longer the flow, higher visco, higher tack, more wetting energy.

Furnace black
Made by burning atomized mineral oil in bricklined furnaces.
Carefully controlled air supply.
Cooled, pigment collected with electronic precipitators (Bag Filters).
Volatile matter lower than in other blacks - lampblack, channel black.
Bluer undertone, higher pH (7-10) than channel black (pH = 2-5).
Less tendency to absorb driers, retard drying than do channel blacks.

Channel blacks
Burning natural gas with limited supply of air.
High color strength and gloss- rarely used- no longer manufactured in U.S.

Lampblack
Burning unsaturated residues- creosote oil byproduct from distillation of coal tar
Dull finishes.

Diarylide yellow
Widely used in many types of inks.
Highly transparent to red and green light, absorb blue effectively.
Easily ground in all types of ink mills.
Small particle size- easily dispersed –good flow properties.
High tinctorial strength.
Some diarylide yellows – for heat- resistant inks- high tinctorial strength and brilliant tones
Poor to fair lightfastness.
Less opaque, so for opaque ink- mixed with TiO₂.

Hansa Yellow
Yellow 1- most commonly used Hansa yellow.
Tinctorially less strong.
Less heat resistant than diarylide.
Flow well, better lightfastness than diarylide.

Phtalocyanine blue
Most important pigment for process blue- cyan inks.
Resistant to chemicals, solvents, very lightfast.
Absorbs blue and green light- making cyan too gray.
Bronze appearance to printed ink.

Reflex or Alkali Blues
Can retard drying of oil-based systems, still very popular.
Used also as a toner for C- black inks.
High tinctorial strength, good working properties, typical for litho inks.
Tend to bleed in alcohol.

Lithol Rubine
Azo red- most commonly used azo rubine pigment.
Litho rubine- publication gravure.
Potential bleed in dampening solutions, scum.

**Rhodamine**
Bluer-more magenta than rubine, more expensive.
Magenta inks prepared from rubine or rhodamine or blends
Poorer lightfastness and alkali resistance than rubines.

**Fluorescent pigments**
Fluorescent pigments – dyes- poor lightfastness, poor flow.
Used for screen printing.
Dispersed in inert, insoluble resins that are ground to small size to produce “fluorescent pigments”.

**Inorganic pigments**
Formed by precipitation- settle out.
Filtration, washed from soluble salts, either flushed into varnish or dried.
Not pure chemical compounds-complex mixtures.

**White pigments**
\( \text{TiO}_2 \) - opaque pigment.
Extensively used - Package printing, one of most widely used of all ink pigments.
Anatase- more stable, softer texture - gravure systems.
Rutile- higher refractive index, greater opacity, more abrasive.
\( \text{TiO}_2 \) – high specific gravity, size 0.2 - 0.3 micron - piling unless properly formulated.
Whitest and most opaque pigments known.
\( \text{TiO}_2 \) – fairly readily ground on most ink mills.
Widely used in flexo and gravure.
\( \text{TiO}_2 \) – Outstanding whitness and opacity- replaced other white pigments.

**Colored Inorganic Pigments**
Inexpensive, good opacity, lightfastness, can exhibit poor texture and working properties if not correctly formulated.

Cr, Pb : chrome yellow, molybdate orange, cadmium yellow, red- many good properties
Limited use of Pb = lead environmental regulations.

**Iron blues**
Prussian, Berlin, Bronze, Chinese blue.
Different shades- due to different manufacturing conditions.
Iron blues use decreases, phthalo blues – more economical.

**Ultramarine blue**
S, \( \text{SiO}_2 \), china clay, carbon, soda ash. Inexpensive.

**Magnetic black**
Magnetic ink Character Recognition \( \text{Fe}_3\text{O}_4 \) feroosferic oxide in special crystalline form. Bank checks.

**Metallic pigments**
Bronze: copper zinc alloys from 100% copper to 70% copper: 30% zinc.
Gold inks: bronze powders.
Silver inks- aluminum.
Coarse particles, create runnability problems.

**LABORATORY 3: PUBLICATION GRAVURE INK**
**GOALS:** Prepare press ready Yellow, Magenta, Cyan, black inks with/without extender. Observe how extender affects print density. Adjust ink to target density on LWC paper grade. Print on gravure K-proofer with yellow, magenta, cyan and black ink on LWC, SCB and newsprint grade. Determine reflective density, gloss, mottle, and color using CIE \( L^*a^*b^* \) color coordinates. Discuss how the paper quality affects the print.

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**Adjustment of Reflective Density for Gravure Ink**
Take small amount of virgin ink, dilute with toluene to efflux time of 22 s (Shell #2 cup). Print using K-proofer.
Measure density of solid areas.
Take the same amount of virgin black ink; add extender (about 1/3 of original ink volume). Dilute with toluene to efflux time of 22 s (Shell #2 cup). Print by K-proofer. Measure density of solid areas.
Reflective Density

Instrument: X-Rite 408 Reflection Densitometer
Samples: Measure magenta and black solids only
Take 10 measurements of density at every sample. Determine Average Reflection Density [%] and Standard Deviation of Reflection Density [%].

Principle: Densitometers measure difference between light projected onto (through) sample and amount of light reflected back (or transmitted by sample).

Reflection and Transmission Densitometers.
Reflection densitometers- measure reflected light.
Transmission densitometers- transmitted light – for transparent film measurement.

Reflection densitometer: red, green, blue filters to represent different thirds of visible light spectrum.
Complementary filters:
- Blue filter for yellow ink
- Red filter for Cyan (blue) ink
- Green filter for Magenta (red) ink

When complementary colored filters placed over the inks, they appear Black (or shade of gray). Densitometers “see” in black and white!

Color values are not referenced to a model of human vision.
Densitometric measurement of color can be calculated by colorimeters and spectrophotometers, not vice versa!
Tabular data or spectral curves
Reflective density data from 0 to 2.0
Reflection densitometer uses incident light source (tungsten filament lamp) to illuminate the print either at 45 or 90 degrees
Light reflected from the print recorded by photocell and numerically displayed – digital display (analog).
Assessment of color- not linear, but nearly logarithmic relationship
Density related to reflectance as follows:
\[
D = \log_{10} \frac{1}{R}
\]
Where reflectance \( R = \frac{R_1}{R_w} \)
\( R_1 \) = Intensity of light reflected from print
\( R_w \) = Intensity of light reflected from white paper
And density \( D = \log_{10} \frac{R_w}{R_1} \)
Densitometers equipped with computer chips – calculate density, dot gain (tone value increase), ink trap, print contrast. Densitometry – used for controlling color at press.

Specular Gloss

Take 10 measurements of ink film gloss and 10 measurements of paper gloss.

Delta gloss is calculated as: Ink gloss – Paper gloss [%].

Instrument: Gardener Gloss Meter. Gloss reading: [%] of standard
Gardener Gloss Meter consist of: Light source, Collimating lens (parallel beams), Slot (limit the parallel beam).
Method of directing the beam against the paper specimen at fixed angle of incidence
Method for measuring the amount of light reflected from the paper (angle of incidence equals angle of reflection).
Working standard: black polished glass (100% gloss).

Gloss is qualitative property which cannot be expressed readily in fundamental therms. Related to:
Luster - sudden selective reflection of light (pleasing effect)
Glares - undesirable reflection of excessively bright light (unpleasant, blinding effect)
Gloss: Characteristic of paper or printed surfaces which causes to reflect the light at given angle of reflection in excess of the diffuse reflection at that angle.
Gloss: Degree to which the surface simulates a perfect mirror in its capacity to reflect incident light
Specular reflection refers to the portion of the incident light which is reflected from the surface of an object with an angle of reflection being equal to the angle of incidence.
The amount of specular reflection is determined by:
The index of refraction of the object,
The wavelength of the incident light,
The angle of incidence.
Parallel beams of light striking optically flat surface at the same angle of incidence will be reflected as parallel
beams. Diffuse scattering—occurs at non-flat (rough) surfaces.
Leveling off (Calendering), filling the valleys by coating.
Print gloss measurements: 60° from the normal to sheet (Best compromise for all prints).
The amount of specularly reflected light increases with increasing angle of incidence.
Gloss can be measured at 20°, 45°, 60°, and 75°.

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**Ink Mottle**
Mottle is defined as the unevenness in print density or print gloss. Mottle = Substrate ability to produce an uniform flat printed tint.
Mottle - affected by non uniform wetting and penetration of ink into substrate.
Mottle - affected by surface tension properties of substrate.
Mottle caused by poor paper formation (coated papers and board).
Calendering and wet pressing affect variation in base sheet structure.
One result of calendering- reduction of non-uniformity in z-direction (Roughness).
Smoother sheets believed to be more receptive to ink – more uniform ink coverage.
Negative effect – random densification of surface layers of paper
Mottle: easily to recognize, difficult to measure

**Equipment for mottle determination:** Tobias Mottle Tester: MTI measures the mottle by measuring the variation in reflective density of a sample at controlled ink film thickness.
The variation of density over the area of the sample = indication of sample mottle. Mottle index. Regular densitometers – accuracy of 0.01. To measure mottle – accuracy of 0.001 is needed.

**Tobias Mottle Tester:**
4 main components:
A probe (measurement head- gloss head or density head)
Rotating drum that carries the sample
A microprocessor performing all control and analysis functions
A video display monitor
The probe performs the actual density measurements.
Probe: illumination source, an optical measurement system, and associated electronics.
Illumination source: produces small area of light of controlled intensity, which defines the area to be measured.
Optical measurement system: detects the amount of light that is reflected by the sample from the illuminated spot.
Electronics convert the output from the measurement system to a signal that can be analyzed by the microprocessor.
The sample is mounted on the measuring drum. The drum rotates under the probe for scanning.
Electronics-microcomputer controls: Scanning, recording, analyzing, and displaying the data.
The MTI uses standard densitometric technique of illuminating a 3 mm diameter circular area with a beam of light that is perpendicular to the sample surface and measuring the light that is reflected from the surface at the angle of 45 degrees.
Mottle tester measures mottle by analyzing variation in the reflective density with accuracy of 0.001 units. System is calibrated to give output that is 1000 times the conventional density reading. (Density of 0.8 produces a reading of 800). Adjacent sample areas 0.15 mm, continuous reading).
Density readings- at high speed, multiple reading of each sample area. Readings are then averaged to produce single data point for each area. Mottle tester filters out the variations in density occurring gradually over large distances, and measures those that occur over small distances.
MTI = average deviation of density per processed data points
MTI takes up to 20 scans. Each scan can be up to 500 data points. Each data point is the average of a number of measurements (Typically 64) of single sample area.
Sample can cover whole drum, ½ or 1/3 of the drum.
The MTI uses standard densitometric technique of illuminating.

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**CIE L*a*b* Color Coordinates**
Equipment: Datacolor Datamaster Spectrophotometer
Calibrate the instrument according to instructions at computer screen. Measure yellow, magenta, cyan, and black color, two times each. Record the color coordinates at D65 light source only.
Measurement of L* a* b* values of color, so called color coordinates. L* refers to lightness of color L=100 white, L=0 black; a* denotes degree of redness or greenness, b* indicates the degree of yellowness or blueness of the color.
LABORATORY 3: PUBLICATION GRAVURE INK

GOALS: Prepare press ready Yellow, Magenta, Cyan, black inks with/without extender. Observe how extender affects print density. Adjust ink to target density on LWC paper grade. Print on gravure K-proofer with yellow, magenta, cyan and black ink on LWC, SCB and newsprint grade. Determine reflective density, gloss, mottle, and color using CIE L*a*b* color coordinates. Discuss how the paper quality affects the print.

