Training module: FINISHING, PRINTNIG and FUNCTIONALIZATION
Course: Basic Principles of Textile Printing

The course is developed under Erasmus+ Program Key Action 2:
Cooperation for innovation and the exchange of good practices Knowledge Alliance

ICT IN TEXTILE AND CLOTHING HIGHER EDUCATION AND BUSINESS
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COMPOSITION of the Printing Paste

- Thickeners, chemical and physical characteristics, selection
- Rheological properties of thickeners and printing pastes

Thickening agents play a paramount role in the formulation of printing pastes, ensuring through the modulation of the rheological properties, sharp and clean drawing patterns, by preventing dye migration, a homogenous distribution of the printing paste on the screen and its uniform flow through the screen openings. The selection of the thickening agent is determined by the fabric to be printed, the printing conditions, and, above all, the type of dye used.

ICT in RHEOLOGY

Stand-alone rotational viscometer with software package
LIMS Bridge software which allows for automatic method selection and data export
The V-Collect data software - automatic data export in an xls file, ready for further analysis or graphical illustration.
BASIC COMPOSITION OF EACH PRINTING PASTE

- Each printing paste contains three basic ingredients:
  - Dyestuff
  - Thickener
  - Auxiliaries

Thickeners

- The most important and most responsible ingredient of any printing paste is a thickener. The thickener allows dyes and other components of a printing paste to be printed onto textile substrate in the contours of the desired pattern (prevents spillage of printing paste outside the contours defined by the pattern).

- The three most important properties of thickeners: it acts as a mechanical carrier of dyes and auxiliaries (must not chemically react with any ingredient in the printing paste); it overcomes the capillary forces of the fabric; retains the ink and other ingredients of the printing paste in a homogeneous paste.
Thickener requirements: In the selection of thickening agents, it is necessary to take into account requirements other than viscosity, which can usefully be classified in five categories: print paste stability, good adhesion of the dried thickener film, minimum effect on colour yield, ease of removal and acceptable cost.

The additives and thickener in the printing paste act as auxiliaries, which means that they indirectly help the reaction of the dye with the fiber, ie the binding of the dye with the fiber. Additives and thickener, as auxiliaries, ensure maximum ink utilization, but are also responsible for the stability of the printing paste, and for the final appearance of the print.

All suitable Thickeners for textile printing can be divided into a four basic groups:

1. Based on origin
2. According to solubility
3. Based on the dry matter content
4. According to rheological properties
Natural, organic, plant origin thickeners are widely used in textile printing:

- **Starch based** thickeners (polysaccharides): corn, potato, rice, wheat, carob flour, tapioca.
- **Alginates** are salts of acidic seaweed, depending on the depth from which the algae are extracted, thickeners are divided into alginates and carrageenans. Alginates with a high degree of strength are used, in addition to printing, in food as gelatin, and in the processing of drugs for making soluble capsules.
- **Natural gums** (gum arabica, tragacanth gum)
- **Caoutchouc** juices
**ALGINATES:** Sodium alginates have become very important for print paste thickening because of their ready solubility, even after high-temperature fixation treatments. They are especially important for pastes of reactive dyes because the extent of interaction is very small. This is due to the absence of primary hydroxyl groups and to the repulsion of dye anions by the ionised carboxyl groups of the polymer under alkaline conditions.

**GUM ARABIC:** Wounds in the bark of acacia trees exude a gum that has interesting properties. The polysaccharide in the gum is extremely soluble in water (50%) and shows Newtonian behaviour. Gum arabic has been used as an adhesive more than as a thickening agent, for which purpose concentrations as high as 40% may be required. Mixing with starch is not recommended as the polymer may separate. Karaya gum (20%) has been used as a cheaper alternative. Crystal gum is a pre-swollen and purified material made from vegetable gums such as Karaya, to be readily soluble and more reproducible in properties than the original gum.
**STARCH** is a macromolecule of high molecular weight, belongs to the group of polyglucosides. It is composed of glucopyranose parts interconnected by a 1,4 - α glucoside bond. As thickeners, starches are not acceptable because they are prepared by cooking, separating two components, which are different in chemical structure and molecule size. The gel component affects the stickiness of the film, and the salt component affects the uniformity of the impression. In quality thickeners, these components are present in equal proportions. In the preparation of starches, this ratio varies depending on the temperature and cooking time, so today starches are etherified and esterified. The most famous of such ethers is the ether of carob flour. Starchs with a free OH group are not recommended for use with reactive dye printing because the dye would react with the OH group, chemically bind and could not react with the textile substrate already in the printing paste.

Although starch has certain disadvantages for use as a thickening agent, it does have the advantage of giving high colour yields. This is the result of its aggregation and very limited penetration into textile yarns and therefore the retention of dye on the fabric surface. However, it is usually desirable to reach a compromise between high colour yield, with substantial susceptibility to crush and poor levelness, on the one hand, and low colour yield with good penetration, little crushing and good levelness, on the other. A traditional method of achieving such a compromise was to use a mixture of starch and gum tragacanth.
The BRITISH GUM is produced by heating dry starch at 135–190 °C, with stirring to achieve uniform roasting, for 10 to 24 h. The process can be accelerated by addition of trace quantities of acid. The use of more than trace quantities of acid leads to more hydrolysis and the formation of the so-called dextrins, which are of low relative molecule mass and can be used as adhesives. British gum pastes have good stability to alkali and have been used for printing vat dyes. For reducible azo dyes, additions of oxidising agent must be made to avoid destruction of dye. In resist printing, when a high-solids-content thickener is desirable to act as a physical barrier, British gums have often been selected.

