Wet Processing Technology –III

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- Why Pigment Printing is Important
- A good quality pigment print is characterized
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Pigment Printing

In pigment printing, insoluble pigments, which have no affinity for the fiber, are fixed on to the textile with binding agents in the pattern required. This description is perhaps oversimplified, but it does obviously set pigments apart from dyes that are absorbed into the fiber and fixed there as a result of reactions specific to the dye.

Historical Development of Pigment Printing:

- Until 1937 natural polymers as binders and thickeners (starch, glue)
- Around 1937 emulsion thickening
- Around 1960 use of aqueous self-crosslinking dispersions as binders
- Around 1970 development of synthetic thickening agents based on acrylic acid
- After 1980 ecological improvements (e.g., emission)

Why Pigment Printing is Important:

- The pigment can be applied to all fibers potentially and it is the only coloration to glass fiber, fabric and polyester
- No wet treatment is required, so drying and curing is applicable to all fiber.
- Extensive color range of highly light fast colors
- Possible to produce good combination shades on blended fiber in one padding operation
- Application procedure is simple
- No change of hue of colorant throughout processing
- Less expensive

A good quality pigment print is characterized by:

- Brilliance and high color value relative to the pigment concentration in material
- Minimum stiffening in the handle of the textile
- Generally acceptable fastness properties.

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Components of a pigment printing system:

A pigment printing system consists of three essential components:

- **Pigment dispersion:** Specific pigments are treated in a grinding mill in the presence of suitable non-ionic surfactants. A particle size of 0.1-3 µm is typical. Generally, the pigment pastes are aqueous based and contain the dispersing agent, humectants (to prevent evaporation and drying out).
- **Binders and cross-linking agents (polymers):** The binders used in pigment printing systems are film-forming substances made up of long-chain macro molecules which, when heated with a suitable acid-donating catalyst, form a three-dimensional structure in the pigment.
- **Thickeners and auxiliary agents:** These give the required print thickening power (rheology).

Binder:

The binder is a film forming substance made up of long–chain macromolecules which, when applied to textile together with the pigment, produce a three dimensionally linked network.

Binder- CH_2-OR + HO-Textile Binder –O- textile + HOR

Where R is H or CH_3.

The links are formed during some suitable 'fixing' process, which usually consist of dry heat and a change in pH value, bringing about either self-crosslinking or reaction with suitable crosslinking agents. The degree of cross linking should be limited, to prevent the macromolecules becoming too rigidly bonded, thus preserving some extensibility. The important criteria, which ensure that the pigment within the crosslinked binder film is fast to wear and cleaning, are elasticity, cohesion and adhesion to the substrate, resistance to hydrolysis, as little thermoplasticity as possible and absence of swelling in the presence of dry cleaning solvents.

Required properties for Binders:

- Should be film forming
- Should be water swell
- Should not be too thermoplastic
- Should have atmospheric stability
- Should be colorless and clear
- Should be of even thickness and smooth; neither too hard nor too stiff.
- Should have good adhesion to substrate without being tacky.
- Should possess good resistance to chemical and mechanical stress
- Should be readily removable from equipments
- Should provide good color yield
- Should be non toxic

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Types of Binders:

- **According to the origin**
  - Natural: glue, gelatine etc
  - Synthetic: acramin binders

- **According to chemical groups**
  - Acrylic binders: These are normally an aqueous dispersed co-polymer of butyl acrylate and styrene, having N-methylol acrylamide groups for cross-linking purposes.

Some of the more important properties of this type of binder are:

- Good resistance to ageing by light
- Good heat stability
- Generally a harsh handle
- Good solvent resistance

  - **Butadiene co-polymer binders :** They are made by emulsion co-polymerisation with acrylonitrille and N-methylolmethacrylamide. A typical butadine type of binder would consist of 45% aqueous dispersion of a co-polymer of 70% Butadiene 26% acrylonitrile & 4% N-methylon methacrlamide.