Adjustment of Reflective Density for Gravure Ink
Take small amount of virgin ink, dilute with toluene to efflux time of 22 s (Shell #2 cup). Print using K-proofer. Measure density of solid areas.
Take the same amount of virgin black ink; add extender (about 1/3 of original ink volume). Dilute with toluene to efflux time of 22 s (Shell #2 cup). Print by K-proofer. Measure density of solid areas.

Reflective Density
Instrument: X-Rite 408 Reflection Densitometer
Samples: Measure magenta and black solids only
Take 10 measurements of density at every sample. Determine Average Reflection Density [%] and Standard Deviation of Reflection Density [%].
Principle: Densitometers measure difference between light projected onto (through) sample and amount of light reflected back (or transmitted by sample).

Reflection and Transmission Densitometers.
Reflection densitometers- measure reflected light.
Transmission densitometers- transmitted light – for transparent film measurement.
Reflection densitometer: red, green, blue filters to represent different thirds of visible light spectrum.
Complementary filters:
Blue filter for yellow ink
Red filter for Cyan (blue) ink
Green filter for Magenta (red) ink
When complementary colored filters placed over the inks, they appear Black (or shade of gray). Densitometers “see” in black and white!
Color values are not referenced to a model of human vision.
Densitometric measurement of color can be calculated by colorimeters and spectrophotometers, not vice versa!
Tabular data or spectral curves
Reflective density data from 0 to 2.0
Reflection densitometer uses incident light source (tungsten filament lamp) to illuminate the print either at 45 or 90 degrees
Light reflected from the print recorded by photocell and numerically displayed – digital display (analog).
Assessment of color- not linear, but nearly logarithmic relationship
Density related to reflectance as follows:
Density D = log 10 1/R
Where reflectance R = R_t/R_w
R_t = Intensity of light reflected from print
R_w = Intensity of light reflected from white paper
And density D = log 10 R_w/R_t
Densitometers equipped with computer chips – calculate density, dot gain (tone value increase), ink trap, print contrast. Densitometry – used for controlling color at press.

Specular Gloss
Take 10 measurements of ink film gloss and 10 measurements of paper gloss.
Delta gloss is calculated as: Ink gloss – Paper gloss [%].
Instrument: Gardener Gloss Meter. Gloss reading: [%] of standard
Gardener Gloss Meter consist of: Light source, Collimating lens (parallel beams), Slot (limit the parallel beam). Method of directing the beam against the paper specimen at fixed angle of incidence
Method for measuring the amount of light reflected from the paper (angle of incidence equals angle of reflection).

Working standard: black polished glass (100% gloss).

Gloss is qualitative property which cannot be expressed readily in fundamental therm. Related to:
Luster - sudden selective reflection of light (pleasing effect)
Glare - undesirable reflection of excessively bright light (unpleasant, blinding effect)

Gloss: Characteristic of paper or printed surfaces which causes to reflect the light at given angle of reflection in excess of the diffuse reflection at that angle.

Gloss: Degree to which the surface simulates a perfect mirror in its capacity to reflect incident light

Specular reflection refers to the portion of the incident light which is reflected from the surface of an object with an angle of reflection being equal to the angle of incidence.

The amount of specular reflection is determined by:
- The index of refraction of the object,
- The wavelength of the incident light,
- The angle of incidence.

Parallel beams of light striking optically flat surface at the same angle of incidence will be reflected as parallel beams. Diffuse scattering- occurs at non- flat (rough) surfaces

Leveling off (Calendering), filling the valleys by coating

Print gloss measurements: 60° from the normal to sheet (Best compromise for all prints)

The amount of specularly reflected light increases with increasing angle of incidence. Gloss can be measured at 20°, 45°, 60°, and 75°.

Ink Mottle

Mottle is defined as the unevenness in print density or print gloss. Mottle = Substrate ability to produce an uniform flat printed tint.

Mottle - affected by non uniform wetting and penetration of ink into substrate.
Mottle - affected by surface tension properties of substrate.
Mottle caused by poor paper formation (coated papers and board).
Calendering and wet pressing affect variation in base sheet structure.
One result of calendering- reduction of non-uniformity in z-direction (Roughness).
Smother sheets believed to be more receptive to ink – more uniform ink coverage.

Negative effect – random densification of surface layers of paper

Mottle: easily to recognize, difficult to measure

Equipment for mottle determination: Tobias Mottle Tester: MTI measures the mottle by measuring the variation in reflective density of a sample at controlled ink film thickness.
The variation of density over the area of the sample = indication of sample mottle. Mottle index. Regular densitometers – accuracy of 0.01. To measure mottle – accuracy of 0.001 is needed.
Tobias Mottle Tester: 4 main components:
- A probe (measurement head- gloss head or density head)
- Rotating drum that carries the sample
- A microprocessor performing all control and analysis functions
- A video display monitor

The probe performs the actual density measurements.

Probes: illumination source, an optical measurement system, and associated electronics.
Illumination source: produces small area of light of controlled intensity, which defines the area to be measured.
Optical measurement system: detects the amount of light that is reflected by the sample from the illuminated spot.
Electronics convert the output from the measurement system to a signal that can be analyzed by the microprocessor. The sample is mounted on the measuring drum. The drum rotates under the probe for scanning.
Electronics-microcomputer controls: Scanning, recording, analyzing, and displaying the data.
The MTI uses standard densitometric technique of illuminating a 3 mm diameter circular area with a beam of light that is perpendicular to the sample surface and measuring the light that is reflected from the surface at the angle of 45 degrees.

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DOCTOR BLADES
After the recessed cells of the cylinder are covered with ink, a blade must wipe away the excess ink before it reaches the printing nip. This blade is called a doctor blade. The correct application of the doctor blade is critical in gravure printing.

Composition. Typically, doctor blades are made of high quality stainless steel. More recently, alternate materials, such as plastic and ceramic are being used. The carbon steel used for doctor blades must be clean and free of any imperfections. Stainless steel blades are often used with corrosive liquids. Plastic and ceramic blades are also non-corrosive and non-abrasive.

Shape. Steel blades are approximately .004 - .015 inches thick, and from 1-3 inches wide. The thickness tolerance is +/- .0002 inches. Blade hardness is between 500 and 600 Vickers. Plastic blades are up to .060 inches thick. Steel blades have a much longer life than plastic blades.
Doctor blades are called blades because the edge that is in contact with the cylinder has been shaped (or sharpened). Sharpening can be done in-house or by the blade manufacturer. Blade edges are important because the blade must have a perfectly straight and smooth edge to rest against the printing cylinder. Any blade imperfections will cause streaks and scratches on the cylinder face.
Edges can be of several types, however the most common is a pre-sharpened beveled edge. The blade edge has a flat shoulder and a beveled (or sloped) edge. This blade is usually supplied by the manufacturer. The beveled edge blade is the most common due to its long life and minimal cylinder wear.

Application. The doctor blade must be held in perfect contact with the cylinder to achieve a clean, even wipe. The doctor blade holder is designed for this purpose. Doctor blade holders will vary with press type.
Since doctor blades are thin strips of metal, they are often used with a back-up blade. This heavier metal strip (.015 - .020 inches thick) gives the thinner doctor blade support when under pressure.
The back up blade and doctor blade are clamped together in the doctor blade holder. Holders can be either straight, curved or a clamping type.
Once the blade is mounted into the holder and positioned in the press, the angle at which the blade contacts the cylinder is critical. The best wiping angle is one that minimizes cylinder wear, wipes cleanly, and allows the greatest press speed.

Blade Angle. Two factors affect the blade angle. First is the angle on the blade itself. On beveled edge blades, wear may cause this angle to change. Pre-sharpened blades are used to minimize this problem by controlling the beveled edge thickness.
The second factor, the set angle, is the actual angle that results from the application of the blade to the cylinder by the blade holder. Set angles are typically between 25-35°. The set angle may change due to blade or cylinder wear and ink type. The angle is not a permanent setting. It can be altered to achieve the best wipe under the current conditions.
For example, a steep angle is used to remove more ink from the cells. This is commonly done in four color process printing when large amounts of ink are not needed. A flat angle is used when printing large solids or coatings. This leaves more ink in the cells, resulting in greater transfer.
The distance between the doctor blade and the nip is also important. This distance is called the printing zone. The distance is important to consider because the ink may dry in the cells after the doctor blade wipe but before it reaches the printing nip. Moving the doctor blade closer or farther from the nip can control this problem.
**Application Pressure.** The pressure applied to the blade while in contact with the cylinder is controlled and monitored. It is achieved by gravity, springs, pneumatic or hydraulic pressure. Pneumatic is the most common and provides longer cylinder life. The pressure should be as little as possible to minimize cylinder wear. Press crews should establish and maintain the pressure that provides the most consistency for each press.

While under pressure against the cylinder, the doctor blade encounters deflection. Deflection is a slight bowing of the blade caused by the cylinder motion, pressure, and blade thickness. This deflection must be accounted for when setting the blade angle.

While the blade is in contact with the cylinder, the entire blade assembly moves from side-to-side (oscillates). This movement provides even wear and helps remove any loose debris that may have collected under the blade which may cause streaks. The maximum movement should be about 1 inch and can be adjusted.

**Care.** Doctor blades are extremely sharp and require care in handling. Any nicks or chips in the blade edge will result in streaking or hazing. Additionally, the extremely sharp blade edge needs to be handled carefully to avoid cuts to hands or other parts of the body.

Common print problems associated with doctor blades include print distortion, slurring, screening, snowflaking, scumming (tinting or hazing), streaking and poor color control. Mechanical problems include uneven blade wear and excessive cylinder wear.

**IMPRESSION SYSTEMS**

In order for the ink to be transferred from the printing cylinder to the substrate, there must be a great amount of pressure applied between the substrate and cylinder. This pressure is supplied by the impression roll. Impression roll pressure helps transfer the ink and acts as a backing to the substrate being printed.

**Impression Mechanics.** While the press is at rest, the impression roll is not in contact with the substrate. When the press is started, the impression roll must be lowered into contact with the substrate and cylinder. This is called a conventional, or moving rubber roll impression system. The rubber impression roll moves into contact with the cylinder, creating pressure.

The advantage of a conventional system is the simple mechanics. The disadvantage is that every time the rubber roll is moved, the web tension and register changes. This means the web must be slowed, and the color to color register will be affected. This creates waste and lowers productivity every time the roll is moved.

The impression roll is moved using either a hydraulic or pneumatic pressure system. Pneumatic systems are the most common.

**Impression Pressure.** There are two ways to set the impression pressure. The first is the stop or gap method. This method uses two steel blocks to limit the contact of the impression roll against the cylinder. The blocks "stop" the roll from further movement. This method does not allow an actual impression pressure measurement. The blocks stop the roller at a certain distance. No matter how much pressure is applied, it will move no further. This type of impression pressure setting is desired for lightweight papers, films and foils because it maintains a constant nip width over the entire length of the impression roll.

The second method is the pressure equalization system. In this case the impression roller is able to float, or move, to achieve the correct impression pressure. This floating impression system can automatically compensate for uneven web thickness during printing. Even though the roller may move, this system maintains constant pressure across the cylinder width.

**Creation of Nip.** When the impression system is loaded, a "nip" is created between the two cylinders. The nip area (flat) is the area of actual contact between the two circular parts (roller and cylinder). The nip area extends the length of the roller and has a variable width.

Controlled nip width is desirable for paper, film and foil. It allows for uniform pressure across the entire width of the web.

