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ICT-TEX

Training module: FINISHING, PRINTNIG and FUNCTIONALIZATION

Course: Basic Principles of Textile Printing

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ICT IN TEXTILE AND CLOTHING HIGHER EDUCATION AND BUSINESS

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PRINTING METHODS

All printing methods could be divided into ***4*** basic categories:

1. Direct printing
2. Discharged printing
3. Resist printing
4. Transfer printing
5. Special printing methods

Basic stages of a printing process:

- Preparation of fabric,
- Preparation of printing paste,
- Printing,
- Drying of fabric,
- Fixing with steam or hot air (for pigments)

❑ FIXING METHODS

- ❑ In printing processes, in general, **three basic fixation** methods are implemented: **steam fixation**, **wet fixation** and **hot air fixation**.
- ❑ **STEAM fixation:** The time and conditions for fixation in steam vary with the properties of the dyes and fibres used, ranging from 10 s to 60 min in steam at 100 to 200 °C. Technical and economic factors have encouraged the use of higher temperatures and shorter times, and the change from batchwise to continuous processes.
- ❑ Wool is a natural fiber in which steam fixation is carried out exclusively in atmospheric conditions, for 30 minutes. It takes longer for the wool flakes to swell, to allow the dye to diffuse into the wool fiber and the dye to bind to the fiber. The average duration of steam fixation for other fibers is 10 min.

The industrial steamer with following applications:

- ✓ Saturated steam modus (102°C to 105°C)
- ✓ Superheated steam modus (160°C to 180°C)
- ✓ Hot air polymerizing modus (160°C to 180°C)

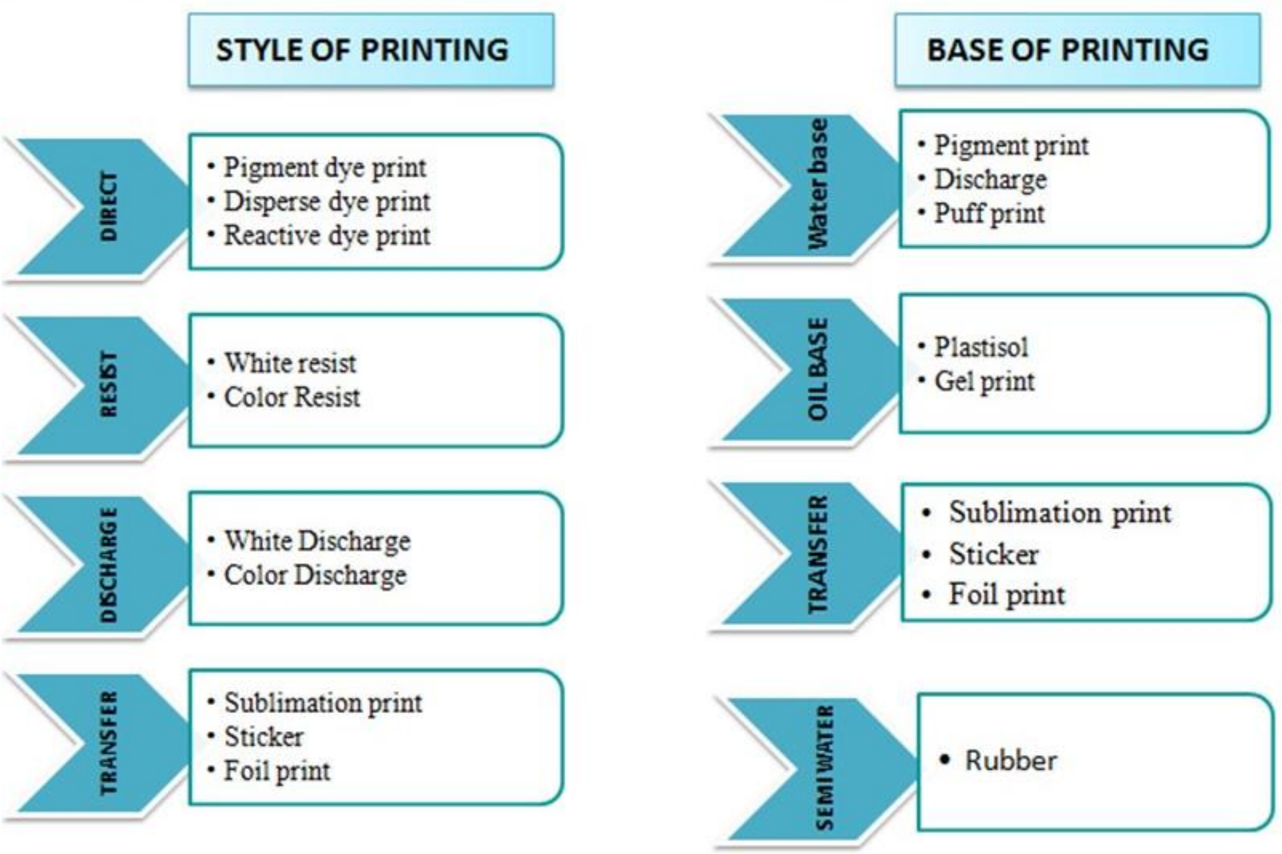
- ❑ **Wet fixing** is applicable for a small group of dyes for some reactive dyes and for leuco esters. Wet fixing is carried out by, after printing, passing the sample through a bath containing additives that allow immediate fixation of the dye to the fiber (shock process).
- ❑ **Hot air fixing** is carried out at a temperature of 130 °C to 150 °C for 5 - 10 min. Hot air fixation is mainly performed in pigment printing. When printing PES fabrics with disperse dyes, thermo fixing is performed at a temperature of 220 °C for 60 sec.