Some of the more important properties of this type of binder are:

- Poor resistance to ageing by light
- Susceptible to yellowing on heat treatment
- Generally a soft handle, particularly on synthetic fibers
- Generally the highest binding action on synthetic fibers
- good solvent resistance

Trade names of binder:

Trade name	Manufacturer	Origin
Acramin	Bayer	Germany
Tinolite, Microfix, orema	Ciba	Switzerland
Helizarine	BASF	Germany
Imperon	Hoechst	Germany

Thickening Systems:

There is a wide range of thickener materials available including alginates, natural vegetable gums, synthetic polymers, or even foams. These materials show sensitivity to factors such as temperature, pH, and salt content.

- Ionic thickener (alginates): Better color yield
- Nonionic thickener (cellulose ether): stable to pH variation and electrolyte content.
- Natural and semi synthetic hydrophilic thickeners:

should not used in pigment printing because:

- When entrapped in binder film, are either soluble in water or swell in presence of water even after fixation.

- They contain large no of polar groups like hydroxyl group and produce a hard film and stiff handle.

- Aftertreatment to remove them is not effective since they are enclosed in the binder film.

Emulsion Thickener:

Two mutually immiscible liquids (oil and water) are stirred to produce an emulsion with the presence of emulsifier. The nature of the emulsifier and the ratio of the two immiscible liquids determine which liquid will be dispersed (the disperse phase) in the other (the outer, continuous phase)

The emulsifier forms a film between the two liquids, reducing interfacial tension. The emulsion stability depends on

- The degree of dispersion
- Type and quality of emulsifying used
- The substance dissolved or dispersed in the dispersed or dispersion medium

Two types of emulsion thickener;

§ **Oil in water (o/w):** kerosene/white spirit in water

§ **Water in oil (w/o):** water in kerosene or white spirit

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Synthetic thickeners:

- A thickener that is made artificially. Synthetic thickeners are typically designed to offer high viscosity at low concentrations, high yield value, shear thinning, stability, integrity over a wide temperature range, and ease of use.
- Synthetic thickeners are efficient at only 1-3 % concentration level while approximately 10% of a natural thickener is needed to give the required viscosity in the print paste.
- Other advantages of synthetic thickeners include rapid make-up since they require no waiting for hydration to occur, sharp print boundaries, and controlled penetration which usually provides greater color value and levelness.

Other Auxiliaries:

- ### Catalysts:

  § **Diammonium phosphate:** - most widely used acid catalyst

  - used in conc. of 0.5% and 0.8% in screen and roller printing respectively
  - when used in correct proportion produces a pH of 3 in fabric and brings a cross linking reaction

  § **Ammonium salts:** sulphocyanide, sulfate and chloride are suitable. Ammonium nitrate: not recommended and it turns polyamide fiber yellow

- ### Urea

These are agents that are added to improve “runnability” on printing machines. Owing to their low volatility these auxiliaries are used sparingly, maximum amounts of 20 parts/1000 being common; otherwise the fastness properties may be adversely affected.

- ### Softening agents

After curing fixation the resultant “handle” of the printed fabric depends on a number of factors:

- monomer composition of the binder
- presence of water-soluble protective colloids (e.g. alginates, etc.)
- extent and type of cross-linking.

By the addition of certain compounds (usually termed “plasticisers”) improves the handle of printed goods.

- ### Cross-linking agents

These agents are universally based on either urea-formaldehyde types (e.g. dimethylolurea) or melamine-formaldehyde types. They are incorporated into printing compositions in an attempt to increase various aspects of fastness, particularly rub and scrub fastness with synthetic fibers. A maximum addition of 10-20 pts/1000 is normally encountered: larger amounts can have a quite marked effect on the “handle” of the fabric

Pigment Printing Recipe and Procedure:

Typical Recipe:

Pigment: 10-20gm

Binder: 40-50 gm

Thickener: 35-50 gm

Catalyst: 5 gm

Dispersing agent 2 gm

Water x ml

Procedure:

- Preparation of printing paste using dispersing agents and thickener and catalyst.
- Application of pigment paste and binding resin together
- Drying at 140 – 150°C
- Curing to fix the resin pigment