Desirable nip widths are shown below:

**TABLE: NIP WIDTHS FOR DIFFERENT SUBSTRATES**

<table>
<thead>
<tr>
<th>SUBSTRATE</th>
<th>NIP WIDTH [inch]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Films and Foils</td>
<td>1/4</td>
</tr>
<tr>
<td>Lightweight Papers</td>
<td>3/8</td>
</tr>
<tr>
<td>Heavyweight Papers and Lightweight Board</td>
<td>1/2</td>
</tr>
<tr>
<td>Boards (20 pts. +)</td>
<td>3/4</td>
</tr>
</tbody>
</table>

The nip width is a function of physical roller characteristics and impression pressure. Physical characteristics include the type of covering, temperature, hardness (durometer), thickness and diameter.
Nip width must be measured and checked each time a new cylinder is loaded. Nip width can be checked by a variety of methods. One is the grease and paper method. Grease, mixed with carbon black, is spread on the rubber impression roller. Paper is inserted between the impression roll and the cylinder, and the impression roll is lowered. When the two contact, the grease leaves a mark on the paper that can be measured. Other methods include impression tape, embossed (textured) foil, and film. These methods are more convenient than paper and grease and are just as effective.

**Impression Roll Construction.** Roller base construction is similar to cylinder base designs. Most are made of durable steel cores with a soft covering. The steel core, or base, must be statically and dynamically balanced like a cylinder base.

Roll balancing is necessary to minimize wear, control web runnability, reduce vibration and heat buildup, and to assure proper contact with the cylinder while the press is running. Any distortion of the roll will affect printability and may cause damage to the roll.

**Impression Roll Material.** The soft covering that surrounds the steel core can be made of several rubber types. The type of rubber will depend on the solvents that are used. Most rolls are constructed of natural rubber, neoprene, and Buna N (synthetic rubber). Natural rubber rolls are recommended for alcohol and water type inks. Buna N rolls are suggested for inks that contain alcohol, toluene and normal butyl acetate.

The hardness (or durometer) of the roll is also very important. Hardness is measured on a "Shore A" scale. Soft rubber rolls are about 50 durometer and hard rolls about 90 durometer. The desired durometer of a roll is dependent on the substrate to be printed. The following chart shows preferred roll durometer for a variety of substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Shore A Durometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foil, Film</td>
<td>50-65</td>
</tr>
<tr>
<td>Coated Papers</td>
<td>70-80</td>
</tr>
<tr>
<td>Plain Paper</td>
<td>75-85</td>
</tr>
<tr>
<td>Boxboard</td>
<td>80-90</td>
</tr>
</tbody>
</table>

Proper impression roll durometer is important. Too soft a roll can lead to deformation (distortion), web handling and rubber deterioration problems. Not using the correct durometer rolls reduces quality and productivity. The durometer of the roll should be checked periodically because it will change with age and use.

**Deflection.** All rollers will deflect. Deflection means that the roll will bend and curve. This is a result of its own weight and the pressure that is applied on it. Since the ends of the roll are secured in the bearings, the middle of the roll will bend. Deflection is more apparent in wider presses (over 60”).

A technique used to reduce deflection requires that a bevel be cut into the rubber at the end of the impression roll. This end cut is used to minimize swelling at the ends of the roll, which then reduces deflection. An appropriate nip area, or flat, should have a rectangular shape. When the roll is deflected, this shape takes on an hourglass shape (wide at ends and thinner in the middle). Since this deflection will affect the print quality, back up rollers are used to minimize this problem. Back up rollers provide support over the entire roll so deflection will not occur. Problems associated with deflection include excessive heat build up, roller breakdown, tension problems and register trouble.

**ELECTROSTATIC ASSIST**

When printing, the main purpose of the impression roll is to force the substrate into contact with the printing cylinder. This contact should be enough to allow the ink to transfer from the recessed cells. Sometimes the ink does not transfer to the substrate, causing a condition known as skipped dot or snowflaking. There are several reasons the ink does not transfer. The most important is the roughness of the substrate surface. In other words, the pits or cavities in the substrate surface are larger than the individual cylinder cells and they simply do not come into contact with each other. Additional reasons include the shape of the cell, ink drying speed and viscosity, and improper impression pressure.

**Operation.** Electro Static Assist (ESA) was developed by the Gravure Association of America to help eliminate skipped dots. ESA is a process that uses electric charges to force the ink into contact with the substrate. This is accomplished by developing an electric field, either positive or negative, between the impression roll and the print cylinder. By charging the impression roll and grounding the print cylinder you can produce the electrostatic field. ESA systems are manufactured by Hurletron in the United States. The Hurletron system applies a charge to the conductive rubber impression roll. This conductive rubber roll is called an applicator.

Once the electrostatic field is applied, electrostatic forces cause the ink in the recessed cell to be drawn up out of the cell into contact with the substrate. ESA efficiency depends on the condition and age of the rubber impression roll,
and the cleanliness of the applicator contacts. Heat will also affect the way the ESA works. Too much heat on the
roller will reduce electrical efficiency.

**INK DRYERS**
Gravure- very fluid inks- need to evaporate a lot of solvent. Also, ink coming to next print station must be dry.
Some applications- extremely dry ink- to avoid trapped odor.
Some inks- 100 % solids- hot melts, UV curable, EB curable.

**Solvent Ink Film formation**
Most inks- solvent integral part of composition. Solvents released by diffusion process- solvent molecules uniformly
move through the film
Evaporation rate- constant – free flow throughout the low viscosity fluid.
Film becomes thicker, viscosity increases, solidification process.
Diffusion rate in semi-plastic mass – much lower than in less viscous ink.
At some point- diffusion slow enough to affect the evaporation rate.
Less energy to evaporate the first 80% of solvent in the wet layer, than to remove the last 20%.
The last 5% is extremely difficult to remove. Tendency of ink film to retain solvent.
(Contaminate contents of food package).

**WATER BASED INKS**
Little or no solvent, therefore little or no explosive hazard.
Water- evaporates more slowly as relative humidity raises.
T of the supply air- well over boiling point of water.
Trace of water remaining in ink film- 0.3%- can make product unacceptable
Tendency- 0.1mg/m² retained.
If 1% water retained- does not matter- no odor. WB inks not re-dissolvable (solvent inks are).

**SOLVENT AND WATER BASED INKS DRYING COMPARISON**
Solvents- much more volatile than the water.
Less energy to change solvent into vapor than water- into vapor.
Amount of heat energy required to raise one gram of liquid one degree C specific heat SH
SH of solvents…. 0.35
SH of water….. 1.00
3x more energy to raise the T of water than T of solvent.
The amount of E required to transform 1 kg of liquid at vaporization temperature to vapor is LATENT HEAT LH
LH for solvents ….cca 200 kCal/kg
LH for water…….cca 900 kCal/kg
More than 4x more heat for evaporation of water than solvent- great deal more E to evaporate WB ink.
It does not mean that WB needs 4x more E- because at the the same thickness of ink film much less water is needed
to be evaporated at WB than SB ink- there is higher level of solids in WB inks. Water escapes more easily from ink
film than solvent.

**Skinning- crusting**
Creation of an undesirable surface layer-skin over the wet deposit- can be serious problem with both WB and SB.
Skin inhibits the passage of solvent (water) vapors- additional E needed to force them through crust. Aqueous inks
tend to crust more easily than SB.
Gradual solvent (water) release- the only way- to prevent blistering, pinholes, and diluent entrapment.
Water based inks can be run at rate equal to or faster than solvent based ones.

**DILUENT LOADS ON DRYER**
Solvent or water load = total amount of diluent which must be evaporated in one hour-expressed in kg, lb., l, gal per
hour.
Best- to use the weight of diluent [g/m²] or [pounds/ream].
Weight= dry weight. 3g/m²-means dry weight.
Solvent weight- relative to water- specific gravity SG. Water SG=1
1 micron thick material with SG=1 will weight 1g/m².
Coatings measured by dry weight g/m² or lb/ream

**INK LAYDOWN VALUES**
How much ink is laydown on material to produce 100% solids in gravure?
Answer depends on type of material.
Tonal quality of ink film depends on pigmentation, percentage of solids in diluted ink.
The tonal quality of solidified ink - density and thickness. Material being printed - non-absorbent - ink film remains on surface - darkest tonal density. The same ink film applied onto slightly absorbent substrate - ink absorbs - reduces ink layer. The same ink applied to very absorbent surface - thinnest film - resulting tone - the lightest. 2 remedies - to increase the pigmentation - too expensive, to increase % solids - darker tone - this increases the viscosity of the ink - too high visco - interfere with printing system.

To create equally dark tones at all types of substrates - to apply a thicker wet layer on more absorbent substrates.

**TABLE: Solvent Ink Mileage (Ink Application Chart)**

<table>
<thead>
<tr>
<th>Substrate type</th>
<th>Area for 1 kg of wet ink [m²]</th>
<th>Area for 1 lb of wet ink [ft²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Films with dye inks</td>
<td>200</td>
<td>970</td>
</tr>
<tr>
<td>Films with pigment inks</td>
<td>165</td>
<td>800</td>
</tr>
<tr>
<td>Coated Papers</td>
<td>150</td>
<td>750</td>
</tr>
<tr>
<td>Uncoated Paper, Boxboard</td>
<td>135</td>
<td>670</td>
</tr>
</tbody>
</table>

Solvent Ink Mileage - Ink Application Chart – for obtaining a uniform tone for rotogravure. Heavier wet ink layers used for more absorbent substrates to create the same tonal density. 150 lpi cylinder, 37 micron deep cells for printing 100% tone with 22% solids ink. Different gravure cell will create different ink mileage.

We must divide the area, which will 1 kg of ink cover in order to find ink laydown values for different materials. To purchase a new press - (dryer) - estimated ink laydown values under maximum operating conditions must be determined.

**TABLE: Solvent Ink Laydown Values**

<table>
<thead>
<tr>
<th>Substrate type</th>
<th>g/m²</th>
<th>lb/ream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Films with dye inks</td>
<td>6.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Films with pigment inks</td>
<td>6.1</td>
<td>3.8</td>
</tr>
<tr>
<td>Coated Papers</td>
<td>6.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Uncoated Paper, Boxboard</td>
<td>7.4</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Typical solvent gravure ink would have 20-25 % solids by weight, means it has 80-75 % solvent in it. Avg = 6.24 g/m² of solvent in ink. To find out the solvent load - how many m² or reams will be printed, and than multiply that with solvent laydown values.

Example: 53” press (1.35m) Production speed 300m/min 1000ft/min² Area of web produced per hour : 1.35 x 300 x 60 = 24,300 m² [83.4 reams] Solvent load 6.24 g/m² 6.24 g/m² x 24,300 m² = 151.6 kg/hour New printing press must be capable of evaporating 151.6 kg/hr solvent, which is 325.3 lb/hr (to apply 100% ink coverage).

Not every color - 100% coverage first and last station – surface printing background color first, reverse printing - last.

First and last station must be sized to dry full coverage, second - though next to the last - 50% coverage. Water based inks - 50% solids, WB inks - more pigmentation - much less WB ink is applied than solvent ink. The average solvent load is about - 4.0g/m² Shallower cells for WB inks - 20 micron depth (40 micron for solvent based). The average water load is half- 2.0g/m² 24, 300 m² or 83.4 reams/hour, the total water load for 100% ink coverage is 48.6 kg (151.6 solvent load). The water load is about 32% solvent load.

**EVAPORATION PRINCIPLES** Energy must be emitted from the drying chamber, transferred to the wet layer, for vaporization to occur. The released solvent and water must be evaporated to surrounding air, and then extracted from the drying chamber. Heat transferring action followed by mass transferring action to dry a wet layer. Heat transfer Q is amount of kilocalories kcal/hr or Btu/hr British thermal units that is implanted in the wet coating under specific operating conditions

\[ Q = h A (T_{\text{air}} - T_{\text{surface}}) \]
Heat transfer portion of the drying process - ability to raise the temperature of wet layer to its evaporation point - mass transfer can begin.