❑ **Industrial hot air dryer**

❑ **Tunnel hot air dryer for smaller production**

Recommendation: Textile Printing, Ed. Leslie W. C. Miles, published by Society of Dyers and Colourists, ISBN 0 901956 79 1.
Chapter 8: Fixation and Aftertreatment Process

- Unlike printing techniques, which involve the application of certain technology and related tools, and are divided into **stock printing**, **machine printing with flat screens**, **rotary** and **digital** printing, **printing methods** are divided **based on how the print effect is achieved on the fabric**, so they are divided on **direct printing**, **discharge printing**, **resist printing** and **special printing methods**.



STYLE OF PRINTING

DIRECT
- Pigment dye print
- Disperse dye print
- Reactive dye print

RESIST
- White resist
- Color Resist

DISCHARGE
- White Discharge
- Color Discharge

TRANSFER
- Sublimation print
- Sticker
- Foil print

BASE OF PRINTING

Water base
- Pigment print
- Discharge
- Puff print

OIL BASE
- Plastisol
- Gel print

TRANSFER
- Sublimation print
- Sticker
- Foil print

SEMI WATER
- Rubber

- It should be noted that the latter group, **special printing methods**, **does not imply special methods**, but the name refers to the **specificity of the effects achieved and which do not belong to the standard effects** achieved by conventional printing techniques and methods.

❑DIRECT Printing with DYES

✓ COTTON Printing with DIRECT DYES

- ❑ In printing processes, **direct dyes** are used **in combination with some of the natural thickeners**. After printing and drying, **they are fixed with steam**. During fixation, the thickener in the printing paste and the fiber swell, re-dissolving the dye (which has solidified in the inter-drying phase) and diffusing from the printing paste layer into the fiber, where it binds with hydrogen and van der Waals bonds. After a certain fixation time, a balance is achieved between the dye in the fiber and on the surface of the fiber (in the paste layer).
- ❑ During the final wash, the unfixed ink together with the excess printing paste and thickener is washed away, which can lead to unwanted staining of unprinted parts of the textile material. At the same time, the balance that was established in the fixing phase, and before washing, is now disturbed, due to the migration of dye from the fibers into the rinsing fluid.
- ❑ For these reasons, in the printing of cotton with direct dyes, it is necessary to use fixatives, which are added as an aid to the printing paste.
- ❑ Active quaternary ammonium cation acting with dye anions may be used. Then larger, less soluble complexes are formed in the fiber, which are less mobile and contribute to greater usability of the print, but there is a decrease in resistance to light. But in general, it can be said that direct dyes are not too important in textile printing, if they are used, it is mostly for cheap products.

✓ COTTON Printing with VAT DYES

- The mechanism of binding of **vat dyes** depends on the process of converting insoluble vat dye into water - soluble leuco form, under the influence of alkali and reducing agent. The formed, soluble leuko compound diffuses from the thickener into a fiber that swells during fixation. By oxidation, the dye is then converted back into its insoluble form within the fiber itself, resulting in very good fastness properties and usability.
- Printing with vat dyes in leuco form is a very demanding process, because due to exposure to air during and after printing, too rapid oxidation occurs. Therefore, an air-stable reducing agent must be used, or a method is used in which the reducing agent is added subsequently at a later stage of printing.
- In 1905, it was discovered that the compound sodium formaldehyde sulfoxylate CH_2OHSO_2Na (Rongalit) has satisfactory stability and has a reducing effect under saturated vapor conditions during the fixation phase. A paste containing such a compound can be stored for a long time without a slight loss of reducing properties. As an alkali, potassium carbonate has shown better applicability in vat dye printing, which also has the property of better solubility, which is also an advantage.