Affect of curing on PET:

Temperature	Time	Strength loss
205°C	1 min	0%
220°C	1 min	0%
235°C	1 min	2%
245°C	1 min	5%
260°C	1 min	13%

Problems of Pigment Printing:

- Adverse effect due to binder as it changes texture of fabrics.
- The quality of printing or dyeing depends on the characteristics of binder used to affix the pigment even more than the properties of pigment.
- Some solvents used in emulsion like kerosene, white spirit cause problem like flammability.
- The chemical and physical influences on the binder and print paste can interfere during production and processing resulting in sticking especially in roller printing.
- The gumming up of equipments, odor, air and water pollution
- Difficulty in obtaining the necessary wet treatment fastness and abrasion resistance with certain products, may not be obtained pigment printing or dyeing.

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Pigment Dyeing on Fabric:

Typical Recipe;

Pigment: 10-20gm/L

Binder: 40-50 gm/L

Thickener: 35-50 gm/L

Catalyst: 5 gm/L

Thickener: 2 gm/L

Dispersing agent: 2 gm/L

Procedure:

- Binder is weighted and diluted with cold water
- Pigment and thickener is added with cold water
- Catalyst solution is added
- Dispersing agent is added
- The dyeing liquor is well filtered and stirred; material is padded
- The material is dried at 70 -100°C in hot flue steam but no use of cylinder dryer.
- Curing is done at 150°C, 2-3 min

Precautions:

- **No alkalinity:** The fiber to be dyed should not be alkaline
- **No OBA:** OBA may produce faulty shade
- **No formation of skein:** Binder should not be allowed to form skein which ultimately give specky shade

Typical procedure for Garment dyeing:

- First bleach the material then treat with a synthetic mordant cationising agent at pH 7
- Rinse at 60°C at a rate of 2°C/ min for 20 min
- Cold rinse
- Apply pigment at 7O°C (pH 5) for 20 min
- Add salt, acid and raise temperature when necessary
- Now use binder 4% for 10 min at 70°C
- Cold rinse with 1 gm/L soap wash for 10 min at 65°C
- Cold rinse and dried

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Pigment

Pigments implied general insolubility and complete insolubility in water.

Difference between dye and pigment

The difference between dye and pigment is not a clear one. Most organic pigments are closely related to dyes with respect to their chemical structure and there are dyes which become pigments after application. Vat dye is a dye when used in dyeing but a pigment when used in printing.

	Dye	**Pigment**
Solubility in water	All dye must be soluble during process	Almost insoluble
Affinity	Possess a specific affinity towards fiber	Have no affinity but used as coating
Chemical nature	Organic and few are metallic	Most are metallic or organometallic.
Application	Through water medium	Through adhesive or binder

Uses of Pigment:

1. Pigments are used for coloration of a very broad and diverse number of materials
2. Surface coating for interior, exterior, automotive and other application
3. Paints based on olegoresinous liquid and water emulsion
4. Printing ink for papers (lithographic, rotogravure and flexographic systems (and for other materials such as metal plates, foils, artists and writing material)
5. Coloration of plastics and rubber
6. Textile printing
7. Coloration of manmade fibers by mass pigmentation before fiber formation (dope dyeing) etc.

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Required Properties of pigments:

1. They should have covering power which is influenced by particle size
2. Should be inert, stable and have long life
3. Should have capability of mixing
4. Good wet fastness, light fastness and abrasion resistance
5. Good resistance to acid, base, perspiration, chlorine, peroxide and gas fading
6. Good solvent resistance (insoluble in water, CCl_4, $Cl_2C{=}CHCl$)
7. Suitable brilliance, hardness and stability
8. Suitable characteristics for good dispersion including particle size and distribution, electrical charge (most are negatively charged particle), specific gravity, purity and crystalline structure, conditions of precipitation of the pigments
9. Should be applicable to all fibers.