Heat transfer curve - straight-line function.

After energy is in the liquid, the removal of the diluent begins - the process is referred to as mass transfer.

\[ X = K_x \cdot A \cdot (P_{air} - P_{surface}) \]

Where

- \( X \) – evaporation rate in kg/hr, or lb/hr
- \( K_x \) – mass transfer coefficient
- \( P \) – vapor pressure

Mass transfer - nonlinear. Factor affecting mass transfer - boundary layer.

Boundary layer of air – present on each moving web.

The ability of drying system to reduce the thickness of boundary layer determines how efficient the dryer is.

Intersection of heat and mass transfer curves - drying rate for specific temperature.

Drying rates are specified in the quantity of water that can be evaporated per m² per hour.

\[ Q = h \cdot A \cdot (T_a - T_s) \text{ watt/sec} \]

Mass out

\[ M = k \cdot A \cdot (P_{air} - P_{surf}) \text{ kg/sec} \]

Vaporization commences at the surface of liquid - works way down when heat applied only on top side.

Ink film enters the dryer - heating up to evaporation \( T \).

Vaporization occurs - \( T \) is reduced (cooling process).

Under ideal condition, vaporization from the middle layer begins when the top layer is cool - this prevents crusting.

Crusting - vapor molecules below the skin require greater pressure to force the way through - air dryers use higher air velocities and Temp in the middle sections than at the entrance.

Crust semi-plastic - pinholes are created. Solid crust - pinholes may stay open - inks thermoplastic - softening the crust - pinholes close.

A dryer can only be used to about 33-50% of its rated efficiency - because high velocity air disturbs the surface of wet layer and excessive evaporation rates will trap solvents in the solidified layers.

**BOUNDARY AIR LAYER**

The layer immediately above the liquid – boundary air layer:

Laminar zone

Buffer zone

Turbulent air layer located immediately above boundary layer.

The heat is transferred through the boundary layer by conduction and convection.

Released vapors are removed by diffusion and convection.

Convection heat transfer efficient in turbulent and buffer zones - in these zones uniform air \( T \) and released vapor.

Very little convection takes place in laminar sublayer.

Laminar - heat conduction and vapor transmission - means of transferring \( E \) and vapors.

Conduction - inhibits the drying action - its resistance proportional to laminar layer. Anything to reduce the laminar layer - will increase the heat, mass and transfer rates.

The use of medium and high velocity air jets to penetrate and disturb the laminar layer - best method to reduce the laminar layer thickness.

**AIR FLOW SYSTEMS**

Large volume of heated supply air to solidify wet layers, larger volumes of exhaust air to extract the vapor-laden air.

Vertical airflow systems, hole, tube and slot type dryers.

Hot air expelled downwards - vertically - onto wet ink - all of these are classified as impingement dryers.

Medium to high velocity hot air streams to penetrate and disturb the laminar flow - which reduces the thickness of the laminar layer and enlarges the buffer and turbulent layers.

The vapors collect above the wet layer tend to saturate the air.

This inhibits the passage of heat to the liquid as well as the flow of vapors from inside to wet layer.

The impinging air breaks up the boundary layer, scatters the concentration of released vapors, lowering the external
vapor pressure. The low-pressure exhaust system has chance to extract the diluent air from the immediate area around the moving web to the exhaust manifold. A hole dryer – impingement dryer in which vertical air streams are expelled from holes. The bottom of the air plenum has a series of holes in it, they are spaced to cover the entire web area as it flows through the dryer. A supply air plenum is a sheet metal enclosure inside the dryer, in which the air is under greater pressure than the air surrounding it. Air passing through the holes tends to spread. Major advantage of hole dryers is that 100% area is under the influence of the circular air blast at all times. The hole dryer is the least costly to print. Two principal disadvantages: the impinging air velocity is the lowest of any type of the dryer. The overlapping air pattern causes some areas to receive more energy than others – overdrying in some sections. Overlapping airflow from hole and tube dryers will cause streaks in the direction of web flow. Hole dryers- more often used on flexo presses. Slot dryers- most efficient.

**ROTOGRAVURE DRYERS**
The length of dryers- function of amount of ink or coating coverage that the unit was specified to. 
**Single chamber** dryers – 50 % ink coverage or slow presses. Length- 1000-1600 mm 40-60". 
Circulator- supply fan mounted on the side of the unit. The cover swings from the bottom – easy access for roller cleaning and web threading. 
All gravure dryers should have some movable covers, which allow the operator to work inside the dryer.

**Dual chamber** – total length 2000-3000 mm (6.5-10 ft). 100 % coverage must be designed to allow the web to exit halfway through the dryer. 
Circulator mounted on each chamber or one larger supply fan mounted at the side of the unit- single larger supply-less vibration.

**EXTENDED DRYERS**
Extended or super-extended dryers- about 5-8 meters (15-25 ft). IR heater – to preheat the wet inks before entering drying chamber.

**DRYER FUNCTIONING**
TIME- most important
TURBULENCE- air impingement
TEMPERATURE
Heat increases drying speed. Excess heat- printed substrate can shrink, curl, become brittle. Ink can skin over- trap solvent in the ink, causing odor, picking on subsequent rollers. 
Dryers- airflow can be controlled at specific sections- zones. 
**Single- zone** the T= const throughout the unit. 
**Multi-zone** operates independently or with air recirculation from one zone to another within the unit- water based inks, water-borne adhesives, gravure coatings. Heat increases the process, excessive heat- shrinkage curl, brittleness of substrate. 
Dryers- constructed in specific sections “Zones” of the drying unit. 
Single zone unit the temperature and air flow are same throughout the unit.
Multi-zone dryers can operate independently or with air recirculation from one zone to another within the unit. Individual temperature controls for different zones make multi-zone dryers suitable for water-based inks, water-borne adhesives, gravure-applied coatings.

**DRYER LIMITATIONS**
Cleanable, dimensionally stable over many years- complex system of air nozzles
Drying parameters put into formulas to predict results. Specification of inks, substrates, coatings. Then calculation of dryer’s potency, from that the operating speed which the dryer will support under those conditions. 
Volume of air to solvent must not fall below certain limit.
The air exhaust volume may not be reduced unless a LOWER EXPLOSIVE LIMIT (LEL) detector is used. **LEL- Lower Explosive Limit** is concentration of flammable vapors below which they are too lean to ignite. Supply air can be from 100% fresh air to 100% recirculation air. Recirculation air economizes on heating energy- it can aggravate the clogging of supply air nozzles with paper dust. Air recirculation filters must be cleaned weekly.
Supply air must not deflect the web, for tension changes would vary the nip to nip distance. On presses running foils, films- rollers support the web at each nozzle.

HEAT SOURCES
Steam, gas, electric, hot liquid, gas/ oil, waste heat from incinerators.
Steam- traditional – used in all publication gravure applications.
Steam coils- 100% recirculation loop.
Maximum heat- 250-320°F depending on steam pressure and type of coils
Steam heat is slow and steady.
Electric heat similar characteristics to steam heat- higher energy cost.
Heating coil temperatures can ignite airborne dust or solvents.
Gas- (methane) is cheap, favorite for packaging presses- pipeline infrastructure to deliver gas to any location
Gas- one third to one fifth the cost of electricity.
Gas heaters- can achieve high temperatures with quick warm-ups.
Need fresh air for combustion.

OTHER DRYING METHODS
All mentioned methods use air as the heat transfer medium and for the mass transfer of vapors outside the dryer.
Air – most versatile heat transfer medium and for the mass transfer of vapors outside the dryer.
IR, UV and EB technologies used for certain specialized operations.

ENVIRONMENTAL CONSIDERATIONS
A typical packaging press evaporates ½ to 1 gallon of solvent per minute. It is 450 lb per hour. Press operates 5,000 hours in a year- it is over 1, 000 t of solvent per year.
At present, press producing over 100 tons of solvent per year must have pollution control devices.
Solvent recovery, fume incineration, or use of water based inks and coatings.

SOLVENT RECOVERY
Purpose of solvent recovery- to remove evaporated solvents from dryer exhaust air and the pressroom air and collect the solvent for reuse. Fans remove the solvent-laden air.
Air channeled through duct work to one or several adsorbers -beds of activated carbon pellets.
The pellets adsorb the solvent as the air is forced through them.
The cleansed air passes out the adsorber into the atmosphere.
After the bed is reasonably saturated with solvent, steam is forced into the absorber –solvent vapor is forced out of the carbon and into the steam.
The solvent-vapor steam is cooled down and condensed into liquid state.
Mixture is piped into a decant tank, the solvent and water separate into distinct layers (solvent is lighter than water).
Solvent- siphoned out off the top into a collection tank for disposal (Reuse).
Nonpolar solvents- not miscible with water.
Recovered solvent can be reused directly.
Recovered water- traces of solvent.
Packaging and product gravure- use polar solvents or mixtures containing polar solvents. Partially miscible with water. Recovered solvent contains some water and decanted water contains solvent.
Capture efficiency- the ability of solvent recovery unit to get as much exhaust air as possible.

INCIERATION
Incineration- other option. Good pollution control method when solvent recovery is not feasible.
Incineration – burns high-boiling point solvents.
Incinerators- small enough for one small press, where solvent recovery is not economical for single press.
The heat from incinerators can be reused- to preheat successive batches of solvent laden air which is to be incinerated at around 1, 450°F.
The tail gases can be used to heat dryers or winter time fresh air.
Dryers with incinerators can be identical to those with solvent recovery. LEL controls, LEL indicators are essential for keeping the exhaust rates low and safe.
Incinerators can operate at much lower temperatures if a catalyst is used to trigger the oxidation of hydrocarbons.
Catalysts- Pt platinum and palladium- initiate the catalysis of oxidation at 650°F.
Manganese dioxide and cerium oxide blends bring down to 450°F.
Solvent capture limits- 92-98 % recovery crucial for recovery and incineration.
Tracking tonnage of purchased, used, recovered and reused. Control devices, their maintenance. Water based inks more appealing???
BASICS OF COLOR SEPARATION
Converting continuous tone color into printing cylinders, printing plates- is called
COLOR SEPARATION
E.g. gravure printing press- prints one color and desired density in one printing unit
Innumerable hues, variations in color- converted into 4 color separations- later to printing cylinders-to print by
primary ink pigments.
Four transparent printing inks- primary.
Overlapped- create secondary and overprint colors.
Yellow, magenta, cyan, black - for them must be made color separations.
Color separation: Traditional camera techniques- using filters to separate colors;
Electronic color scanner- filtered photomultiplier tubes.
Results are quantified-for future reference.
Current technology- high standards.
COLOR THEORY
Human perception- customer- subjective judgement.
All colors- contained in white light source- reflected from substrate.
4 variables in color reproduction: light source, colored object, human eye, human brain.
STANDARD WHITE LIGHT SOURCE
Light – mixture of all colors; variation in source can make the same subject appear different
Incident (projected); or reflected.
Ideal = average daylight; not available at different locations at different time of day.
Light- combination of all wavelengths of energy.
Light- travels at speed of 186,000 miles/sec.
Passing the light through glass prism- different wavelengths refract at different angles- rainbow of colors visible to
eye is created.
Unit to measure the wavelength- nm nanometer 10^-9 m.
Visible spectrum- 400-700 nm violet (blue)- to red.
Light sources for viewing the color- white light sources- imbalance of hues.
White light – standardized- spectral energy distribution- balanced amount of red, blue and green light.
Industry standard- controlling spectral energy distribution = color rendering index = 90
2 different light sources conform to this standard- allow any copy to be viewed under the same conditions.
Color temperature- measured in degrees of Kelvin.
0°K= - 273.1 °C absolute zero - (temperature at which radiator would emit no light).
Many different light sources available - imperative to view or evaluate color reproduction under standard source.
Industry standard light source: 5000 °K: average daylight 10:00 am- 2:00 pm northern hemisphere.
Some gravure plants- Roto News- at 7500 °K- due to color absorption factor of substrate.
Current industry trend- use 5000 °K for all color reproduction work.
Quality control: GATF/RHEM indicator - patch with 2 alternating magenta strips- metameric in nature. When placed
under standard 5000 °K light strips appear as 1 color- comprised of different mixes of color.
Commercially available viewing booths- standard illumination.
COLORED PIGMENTATION
Colored substance- second variable ( original camera copy, color photograph, transparency)
Printed reproduction- ink pigment- way how it interacts with light.
Hue- appearance- comes from pigment absorption of white light.
Printing inks- 3 process colors- yellow, magenta, cyan - each absorb 1/3 of visible light spectrum.
Allowing residual 2/3 to be reflected
E.g.: yellow ink- absorbs blue, reflects red and green light- combine- create yellow to the eye
3 subtractive primary colors overlap- create black- total absorption- no reflection.
Black-referred to as a color- is not a color- rather : total absence of reflected light.
Why printers use black: 3 primary are not ideal- not able to absorb 100 % of light.
To overprint 3 process colors- over one another- produces muddy black-
Fourth color – black required- pure black- more economical, accurate.
ADDITIVE COLOR
Creation of color separation based not on behavior of pigments - but on behavior of light itself.
3 primary colors - red, blue and green - additive in value.
3 additive colors of light combined in equal % - form white light.
COLOR CORRECTION FOR COLOR IMPURITIES
Ink pigment- not perfect in absorbing 1/3 of visible spectrum, and perfectly reflect other 2/3.
Adjustment during separation-color correction.
Understanding ink deficiencies.
Yellow- best and purest pigment on the market.
Yellow would almost totally absorb the blue 1/3 of spectrum, reflect red and green.
Second purest- magenta- impurity is often yellow.
Least pure- cyan- appears to have magenta impurity- would have also yellow.
Major impurity- magenta, minor yellow.
Color being impure- pigment can still be chemically pure individual.
Color impurities in pigments cannot be removed- purpose of color correction- to reduce the amount of ink being printed in those regions of each separation where they overlap.
Yellow separation receives most color correction- yellow is already contained in magenta and cyan.
Process inks- vary from one to other manufacturer.
Color separators must know the ink/pigment impurities for each client before performing color correction.