- Vat dyes that are standardized for use in printing must be smaller in particle size and in crystalline form to achieve the maximum level of reduction. Of the thickeners, the British Gum thickener is recommended (product obtained by heating dry starch to a temperature of 135 - 190ºC, with constant stirring, 10 to 24 hours), due to its stability and resistance to alkalis, which are an integral part of printing paste.
- The vat printing process can be approached in two ways, called s**ingle-phase** and **two-phase** methods. The **single-phase method** implies that the printing paste contains a reducing agent and alkali, and the vat dye is immediately converted into a soluble form. Such a paste is used for printing and, after drying, oxidation and steam fixation is performed. In the **two-phase method**, it is advantageous to avoid premature oxidation of the vat dye by applying the dye and the reducing agent to the material to be printed, separately, in two phases. First, the textile material is printed with a paste which contains only thickener and dye (**phase I**). After drying, the material thus printed is passed through a fleet containing a reducing agent and alkali (**phase II**). After phase II, oxidation and steam fixation are performed. Steam fixation is applied in the so-called air-free system (without the presence of air). In such a method, Na-dithionite (hydrosulfite) can also be used as a reducing agent, because the exposure to air during the procedure is reduced to a few seconds. **This method is applicable to the whole spectrum of reducing dyes, and starts by printing only the thickener dye in the first phase.**

- The disadvantage of this method is the possibility of the appearance of dye spills during impregnation with alkali and reducing agent. To avoid spillage, the use of thickeners that coagulate in the presence of alkali is recommended. The degree of coagulation must be controlled to ensure optimal removal of excess thickener in the final stage of washing. Also, the impregnation conditions must be optimized so that the passage time of the printed fabric through the bath containing alkali and reducing agent is as short as possible.

✓ COTTON Printing with REACTIVE DYES

- Reactive dyes bind to cellulose fiber via a covalent bond, which allows the use of dyes that, unlike direct and vat dyes, are low molecular weight and good solubility. Such dyes give more brilliant colors, diffuse faster into the fiber, and in hydrolyzed form can be easily removed in the final stage of washing (removal of excess unbound dye). Even with reactive dyes, two printing methods can be performed: **single-phase** and **two-phase** process.
- When using reactive dyes, a certain pre-treatment of the textile material must be carried out, which involves detailed starching and removal of impurities from the cellulosic material, which can cause weaker and uneven bonding of the dye. Complete or partial mercerization is also recommended, as a relatively small number of reactive dyes give good dyeing characteristics on non - mercerized cotton.

- ❑ **Single-phase printing method with reactive dyes** - **„All in one”** method: paste preparation - by direct dissolution of reactive ink in printing paste (possible due to good solubility of reactive inks).
  - ✓ **Dye pre-dissolution:** the reactive dye is mixed with urea with a minimum amount of warm water. Sodium bicarbonate is added to the printing paste as an alkali, when the dye is completely dissolved in the thickener. If the dye was previously dissolved with the addition of warm water, the paste should be cooled to room temperature before adding the alkali.
  - ✓ **Thickeners:** Alginates (the only natural thickeners suitable for printing with reactive dyes). Due to the high price of alginate and limited availability on the market, the possibility of using anionic synthetic thickeners has recently been tested. Since acrylic acids (synthetic thickeners are acrylate-based) do not react with reactive dyes, dye application and dye retention on the material surface is even better than with natural thickeners (alginates), but the disadvantage is the difficult phase of rinsing and removing excess thickener and unbound dyes.
  - ✓ **Alkali:** Sodium bicarbonate (Na_2CO_3) is the most commonly used, inexpensive, and provides optimal printing paste stability for most reactive pastes. In the case of high - stability reactive dyes, sodium hydroxide (NaOH) can be used in addition to sodium carbonate - stable reactive dyes tolerate conditions of high alkalinity well, and the addition of NaOH enables better coverage and application of dyes on the material.

- ✓ For less stable reactive dyes, a reduced amount of bicarbonate is used or Sodium trichloroacetate can be used. The reactivity of the ink and the required stability of the printing paste must be taken into account when choosing the alkali.