Physical/Chemical Properties of Pigments:

Chemical Structure	Inorganic oxide, salts, organometallic toners, organic insoluble azo pigments, phthalocyanine metal complexes
Physical state	Very important, decreasing particle size increase color value but decreasing hiding power
Particle size	5-7 micron
Density	Sp gravity range from 1.17- 1.37 for most cases
Melting points	Usual range 110 -175°C
Boiling point	Decompose at 195- 345°C. phthalocyanine pigments sublimes at 500°C
Water solubility	Insoluble for all practical purposes.
Other solubility	Inorganic pigments are insoluble in most solvent
Spectra	Very strong and high, though not comparatively sharp peaks

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Application Properties of Pigments

Fabric dyed	Any fiber can be dyed by selecting a suitable binder, quality greatly depends on binder used to affix the pigment
Fabrics printed	Any fiber by suitable binder even hard to print polyester blends and glass fibers
Disposable fabrics	Well suited for non woven fabrics
Dischargeability	Some pigments are suitable for discharge printing
Alkali fastness	Poor for organometallic azo toners, good for insoluble azo
Heat resistance	Extremely varied. Some are stable up to 200°C and some up to 300°C. optimum for inorganic pigments
Light fastness	Generally very good. Optimum for inorganic pigments
Wash fastness	Generally good to very good
Useful colors	Diarylide yellows and oranges, Hasna yellow, azoic reds, phthalocyanine blues and greens, carbon black, TiO_2 white, violet and browns.
Processes used	Padding for dyeing
Aftertreatment	None required

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Classification of pigments:

- ## According to origin

1. **Natural/Mineral:** Iron ores, clays, chalk etc
2. **Synthetic/chemical:** white lead, ZnO, TiO_2 and large number of inorganic and organic color

- ## According to Reactivity

1. **Reactive pigment:** some pigments on account of the chemical character react with oil, fatty acids and soaps. These are called reactive pigments e.g. ZnO, red lead
2. **Inert pigment:** TiO_2

- ## According to Chemical Nature

1. **Organic pigment:** appx 25% (by wt.) of the world production of organic colorant is accounted for organic pigments. They account for only 4% of total pigment production. Of the total organic pigments production yellow, red and blue tones accounted for 89%.

Most organic pigments exhibit a small solubility, typically in polar solvent. All the organic pigments are soluble in one or more of the four chemical: Chloroform ($CHCl_3$), Methyl alcohol (CH_3OH), Dimethyl formamide (DMF) and concentrated H_2SO_4. Organic pigment consists of:

1. **Azo pigment:**
   - Strong tinctorial strength
   - Good alkali resistance
   - Excellent brightness
   - Cover a wide range with regard to other application properties
   - Poor alkali resistance of certain organometallic pigments make them unsuitable for printing

2. **Diarylide orange and yellows:**
   - Extremely bright color
   - Inferior light fastness
3. **Phthalocyanine**
   - Blue, greens are dominant shade especially in plastic coloration
   - Offer low migration
   - Good temperature stability
   - Excellent light fastness
   - Good heat resistance
   - Excellent alkali resistance
   - Good solvent resistance
   - Used extremely in printing, pad dyeing and dope dyeing

4. **Hasna yellow**

    - Good light fastness
    - Have migration tendency

2. **Inorganic pigment:**

    - They account for 96% (by wt.) of total production. More than half of their production volume is accounted for a single production, TiO_2, the most important white pigment
    - H_2SO_4 is a good solvent for many inorganic pigments
    - They are opaque
    - Less expensive
    - More weather resistant
    - More chemical resistant
    - Insoluble in most organic solvents
    - Highest degree of light fastness
    - Excellent heat resistance

They consist of

1. **Salts**: Sulfates, carbonates, silicates and chromates of many metal elements like, Ti, Zn, Ba, Pb, Sb, Zr, Ca, Al, Mg, Cd, Fe, Mo, Cr etc.
2. **Oxides** of Ti, Zn, Ba, Pb, Sb, Zr, Ca, Al, Mg, Cd, Fe, Mo, Cr etc.
3. **Metal Complexes**: Naturally occurring oxides and silicates.