THE HUMAN EYE
3rd variable in color sensation- reaction of human eye.
Retina of human eye-2 types of sensors- rods and cones.
Rods- reduced illumination – existing colors are transmitted as tonal gradation of achromatic vision.
Sensitivity of rods- at dusk- colored objects are silhouetted or gray.
Limited illumination restricts cones from sensing color.
Every individual perceives color differently- based on differences in 6 million cones in eye.
Cones- selective receptors of red, green or blue light or chromatic color.
Color-blindness- 8 % males, 1 % females; Green-red portion of the spectrum.
MENTAL ASPECTS OF COLOR THEORY
Physiological- psychological aspects –subjective part of color evaluation.
Human brain is not capable of remembering color or tone on absolute basis.
Densitometry, colorimetry- evaluation of color- verification of standards.
Person’s ability to view the color is affected by:
Angle of viewing (90 deg- best);
Angle of illumination- 45 deg- standard- or commercial viewing booth;
Distance of viewing- 14-18 in;
Texture of surface being viewed;
Glossy color images vs. flat color;
Size and shape of colored image;
Health, mental attitude.

FATIGUE AND STRAIN
Nerve cells- fatigued- ability to view the color- impaired.
Eye fatigue- long time looking at bright source or color hue.
Fatigue influences next color to be viewed.

SUBJECTIVE MEMORY COLORS
Memory color - key elements in image- blue sky, green grass, red apples-
Each individual recalls those.
Color separations may be rejected due to differences in remembered colors.
Geographical differences, individual background- play important role in the perception of color reproduction.
TRANSMITTED COLORS
Transparent copy- preferred medium for color separation.
Transparent dye, pigment.
Transparent copy- 35mm transparency, or larger transparency.
Transparency- first generation original- sharpest image resolution.
4x5, 5x7 or 8x10 in. transparencies- preferred (enlargement, retouching imperfections).
DYES AND TRANSPARENCIES
Use the same manufacturer’s duplicating film as the original transparency.
Emulsions sensitive to specific memory colors—color may shift at different manufacturer’s film.
Transparent retouching dyes recommended by film manufacturer (match by eye, but produces different spectral sensitivity in the camera).

**REFLECTED COLOR**
Reflection copy—most popular form of black and white copy.
Water color, line drawing, color print, oil painting.
Reflection copy—less popular with color separators—often second generation copy—reproduction.
Original generation of color photograph—color negative.
Each new generation—shifts in color, increased grain, loss of image resolution.
Dye transfer = color photograph made from 3 dyed layers contacted in register.
Expensive, excellent reflection copy.

**INK AND SUBSTRATE**
All colors—on white paper.
Inks filter subtracting pure color from white light—combining the rest.
Each primary color—absorbs its complementary color from white light.
Paper—color cast—also absorbs color from incoming light and reflects the reminder.
White paper—balance of white reflection—warm whites, blue whites—in viewing booth.
The whiteness of paper measured by the degree of equal red, green, blue reflectance under standard illumination.
**Brightness**—reflectivity of substrate at 457 nm.

**MEASUREMENT OF COLOR**
Three dimensional phenomenon:
- **Hue**—actual color (adequately describes the difference between red, orange, blue, yellow).
- **Saturation**—purity of a given hue—its freedom from gray (engine red—brick red = red hue)
- **Lightness**—how light or dark the value is—degree of density

**COLOR MEASUREMENT MODELS**
Efforts—physical color models relied on human perception.
DIN, Ostwald, Munsell systems.
Most common colorimetric measurement is CIE
(Commission Internationale de l’Eclairage; International Commission on Illumination)
CIE defines standard light source, and average observer (average human sensitivity to red, green, blue)
Tristimulus values red = X, green = Y, blue = Z, changed into chromaticity coordinates
x(hue) = X/(X+Y+Z) y (chroma) = Y(green)/(X+Y+Z)
x, and y used to plot specific color on the chromaticity diagram
Three instruments for measuring the color: Spectrophotometer, Colorimeter, Densitometer

**SPECTROPHOTOMETER**
Reflected or transmitted light—measures along the electromagnetic spectrum
Instrument produces data as a spectral energy distribution curve—spectrometric curve
Measures: color of the ink
Used also for color matching—metameric color match—different light source—they look different
Spectrophotometer—identifies different spectrophotometric curves in metameric inks
- Illuminates the sample with essentially monochromatic light;
- Measures all the diffusely reflected light at each wavelength;
- Expresses the amount of light reflected as % of diffuse reflectance at the same wavelength by white reference standard.

**COLORIMETER**
Measurement of color that uses tristimulus reading similar to that of the human eye
Parallels the way the human eye uses red, green, blue sensitive cones to translate color vision

**INK and COLOR**
First-source of light.
Without light—there is no color to be seen.
Distinct interaction with light produces different color.
Color results from interaction of light and pigment.
Light missing—result-black.
Pigment is missing—result is white.
Color and Light present—How they will be viewed?
Color receptors of eye accept the light reflected by broccoli, cranberry juice, orange. Transform it to electrical impulses. Brain – accept it as color. 

**Color and Light**

Light from sun appears to be white- composed of several colors –when in equal portions- appear white. Light – radiant energy – travels in waves. 
400-700 nm, wavelength determines the color. 
E.g. beam of 430-450 nm – bright blue light. 
630-650 nm - engine red. 
Two beams overlap-result-lighter color (light being added to light). 
Green, blue and red light combined: 
Area of blue and red combination - magenta (Green missing) 
Green and red combination -yellow (Blue missing) 
Blue and green - cyan (Red missing) 
Any color can be produced by combination of green, red and blue light: Additive primary colors 

**Pigments and Light**

Subtractive system- description of interaction of light and pigment. 
Chemical composition of pigments causes partial absorption of light. 
Selective absorption causes that white light is disturbed and color is produced 
All light is absorbed – black sensation. 
All of the light is reflected - white sensation. 
Primary colors of the light – red, blue, and green. 
Combination of equal amounts of two primaries - secondary color in additive system: Cyan, magenta, yellow.

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**CHEMICAL PULPING**

**Delignification:** breaking down the chemical structure of lignin 
**Kappa number:** measure of the lignin content in the pulp 
**Pulp viscosity:** measure of the average chain length of cellulose (DP- degree of polymerization) 
**Fiber Liberation Point:** (130-180°C) – occurs when sufficient lignin has been removed during pulping- chips are broken apart into fibers with little or no mechanical action. 
**Full chemical pulp:** produced by chemical methods only; yield about 50%, lignin content 3-5 % 
**Unbleached pulp:** full chemical pulp as it comes from the pulping process, light to dark brown in color 
**Bleached pulp:** white pulp produced by bleaching full chemical pulp 
**Dissolving pulp:** bleached chemical pulp; yield 30-35%, high cellulose content (95% or higher) 
Kraft process with acid prehydrolysis or acid sulfite process; Improved cellulose purity achieved by a cold alkali extraction. Used for cellulose derivatives production (rayon, Cellulose acetate, cellophane). 
**Kappa number:** consumption of 0.1 N KmnO4 in milliliters consumed by one gram of pulp in 0.1 N sulfuric acid (H2SO4) used to monitor the degree of delignification of chemical pulps after pulping and between bleaching stages. 
Klason lignin, acid soluble lignin: gravimetric, direct method; KL- residue after total acid hydrolysis of carbohydrates portion of wood/pulp. Acid soluble lignin can be estimated spectrophotometrically (UV region). For hardwood pulps: Klason lignin, % = 0.15 x Kappa number

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**KRAFT PULPING**

Full chemical pulping with NaOH and Na2S, pH above 12 , 160-180 °C , 800 kPa (120 psi), 0.5-3 hrs 
Useful for any species of wood, high strength of pulp, tolerant to bark, efficient energy and chemicals recovery cycle 

Disadvantages: difficult to bleach compare to sulfite pulps, low yields (carbohydrate losses), sulfur compounds- extremely offensive odor 80% of lignin dissolved, 50% hemi, 10 % of cellulose 

**Grades:** 
**Soft cooks**- (for bleached grades) lignin content 3.0-5 .2 % (20-35 Kappa #) 
For softwoods, or 1.8-2.4 % lignin (12-18 Kappa #) hardwoods 
**Medium soft cooks**- (bag papers) lignin- 5.2-7.5% (35-50 Kappa #) 
**Hard softwood cooks**- 9-11 % lignin (65-70 Kappa #)- top liner boards 12-16.5 % lignin (80-110 Kappa #) – bottom liner
Digester:
Pressurized vessel for cooking chips into pulp

A. BATCH DIGESTER

70-350m³
Mill has a bank of 6-8 digesters

Heating:
- Direct- with the steam, dilutes the cooking liquor, changes the liquor to wood ratio, bad uniformity of cooking-disadvantage
- Indirect- cooking liquor heated outside the digester, heat exchanger. More uniform heating and cooking.