LOCUST BEAN GUM is a nonionic polysaccharide, pH has little effect on the viscosity over the pH range 3–11. Pastes of useful viscosity are obtained at concentrations of about 2%. Additions of sodium salts have little effect on paste viscosity, but complexes are formed with borates, producing gelling that has been exploited in the two-stage fixation of vat prints.

GUAR GUM is chemically similar to locust bean gum (it is also a galactomannan) and like locust bean gum is a very useful thickening agent. In contrast to locust bean gum, guar gum can be dispersed in cold water. Although its cold-water dispersibility is a major advantage, dispersion must be carried out with care in order to avoid the formation of lumps. The hydration of the powder should not be faster than the rate of surface wetting.
SYNTHETIC - POLYMER THICKENERS Copolymers of acrylates have been used more widely. Relatively low-cost copolymers of methacrylic acid and ethyl acrylate, for example, give low-viscosity dispersions in water in which the molecules are randomly coiled. On addition of alkali, the carboxylic acid groups are ionized and the resultant mutual repulsion of negatively charged centers causes extension of the polymer chains and substantial increases in viscosity. The viscosity obtained, however, is critically dependent on the amount of alkali added. The fall in viscosity is a consequence of the polymer going into solution, as a result of the solvation and intermolecular repulsion of the carboxylate ions. This sensitivity to pH was the obstacle for industrial use, so polymers with similar properties have been produced from maleic anhydride and an olefin, cross-linked with a diamine.

One successful commercial product is a liquid dispersion of acrylic polymer particles in a hydrocarbon solvent. It has a high solids content (50–60%) but its mobility is high, and when it is stirred into water a viscous paste is produced.

This thickeners are used in pigment printing.

☑ Synthetic thickener for pigment printing
THICKENER divided based on DRY MATTER CONTENT:

Thickener comes on the market as a dry substance; well ground, of a precisely defined percentage. Percentage indicates the amount of dry matter to be taken per 100 g of distilled water - in order to obtain the exactly declared viscosity of the thickener. As the percentage of dry matter changes, the properties of the thickener also change.

Each thickener has a defined percentage of dry matter and depending on this percentage the thickeners can be:

- Viscous (dry matter content > 9%)
- Medium viscous (dry matter 6 to 9%)
- Low viscous (dry matter 2 to 6%)

The data on the amount of thickener dry matter is used as technical data for the preparation of printing paste. The amount of dry matter affects: membrane thickness and strength in the drying phases; tickiness of paste in fast rotating printing machines and metal rollers (thickeners with a high percentage of dry matter have high stickiness); the amount of condensed water in the steam fixation process on the washability of the thickener. Therefore, high-viscosity thickeners are used for hydrophilic fibers in order to keep water consumption as low as possible (there is a thinner film on the printed surface).
AUXILIERIES:

Auxiliaries can have chemical and physical effects:

- **CHEMICAL effect** - ensure the reaction of the dye with the fiber: salts, reducing and oxidizing agents, pH regulators, dispersants, hydrotrropic agents, crosslinking agents.

- **PHYSICALLY effect** - They affect the sharpness of the print, change the morphological structure in the fixing process (membrane swelling, creation of an amorphous area in the fiber, etc.), affect the washing process, the stability of the printing paste and the diffusion of dye into the fiber: thickeners.

- **pH regulators** (acids, bases, amphoteric salts) allow dye diffusion and fixation. The choice of pH regulators depends on the type of dye and fiber. For cellulose fibers, they are used from neutral to alkaline. For wool, silk and chemical fibers are used from acidic to neutral.
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- **Dispersants** are used in printing with insoluble dyes, whether pigmented or disperse. According to their chemical composition, they are ethoxylated fatty acids. Their mechanism is based on the ability to break down aggregates, i.e., the accumulation of dyes, creating fine dispersions. They are responsible for the uniform distribution of dye in the paste and in the printed area.

- **Hydrotropic agents** create fine dispersions, enable better solubility of the dye and have a positive effect on its application to the textile substrate. The printing paste, although it is a colloidal water system, has too little water to dissolve a large amount of additives. Dissolution is carried out by hydrotropic agents, among which urea is of the highest quality. Urea is a dispersant that has a very high hydrotropic effect. This action can be explained by the ability of urea to bind 7 molecules of dye and (or) water by hydrogen bonds, which affects the breakdown of dye accumulations and increases the solubility of water-soluble dyes.

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\text{Chemical constitution of UREA}
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- **Urea** in the vapor fixation phase increases the amount of condensed water in the printed area, allows stronger swelling of the fiber and the penetration of dye into the fiber. In warm storages, especially on summer days, urea maintains a constant viscosity of the printing paste, preventing water from evaporating from it. In the fixation phase, urea decomposes into nitrogen and carbon compounds, which are found in water during rinsing. This is why urea has become unacceptable today at a time of high environmental awareness. *Polyvalent alcohols and etherified compounds are used as its substituents.*

- **Softeners** are auxiliaries that changes the feel of the textile material and the material becomes more pleasant and pleasant to the touch. In practice, selected fabric softeners are added to the printing paste in order to improve the softness of the touch without reducing the color fastness. Softeners based on fatty acid esters, mineral and silicone oils are most commonly used, and more recently silicone micro-emulsions. The printed material becomes softer, more brilliant, the depth of color increases, and in some cases the durability improves.

- **Crosslinking agents** affect the formation of polymer films, can improve its properties and enhance the adhesive bond to the textile surface.

- **Other**, can be anti-aging agents, stabilizers, preservatives, etc. Their task is to ensure stability in the printing paste and later in the fixing phase.