Difference between organic and inorganic pigment

	Organic	**Inorganic**
Solubility	Soluble in organic solvent	Soluble in inorganic solvent
Tinctorial strength	Higher	Lower
Brightness	Higher	Lower
Purity	Higher	Lower
Transparency	Opaque	Transparent
Weather resistance	Less	More
Chemical resistance	Less	More
Fastness	Good	Excellent
Cost	Expensive	Cheap

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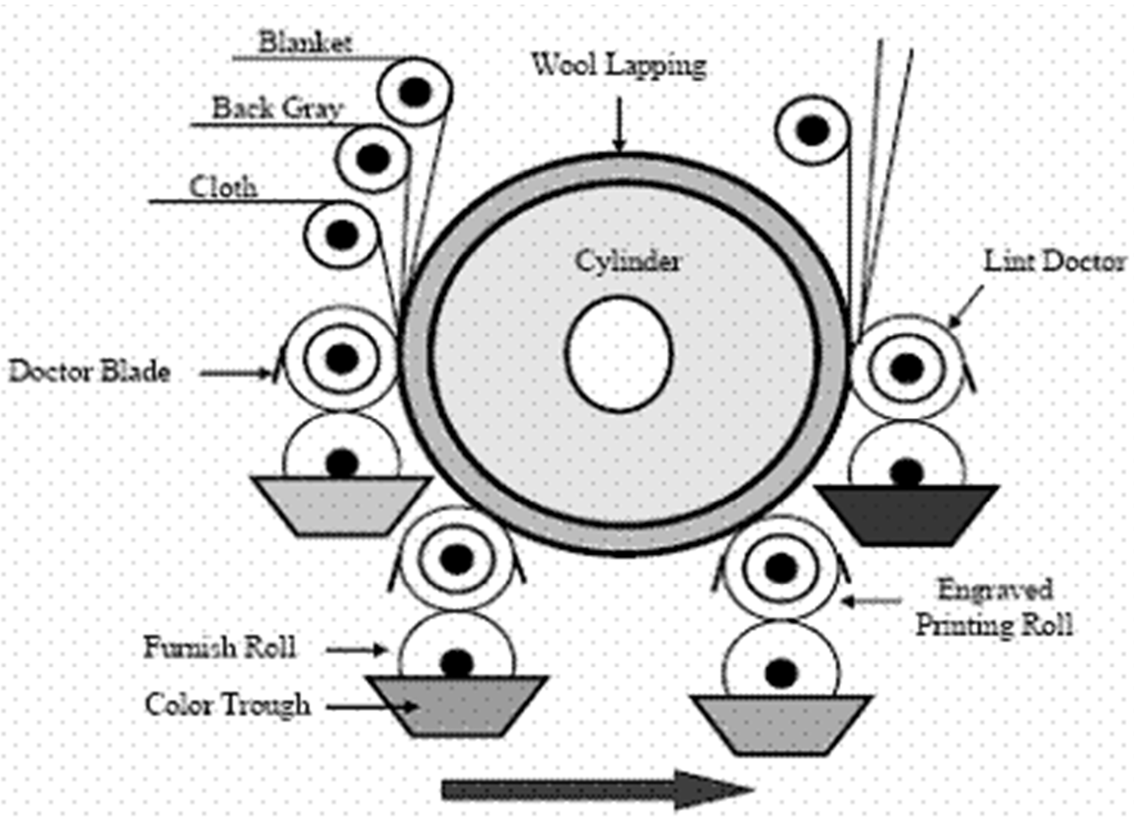
Roller Printing

- Engraved roller printing is a modern continuous printing technique developed in the late 19th and early 20th centuries.
- Until the development of rotary screen printing, it was the only continuous technique.
- The high fixed cost of copper rollers, expense of engraving process, and possible distortion of fabric during printing have led to its reduced use, now being less than 5% of the worldwide textile printing market.
- The fine design detail possible with this technique has always been its main



advantage.

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