Cooking time: time from initial steaming of chips to start of digester blowing

Time to temperature: Time from initial steaming of chips to the point when desired temperature is reached

Time at temperature: Time from when the cooking T is reached until digester blow starts

Cooking sequence:
- Filling of the digester with chips, white liquor, and weak black liquor
- After initial circulation of the liquor (contents settle) additional chips are added
- Digester sealed and heating starts; temperature rises for about 90 min until the cooking temperature is achieved.
- Cookig T is reached- cook at the temperature 0.5-3 hrs
- During the heating time, air and other gases from the digester are vented
- When cook is completed (Kappa #), content of the digester is discharged to the blow tank
- Digester is opened and the sequence is repeated

B. Continuous Digester

Tube shaped vessel, with elements: presteaming, liquor impregnation, heating, cooking, and washing Chips enter and exit the digester continuously More space efficient, easier to control, labor saving, energy efficient than batch digester

Rotary valves help to fill the digester, from atmospheric to high pressure

KAMYR DIGESTER
Vertical digester (One to two vessels) 77 million tons/year
3 zones: heating, cooking, washing

M&D Digester (Messig & Durkee)
Inclined at 45 degree
Kraft pulping of sawdust, acid prehydrolysis (with kraft), and semichemical pulping
Cooking time approx. 30 min
Diameter about 2.4 m- relatively small production levels

PANDIA DIGESTER
Horizontal digester, multi- tube (2-8 digester)
Screw feed
Kraft pulping of sawdust
Semichemical pulping of chips, non-woods (straw), short cooking times

Digester blowing
Continuous digester- @ about 100°C
Batch digester- @ or near cooking temperature 170 °C, pulp loses a significant amount of strength (10-15%)
Vapor expansion in chips is usually sufficient force to cause fiber separation

Blow tank
Large cylindrical vessel
Hot pulp from digester is mixed with agitators with diluted black liquor
Hot gases from BT are recovered by the blow heat accumulator (heat exchanger). Condensates sometimes used as dilution water, in brown stock washing, etc. Non-condensable gases often diverted to the lime kiln for combustion

Liquor to wood ratio
3:1 to 4:1 in full chemical pulping
It is kept as small as possible while maintaining good digester operation including good circulation for even cooking

LIQUOR/WOOD= [TOTAL PULPING LIQUOR MASS]/ [DRY WOOD MASS]

REJECTS, KNOTTER, SCREENER
Rejects portion (knots) not sufficiently delignified to liberate Knotter- coarse screening equipment (3/8 in holes)
Rejects in kraft pulping are repulped. After washing, pulps screened to remove shivers, dirt, contaminants. Shorter fibers (hardwoods) screen more easily than softwoods. Pulp screened prior to washing for improved washing efficiency
**BROWN STOCK WASHERS**

- Rotary vacuum washers
- Drum washers with wire-mesh covered cylinder
- Drop leg of pipe supplies the washer with a vacuum
- As the drum contacts the slurry, a vacuum is applied to thicken the stock
- Typical configuration: 3-4 washers
- 80% of the contaminants are removed at each stage
- Double wire press
- Suitable for market pulp production
- Brown stock washing, washing between bleaching stages, or stock thickening
- Black Clowson
- Continuous, wire countercurrent washer

**KRAFT SPENT LIQUOR RECOVERY**

**A- Evaporation** - concentration of black liquor
- Multiple-effect evaporators (7 pcs)
- Concentrator
  - 15% solids in dilute black liquor (from 1 washing stage) to 65-70% solids after concentrator
  - Steam-black liquor countercurrent flow
- B- Combustion - recovery boiler
  - Burns the concentrated black liquor by spraying it into the furnace through side openings
  - The water evaporates and the organic materials removed from the wood form the char and then burn
  - Fuel value of black liquor (65-70% solids) is 14-16 MJ/kg compare to coal 32 MJ/kg
  - Overall chemical reactions in the recovery boiler in addition to combustion are:
    - \[ 2 \text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \] (Conversion of sodium salts)
    - \[ \text{Na}_2\text{SO}_4 + 4 \text{C} = \text{Na}_2\text{S} + 4 \text{CO} \] (Reduction of make-up chemicals)
  - Firing up black liquor at 65% solids leads to a maximum combustion temperature of 1100-1300°C (2000-2400 °F)
  - The recovery boiler is the largest, single most expensive piece of equipment in a kraft mill costing over $100 million

Molten slag leaves the boiler directly to the green liquor dissolving tank

**Causticizing process**

- Green liquor clarifier
- Slaker \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \)
- Causticizers
- \( \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow 2 \text{NaOH} + \text{CaCO}_3 \)
- White liquor clarifier - digester
- Lime kiln, 3 zones: Drying, heating, calcining
- \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \) (g)
- Causticizing efficiency 78-80%
- Causticizing efficiency = \( \frac{\text{NaOH}}{[\text{NaOH} + \text{Na}_2\text{CO}_3]} \times 100 \) [%]

**LIQUORS**

- Cooking: (Pulping liquor) Black liquor + White liquor + wood moisture
- Black liquor (residual alkali, \( \text{Na}_2\text{S}, \text{NaOH} \))
- White liquor (conc. \( \text{Na}_2\text{S}, \text{NaOH} \))
- Wood moisture \( \text{H}_2\text{O} \)
- Black Liquor: (spent liquor)
- Residual alkali, \( \text{Na}_2\text{S}, \text{NaOH} \)
- Green liquor (after combustion)
- \( \text{Na}_2\text{S}, \text{Na}_2\text{CO}_3 \)
- White liquor- fresh pulping liquor
- \( \text{NaOH} + \text{Na}_2\text{S}, \) (Impurities, salt, \( \text{Na}_2\text{CO}_3 \), water, corrosion, etc.)

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**PULPS BLEACHING**
Bleaching is the treatment of pulp with the chemical agents to increase their brightness. Brightness is a term used to describe the whiteness of pulp or paper, on scale from 0 % (absolute black) to 100 % (relative to a MgO standard which has an absolute brightness of about 96 %) by the reflectance of blue light (457 nm) from paper. Color reversion is the yellowing of pulp on exposure to air, heat, certain metallic ions, and fungi due to modification of residual lignin forming chromophores. Mechanical pulp are particularly susceptible to color reversion, though chemical pulps may experience this when exposed to high temperature. Bleaching sequence is a combination of separate bleaching stages (e.g. CEDED, CEHH, CEHD, OC/DEoDED etc.). Each stage consists of a pump to mix the chemicals with the pulp, a retention tower to provide time for the bleaching chemical to react with the pulp, and the washer to remove the bleaching chemicals and solubilized pulp components.

Lignin content measurement is a vital tool to monitor the degree of cook or to measure residual lignin before bleaching and between various stages of bleaching to monitor the process. Important value for the bleaching chemicals charge. Kappa number test is an indirect method for determining lignin by the consumption of permanganate ion by lignin. (Kappa number is the number of milliliters of 0.1 N KmnO4 consumed by one gram of pulp in 0.5 N sulfuric acid after a ten minute reaction time at 25 oC under conditions such that one-half of permanganate remains unreacted). Klason lignin is the residue obtained after total acid hydrolysis of the carbohydrate portion of wood (cellulose, hemicellulose). It is gravimetric method for determining lignin directly in woody materials. Some part of the lignin remains soluble (“acid soluble lignin”) and can be estimated spectrophotometrically in the UV region of spectra.

**BLEACHING PROCESSES**

are either:

- Lignin removing
- Lignin preserving (conversion or stablization of chromophores [light absorbing funtional groups])

Bleaching chemicals may be:

**Oxidizing**

- Cl: chlorine , ClO2: chlorine dioxide, O3: ozone , O2: oxygen, Na2O2:
- sodium peroxide, H2O2: hydrogen peroxide,
- NaOCl sodium hypochlorite

**Reducing**

- Na2S2O4: sodium dithionite, ZnS2O4: zinc dithionite , NaHSO3: sodium bisulfite

**A / BLEACHING OF MECHANICAL PULPS**

To maintain the yield, lignin preserving bleaching is used. Bleaching of mechanical pulps involves masking the lignin that is present , instead of removing the lignin as is case for bleaching chemical pulps. Bleaching mechanical pulps is often refered to as brightening. Bleaching chemicals may be oxidizing (mainly hydrogen peroxide), reducing (mainly the dithionites) or a combination. Mechanical pulps are bleached with Chemicals designed to alter many of the chromophores. Chromophores are most often conjugated double bonds systems arising in the lignin of pulps.

Fairly limited brightness improvements are realized (6-12 % typically) with a maximum brightness of 60-70 % in a single stage, or up to 75 % in a two stage process. If two stages are used, the oxidative stage is used before the reductive stage or else the oxidant will undo what the reductive compound accomplished.

**a/ Dithionite, Hydrosulfite Bleaching**

Previously, zinc dithionite was used because is very stable. However, zinc is toxic to fish, therefore, the sodium form has replaced the zinc form. Zinc dithionite was prepared in the pulp mill from zinc and sulfur dioxide as follows:

\[
Zn + 2 SO_2 \longrightarrow ZnS_2O_4
\]

Bleaching is carried out at pH 5-6 with chelating agents to prevent metal ions such as iron (III) from coloring the pulp. Bleaching is often carried out in the refiners. The reaction time is on the order of 10-30 minutes. The brightness gain is only 5-8 %. If hydrogen peroxide and dithionite are used in a two-stage process, the dithionite must be the second stage or hydrogen peroxide will re-oxidize those moieties reduced by the dithionite. The reaction of dithionite is :

\[
S_2O_5^{2-} + 2 H_2O \longrightarrow 2 HSO_3^- + 2 H^+ + 2 e^-
\]

Dithionites reduce quinone structures present at lignin macromolecules to hydroquinones.

**b/ Oxidative Bleaching (Peroxide Bleaching)**

Some metal ions, such as Fe3+, Mn2+ and Cu2+, catalytically decompose hydrogen peroxide, so peroxide bleaching is carried out with agents that deactivate these metal ions:
Fe^{3+} \rightarrow H_2O + \frac{1}{2} O_2

Chelating agents, such as EDTA, DTPA or sodium silicate are used. Brightness gain is about 6-20 %. Hydrogen peroxide with sodium hydroxide and/or sodium peroxide (NaOOH) is used to produce the high pH that is necessary to produce the active perhydroxyl ion, HOO^-:

\[ H_2O + HOH \rightarrow (H_3O)^+ + HOO^- \]

Some carbohydrates degradation occurs and is responsible for about half of the peroxide consumed. Color reduction occurs by altering chromophoric groups such as orthoquinones. The pulp is sometimes subsequently treated with SO_2 to neutralize OH^- and reduce any residual peroxide. Yellowing of high-yield pulps

High yield pulps can be bleached, but not permanently. Photoyellowing is mainly due to UV (wavelengths <400 nm) induced free radicals of lignin:

Lignin-OH \rightarrow .Lignin + .OH
Lignin-O-lignin \rightarrow Lignin-O. + .Lignin

UV light is mainly absorbed by an alpha-carbonyl group. The alpha-cabonyl is promoted to an excited state: Carboxyl groups can also absorb energy and convert oxygen from its triplet ground state to an excited singlet that can oxidize aromatic rings.

Stabilization of high-yield pulps. Objective is the prevention of radical formation methods:
- reduction of alpha-carbonyls to alcohols
- etherification or esterification of phenolic hydroxyl singlet oxygen quenchers (compounds that react more rapidly than the lignin with singlet oxygen)
- hydrogenation of double bonds
- UV absorbers

**B/ BLEACHING OF CHEMICAL PULPS (Lignin Removing Bleaching)**

The use of three to seven stages increases the efficiency of bleaching by reducing the amount of chemical required. This is due to the complex nature of lignin; each bleaching chemical is going to react differently with lignin. Since chemical pulps are dark to begin with, bleaching increases brightness up to 70 % with a maximum brightness of about 92 %.

Bleached chemical pulps are insensitive to color reversion, but high temperatures may induce some color reversion. Lignin removal is accompanied by significant losses of pulp yield and strength of individual fibers. However, the strength of fiber-fiber bonding increases after bleaching. Bleaching chemicals are generally more specific to lignin removal than to carbohydrate degradation compared with the chemicals used in pulping. Bleaching is much more expensive than pulping for a given amount of lignin removal. Some of the bleaching chemicals are very specific to lignin removal while others are much less specific and cause appreciable carbohydrate degradation and diminished yield.

Oxygen and chlorine are relatively inexpensive, but not particularly selective for lignin removal. These chemicals are used in the early stages of bleaching to remove most of the lignin. Residual lignin is removed in later stages with expensive, but highly selective bleaching agents like chlorine dioxide, hypochlorite, and hydrogen peroxide.

**Chlorination Stage (C)**

Chlorination is being phased out, due to environmental concerns. Due to its importance for many years, however, lots of what we know about bleaching chemistry is related to the reactions of lignin with chlorine. Elemental chlorine has been used since shortly after its discovery in 1774 by Scheele. Chlorine is manufactured concomitantly with sodium hydroxide by electrolysis of sodium chloride; since these two chemicals are produced together, one often speaks of the chlor-alkali industry. The production of chlorine is summarized as follows:

\[ 2 NaCl + 2 H_2O + e^- \rightarrow Cl_2 + 2 NaOH + H_2 \]

Pressurized, upflow reactors are used since the solubility of chlorine in water is low (4 g/L at STP). Chlorine is not overly specific to lignin, and much carbohydrate degradation occurs through its use. The chlorine reacts with the lignin by:
- substitution
- oxidation
- addition

Oxidation includes reactions with both lignin and carbohydrates. Oxidation of the carbohydrates leads to a decreases cellulose viscosity and decreased pulp strength. Lignin is not removed to a large degree in this stage, and the pulp actually gets darker (with a characteristic orange color). Chlorination produces chlorinated organic materials
including a very small amount of dioxins. Since these compounds are recognized as powerful toxins and carcinogens, their detection in bleach plant effluents prompted a flurry of investigative activity in Europe and North America to identify point sources and corrective measures. The chlorination/extraction sequence was subsequently found to be the major source of these compounds. Many mills have already replaced up to 50% of the chlorine (Cl\(_2\)) with chlorine dioxide (ClO\(_2\)).

Analytical methods include:
- AOX (Adsorbable Organically bound Halogens),
- EOX (Extractable Organically bound Halogens) and
- TOX (Total Organohalogens – when AOX is analyzed together with volatiles).

Specified load limits for chlorinated material, measured as AOX, have either already been introduced or will be valid in the middle of 1990s for pulp mills in many pulp-producing countries including Scandinavia, Germany, Canada and Australia. These limits vary somewhat, but are in the range of 1 – 3 kg AOX/ton of pulp.

**CD Stage**
The CD or CD is a modification of C stage bleaching, where some of the chlorine is replaced with ClO\(_2\). Substitution of 10% of the chlorine is used to prevent over chlorination. Substitution of 50% or more of chlorine with chlorine dioxide at many mills is becoming common to reduce production of dioxins and other chlorinated organic chemicals.

**Extraction Stage (E)**
The E stage is extraction of degraded lignin compounds, which would otherwise increase the chemical usage in subsequent bleaching stages, with caustic (NaOH) solution. The objective of this step is removal of chromophores from previous steps: chlorinated and oxidized lignin fragments are removed this increases the brightness that can be imparted by subsequent bleaching steps better brightness, opacity, softness & mechanical properties limited removal of polysaccharides.

**Chemistry of alkaline extraction**
Removal of chlorinated lignin. Chlorination appears to give three types of lignin fragments: Small molecular weight fragments-these are water soluble and removed in the wash after chlorination. Larger molecular weight fragments-soluble in alkali, at base concentrations of 0.5-1% and pH ~ 12. A portion is insoluble even at severe alkaline conditions. These require more oxidative steps. Removal of chlorinated lignin fragments is thought to occur by one of two mechanisms:
- physical process-time & temperature control the solubilization
- chemical process-base hydrolyzes chlorine in aliphatic & aromatic positions

- Removal of hemicelluloses
- Saponification of fatty acids and resin acids
- Degradation of chain length of polysaccharides

Chlorination and alkaline extraction will remove ~80% of the residual lignin, but the resultant pulp has low brightness due to a relative increase in chromophoric groups. The alkali displaces chlorine and makes the lignin soluble by the reactions such as:

\[
\text{Lignin-Cl} + \text{NaOH} \rightarrow \text{Lignin-OH} + \text{NaCl}
\]

The lignin in the E1 effluent gives a dark color that is ultimately responsible for much of the color of the final mill effluent. Recently oxygen gas has been incorporated into this stage (0.5 % on pulp) at many mills and the term Eo applies. When E stage follows the C stage (E1) it is often used with downflow tower due to the high consistency of pulp (10 - 18%).

**Hypochlorite Stage (H)**
The H stage consists of bleaching usually with sodium hypochlorite solution (NaClO). It is important to maintain the pH above 8 because below this pH hypochlorite is in equilibrium with significant amounts of hypochlorous acid (HOC1), which is powerful oxidant of carbohydrates. Since the pH is high, lignin is continuously extracted as it is depolymerized. Hypochlorite reacts principally by oxidation. The chemical is more selective than elemental chlorine, but less selective than chlorine dioxide. Sodium hypochlorite, which is now used since it leads to less scaling, is made from chlorine as follows:

\[
\text{Cl}_2 + 2 \text{NaOH} \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}
\]

**Chlorine Dioxide Stage (D)**
ClO\(_2\) is relative expensive, but highly selective for lignin. This makes it very useful for the latter bleaching stages where lignin is present in very low concentrations. It is explosive at concentrations above 10 kPa; hence, it cannot be transported and must be manufactures on site. Downflow towers are used to decrease the risk of gas accumulation. The D stage is useful for reducing shive contents. It reacts by oxidation.
Chlorine dioxide is:
- selective oxidant for lignin
- doesn't degrade carbohydrates
- maintains pulp strength
- free radical (has an unpaired electron)
- unstable, explosive, this probably accounts for its reactivity
- best results obtained in later stages of bleaching

**Peroxide Stage (P)**
Bleaching with hydrogen peroxide, $\text{H}_2\text{O}_2$ is not common for chemical pulps. It is usually used for brightening mechanical pulps, but when it is used to bleach chemical pulps it appears as the last stage of a sequence such as C-E-H-P or C-E-H-D-P. It is an expensive bleaching agent, but may be used more frequently as the use of elemental chlorine decreases.

**Oxygen Stage (O)**
Oxygen bleaching or pulping is the delignification of pulp using oxygen under pressure and NaOH. This is an odorless, relatively pollution-free process used prior to chlorination. This is the most inexpensive bleaching chemical to use, but also the least specific for lignin removal. A considerable decrease in cellulose viscosity accompanies this process. Bleaching may be thought of as extended delignification, that is, an extension of the pulping process. Some call it oxygen delignification. It is used before the traditional chlorination first step of bleaching to reduce the Kappa number from 30-35 after pulping (softwood) to 14-18 after oxygen bleaching stage. Bleaching to Kappa numbers below this leads to unacceptable losses of the cellulose viscosity.

The effluent of oxygen delignification can be used in the brown stock washers or otherwise ultimately sent to the recovery boiler because there is no chloride ion (corrosion).

There are two main methods of oxygen bleaching: medium consistency (10-15%) and high consistency (30 %). The high consistency method is more common (in oxygen pre-tower), but with the difficulties, such as the gas in the reactor (pre-tower) contains high concentration of oxygen and volatile organic chemicals such as methanol, ethanol, and acetone that are potentially explosive. Temperature of oxygen bleaching is important to the selectivity of the process with better selectivity at 100 oC than 130 oC.

**Ozone bleaching (Z)**
Ozone is a very strong oxidizing agent and reacts under acidic conditions. Upon reaction, ozone is reduced to oxygen or hydrogen peroxide.

**Advantage:** Production of ozone can be stopped in the case of emergency

**Disadvantage:** Acidic conditions ($\text{H}_2\text{SO}_4$), Low solubility of ozone in water (low temperatures used)

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**REFINING AND PULP CHARACTERIZATION**

Refining – mechanical treatment of pulp fibers to develop their optimum papermaking properties. Refining increases the strength of fiber to fiber bonds by increasing the surface area of the fibers and making the fibers more pliable to conform around each other, which increases the bonding surface area and leads to a denser sheet. Generally a refining is a trade-off between improving fiber to fiber bonding and decreasing the strength of individual fibers. Most strength properties of paper increase with pulp refining, since they rely on fiber to fiber bonding. The tear strength, which depends highly on the strength of the individual fibers, actually decreases with refining. Refining of pulp increases their flexibility and leads to denser paper. This means bulk, opacity, and porosity values decrease with refining.

**Fiber Brushing** - refining at high consistency with a relatively large distance between the refiner plates increases fiber-fiber interactions that are termed fiber brushing. This tends to roughen the fiber surface, with minimal fiber cutting for improved fiber-fiber bonding.

**Fiber Cutting** - Operating refiners at low consistencies with a minimal distance between the refiner plates increases fiber-bar contact, resulting in fiber cutting. This is desired with long-fiber pulps (redwood, cotton etc.) to increase the quality of formation on the paper machine. In most cases, however, it is desirable to minimize fiber cutting to maintain high paper strength.
Drainage – is the ease of removing water from pulp fibers, either by gravity or mechanical means. CSF is a measure of drainage and a useful means for determining the level of refining.

Fibrillation – production of rough surfaces on fibers by mechanical action; refiners break the outer layer of fibers, i.e., the primary cell wall, causing the fibrils from the secondary cell wall to protrude from the fiber surfaces. For example, the surface area of kraft, softwood fibers is on the order of 1m²/g at 750 CSF, but it increases to about 5m²/g at 350 CSF.

Average fiber length – statistical average length of fibers in pulp. Fiber length is measured microscopically (number average), by classification with screens (weight average) or by optical scanners - Kajaani (number average). The coarseness of fibers has an important effect on many properties of paper. Coarseness is defined as the weight per unit length of fiber expressed as milligrams per 100 m.

Pulp used to be treated in beaters, such as the Hollander beater, but now refiners are used. The terms beating and refining are often used interchangeably, but refining is applicable to most modern equipment.

Canadian Standard Freeness, CSF – the CSF test was developed for use with groundwood pulps and was not intended for use with chemical pulps; nevertheless, it is the standard test for monitoring refining in North American mills. Refining decreases the pulp freeness, the rate at which water will drain through the pulp. Refined pulp, therefore, has a low freeness. A high drainage rate also means a high freeness. Obviously freeness is of utmost importance in the operation of a paper machine. A low freeness means that the paper machine will have to operate relatively slowly, a condition that is usually intolerable. There are other freeness tests that are used around the world. Perhaps the most common one is the Shopper Riegler test, which is similar in concept to the CSF test. CSF results depend on the temperature and consistency.

PAPER MANUFACTURE

- Stock Preparation
- Paper Machine
- Paper Converting

A/ Stock Preparation
- the interface between the pulp mill or pulp warehouse and the paper machine
- in integrated mill begins with dilution of the heavy stock at the discharge of the high-density pulp storage chests and ends with the blended papermaking furnish in the machine chest
- in the independent paper mill begins by feeding pulp bales into the repulping system

Objectives:
- to take the required fibrous raw materials (pulps) and non-fibrous components (additives)
- treat and modify each furnish constituent as required
- combine all the ingredients continuously and uniformly into the papermaking stock

Operations:
Repulping – baled pulp (or other fibrous material) is dispersed into water to form a slush or slurry. The operation can be either batch or continuous.
Refining (or beating) - the fibers are subjected to mechanical action to develop their optimal papermaking properties with the respect to the product being made. The operation is usually continuous, but some non-wood and specialty pulps are still treated batch-wise.
Utilization of Wet-End Additives – a wide variety of mineral and chemical agents are added to the stock, either to impart specific properties to the paper product or to facilitate the papermaking process. Preparation is usually carried out batch-wise.
Metering and Blending – the various fibrous and non-fibrous furnish components are continuously combined and blended to form the papermaking stock.
Additional Operations – pulp screening and cleaning, secondary stock preparation system, white water and broke handling systems, etc. Classification of wet-end chemical and mineral additives

Functional additives
- Fillers (e.g., kaolin clays, talc, TiO₂) – improve optical and surface and optical and surface properties
- Sizing agents (e.g., rosin) – control penetration of liquids, help to repel water
- Dry-strength adhesives (e.g., starches, gums) – improve burst and tensile; add stiffness and pick resistance
- Wet-strength resins add wet strength to such grades as towelling and wrapping
- Dyes (dyes and pigments) – impart desired color
- Optical brighteners improve apparent brightness
- Control additives
- Retention aids improve retention of fines and fillers, polymers bind to fines, overcome surface charge
- Drainage aids increase water removal (rate) on wire
- Acids and bases control pH
- Alum \( \text{Al}_2(\text{SO}_4)_3 \) control pH, fix additives onto fibers, improve retention
- Fiber flocculants improve sheet formation
- Defoamers improve drainage and sheet formation
- Pitch control chemicals prevent deposit/accumulation of pitch
- Slimicides/biocides control slime growth and other microorganisms
- Specialty chemicals corrosion inhibitors, flame proofing and antitarnish, chemicals etc.

**B/ Paper Machine (PM)**

1803 – 1807 patents issued to Fourdrinier brothers for improved continuous paper machine
1809 patent issued to John Dickinson for the cylinder paper machine (England)
1817 first cylinder machine in America
1827 first Fourdrinier machine in America

**Sections of PM:**

1. Forming application of slurry to screen
2. Draining water removal by gravity or vacuum
3. Pressing squeezing water out
4. Drying removal of water by heated surface
5. Post drying operations surface processing

1/ Forming section

a) **Flow spreader** – takes the incoming pipeline stock flow and distributes it evenly across the machine from back to front.

b) **Head box** – is a pressurized device that delivers a uniform pulp slurry on the wire, through the slice, at approximately the same velocity as that of the wire. Original headboxes were open, unpressurized, and used hydrostatic head for the necessary pressure. A secondary headbox may be used part of the way down the table to give a top coat of high quality fiber relative to the rest of the sheet. This is done, for example, to produce a white printing surface on linerboard or to put secondary fiber in the middle layer of linerboard, where contaminants such as polymers and wax are hidden. Paper machines operating above 2500 ft/min (800m/min) require a special, high pressure headbox known as a hydraulic headbox.

2/ Draining section

c) **Wire, forming fabric** - endless, moving fourdrinier fabric forms the fibers into a continuous matted web while the fourdrinier table drains the water by suction forces. Continuous loop or belt of finely woven screen made from wire or plastic; the mesh size varies from 40 to 100 mesh (opening per inch). A coarse wire allows faster drainage but gives a coarser paper; as in most aspects of pulp and paper, there is always a tradeoff in goals. The forming media has three functions: 1. to transport the fibers, 2. to permit draining the sheet, 3. to transmit power.

d) **Deckle board** - are used to prevent the stock from flowing off the two sides of the forming fabric when a thick layer of stock is delivered to the fabric by a large slice opening.

e) **Foils** - stationary blades 5-10 cm wide. With stock on the fabric, and the fabric in motion, the suction that develops causes the fabric to drawn down towards the foil surface. Foils have two functions apart from supporting the fabric: 1. to provide hydraulic shear, 2. to give uniform, controlled water removal.

f) **Lovacs, Hivacs** - suction boxes to drain the sheet using low or high vacuum.

g) **Dandy roll** - hollow, light, wire covered roll that rides on the top of the fourdrinier wire just ahead of the suction boxes. This roll has four purposes:
1. to impart a water mark to the sheet,
2. to improve the top surface for printing,
3. to improve formation by mechanical shear,
4. to increase the drainage capacity of the flat wire.

h) **Couch roll** - guide or turning roll for the fourdrinier wire, where the paper web leaves the wire and the wire returns to the breast roll.

It has two purposes:
1. to transmit power to the fabric,
2. to increase the dryness of the sheet applying the suction by the vacuum.

i) **Twin wire formers** – machines that use a jet of stock imparted on two converging wires to accelerate water removal and maintain better web uniformity. These are particularly useful for the high speed machines, where the fourdrinier wet end would tend to give two-side sheet, since both sides are wire sides and the sheet is formed symmetrically on the two sides.

j) **Cylinder machine** – with a cylindrical forming wet end was invented in 1809. the web is formed an a rotating cylindrical screen 36 to 60 in. in diameter and immediately picked off. Typically, 5 to 10 of these operate in series to make a multi-layer sheet. Used to make heavy weight board from secondary fiber, which is not de-inked, for folding boxboard, chipboard and gypsum board. A high quality fiber surface may be added for printing upon.

3/ **Press section**

the sheet is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated (i.e., the fibers are forced into intimate contact). A press is a pair of squeeze or wringer rolls designed to remove water mechanically and smooth and compress the sheet.

4/ **Drying section**

most of the remaining water is evaporated and fiber-to-fiber bonds are developed as the paper contacts a series of steam–heated cylinders. Removing water from the web is accomplished by adding heat to the web and circulating the air. Heat is applied by the pressurized, steam filled circular steel or cast iron dryer drums. The rate of water removal depends on many factors:

1. the temperature and amount of steam entering the dryer,
2. adequate removal of the steam condensate and air from the interior of the dryer,
3. the amount of sheet–dryer surface contact, contact time, and contact pressure,
4. cleanliness of the drum’s exterior and interior surface,
5. type of felt and condition of felt,
6. circulation of hot, dry air.

The initial drums cannot be too hot, otherwise large amounts of liberated steam will cause the paper to cockle. The paper often stretches a few percent in the machine direction while contracting in the cross direction through the course of drying, causing the machine direction to be stiffer and to have a higher tensile strength than the cross machine direction. Sophisticated control of individual dryer motors controls the tension throughout the dryer section and reduces web breaks.

**Dryer hood** - an enclosure around the dryer section and is used to improve drying efficiency by removing the moist air near the surface of the web. If this air is not removed, it quickly becomes saturated with water, preventing further water removal from the web.

**Yankee dryer** - is a large dryer drum (3.5 – 4.5 m in diameter) for drying tissue papers that are not strong enough to endure numerous felt transfers. The Yankee dryer is normally the only dryer used to dry tissue. The creping blade (doctor blade) is the thin metal blade that scrapes the dry tissue off the Yankee dryer.

**Size press** - is located between dryer sections and consists of pair of squeeze rolls mounted horizontally, vertically, or at a 45 o angle. It is used to apply surface size (usually a starch solution) to paper.

5/ **Post drying operations**

k) **Calander** - calander stack is a series of solid rolls, usually steel or cast iron, mounted horizontally and stacked vertically. Dry paper passes between the rolls under pressure, thereby improving the surface smoothness (for example, from imperfections caused by felt marks, cockles, lumps, fibrils, etc.) and gloss and making the caliper more uniform, if not decreasing the caliper and porosity. The bottom roll is called the king roll. The roll above the king roll is the queen roll.

l) **Supercalander** - is similar to the calander but uses alternate hard and soft, heated rolls. Supercalanderering may actually increase fiber bonding with an increase in strength, but the compact sheet has decreased opacity. It is usually done off-machine because of the relatively low speed required.

m) **Reel** - is the last unit on the paper machine that collect the paper. The paper is wound on a spool that rotates against a drum. A new spool is started on a secondary arm before the filled reel is discharged, for changing reels “on the fly”.

**Moisture profile on PM:**

0.3 – 0.6 % - dilute suspension of fibers is applied to an endless wire screen or plastic fabric
18 – 23 % - consistency of the web leaving wet end. Water is removed by gravity, or the vacuum developed by table rolls, foils or suction equipment, and the drilled couch.
35 – 55 % - consistency of the web leaving the press section
94 – 98 % - dryness of final paper leaving drying section
4. **Paper Machine:**
The paper machine operation starts with stock preparation where wood fiber and recovered wood fiber is mixed with water and mineral (commonly clay or calcium carbonate and titanium dioxide). A mixture of 99+% water and slightly less than 1% papermaking material is blended prior to use on the paper machine. Water is drained from the fiber slurry on modern machines in both upward and downward directions to form a web of paper. The web of paper is approximately 20% fiber and 80% water at the point it enters the press section. In the press section, the paper is squeezed between rollers and a felt, reducing its moisture content to 40-50%, at which point it enters the papermaking dryer section. Here steam-heated dryers further reduce the moisture content of the paper to a level of 2-6%. In our high quality machines, a size press coater applies a light coating of starch and mineral (calcium carbonate and clay), which enhances the surface strength and smoothness of the paper. Since this coating is applied in a water suspension, the paper must be dried in the after-dryer section. Finally, the paper is spooled into a giant roll of paper.

5. **Blade Coater:**
In our coated paper processes, a blade coater is used to apply coatings that provide high quality print characteristics for sheet offset, web offset, or rotogravure printing applications.

6. **Supercalender:**
The supercalendering machine is a series of rollers. Paper passes through rollers alternatively made of steel and cotton or a synthetic material. This calendering takes place under high pressure and temperature, and creates a glossy, smooth and attractive surface. After supercalendering, the paper is cut into roll sizes that will eventually be shipped to our web offset or rotogravure customers, or to our sheet converting operation for converting to sheets.

7. **Sheet Converting:**
In the sheet converting operation, rolls of paper are cut into sheet dimensions that are used by our sheet offset customers or by our office paper customers. The converting operation also packages our products and prepares it for shipment to our customers.

*Two other pulping methods are used at Consolidated: Mechanical pulping and TMP. The most common method of mechanical pulping is the groundwood process where wood is pressed lengthwise against a grinding stone. This causes the surface of the wood to abrade away. The fiber is then mixed with water into a slurry. TMP, or thermomechanical pulping, is another important process at Consolidated. In the TMP process, chips are subjected to high temperatures and pressures between rotating disks, which shred wood into fiber bundles or individual fibers. Both of these processes convert 95% or more of the dry wood into pulp.

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**FIBER LENGTH, PRINTING AND STRENGTH PROPERTIES**

Effect of fiber length on paper properties:
- Property Effect on paper as Fiber Length is Increased Decreased
- Bursting Strength increases decreases
- Folding Endurance increases decreases
- Formation becomes wilder becomes less wild
- Print Quality becomes poorer becomes better
- Surface levelness decreases increases
- Surface Smoothness decreases increases
- Tearing resistance increases decreases
- Tensile strength increases decreases
- Effect of refining on paper properties:
  - Property Effect on Property as the Degree of refining is Increased Decreased
  - Apparent Density Increases Decreases
  - Caliper Decreases Increases
  - Compressibility Decreases Increases
  - Dimensional stability Decreases Increases
  - Formation More uniform Less uniform, wilder
  - Ink holdout Greater Becomes less
  - Internal bond strength Increases Decreases
  - Porosity Decreases Increases
  - Smoothness Increases Decreases

**Filler’s Influence**
**Fillers** - beneficial influence on optical properties related to printability. Tend make paper less sensitive to moisture change, improve dimensional stability.
Reduce bulk and stiffness, make paper softer.
Reduce paper strength-burst, fold, tear, tensile, internal bond strength.

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