- ☐ **Fixing:** is the most important phase in the textile printing process, and for reactive dyes it is most important to optimize the fixing time so that no unbound reactive dye remains in the reactive form and thus the unprinted parts of the material are colored. Therefore, the choice of reactive dyes for the printing process will be influenced by the characteristics of the fixing equipment. For high reactivity dyes, fast fixation conditions (shock procedure) can be used, but for low reactivity dyes, the usual temperatures and duration of steam fixation are recommended. Furthermore, the importance of the stability of the realized dye - fiber bond, in alkaline conditions and elevated temperature conditions (conditions of fixing reactive dyes) is expressed in the fixation.

  Fixation of most reactive dyes is carried out with saturated steam at 100 °C for 10 minutes. For dyes with very high reactivity, 1 minute may be sufficient. Faster fixation is achieved by superheated steam at 130 - 160 °C, for 30 to 60 seconds.

  The role of urea in the fixation phase is to retain a sufficient amount of water that condenses at the moment when the cold sample reaches the conditions of superheated steam. The amount of water that urea retains at that time is needed to create the solution necessary to achieve the dye-fiber reaction. In the absence of urea, the yield of dyes is low, while the addition of urea in the ratio of 150 - 200g/kg of paste, achieves maximum yield of dyes.

- In the case of reactive dyes, dye fixation can also be performed with dry, hot air, but in this case it is necessary to optimize the choice of dye (the best results of dye use in hot, dry air fixing conditions are given by high diffusion speed and high reactivity reactive dyes). The high diffusion rate allows the diffusion of dyes and alkalis into the fiber to begin already in the drying process, before fixing. If tunnels with hot air flow are used for fixing then the recommended conditions are 160 - 180 °C, 1 - 3 minutes, and in contact fixing conditions, heated cylinders or presses, a temperature of 150 °C for 3 minutes is recommended.

- **Rinsing:** After fixing, unbound hydrolyzed dye must be thoroughly rinsed without leaving marks on unprinted parts of the material. To ensure the suitability and sufficiency of the usual, routine rinsing procedure after printing and fixing, the percentage of unbound dye on the material should not exceed 10 to 30%. A higher percentage of fixed dye can be achieved with reactive dyes that have two reactive centers in the structure of one dye molecule. This enhances the reaction of the dye with the fiber and leads to 90% fixed dye, compared to 70%, which is commonly achieved in the process of fixing reactive dyes.

- **Two-phase printing method with reactive dyes** – Printing with reactive dyes can be carried out without the alkali contained in the printing paste, and the alkali solution is applied subsequently by the impregnation process, in order to stimulate the process of fixing the dye. This ensures a higher volume of water in the fabric during the fixing phase (min. 50%, as opposed to the usual 20% in single-phase printing), which reduces the need for large amounts of urea (in such conditions, 50 g/kg of paste is enough). **Sodium alginate is recommended as a thickener** for this type of printing with reactive dyes.
  - ✓ In this process, an alkali solution with a high electrolyte content is prepared to prevent color loss and color transition from printed to unprinted parts of the material. Therefore, two types of solution are recommended: **concentrated sodium silicate solution** ($Na_2O:SiO_2$ = 1:2) or **alkali mixture** (Sodium carbonate Na_2CO_3, Potassium carbonate K_2CO_3, NaOH).
  - ✓ Usually, after the process of impregnation with an alkali solution, fixation with superheated steam at 130 °C is carried out for 30-50 seconds, followed by rinsing. With reactive dyes of high reactivity, it is not necessary to carry out steam fixation, but the so-called shock procedure in an alkali solution with a passage of 10 - 20 seconds, followed immediately by rinsing.

❑ The first phase is a thorough rinsing in cold water, in which the dried thickener swells again and allows the removal of its excess. Alkalis, electrolytes, most excess thickener, and surface hydrolyzed dye should be removed in this first phase. This is followed by hot washing at near-boiling temperature, in which the hydrolyzed, unbound dye is removed, not only from the surface but also from the inside of the fiber. This is followed by another cold rinse, which finalizes the washing process.

✓ POLYESTER (PES) Printing with DISPERSE DYES

❑ The only group of dyes suitable for PES printing are disperse dyes (azo, anthraquinone, coumarin and quinoline disperse dyes are suitable for PES printing). Excellent wet resistance properties are achieved, if the fixing processes after printing and the post-processing are carried out correctly. Due to the hydrophobicity and high temperature of the PES glass transition, during the subsequent washing after printing and fixing, the washing liquid does not penetrate the fiber and the unbound dye inside the fiber is extremely difficult to remove.

- Further problems can occur if there are residual amounts of non-ionic agents on the surface of the fibers (agents commonly used in the pre-treatment phase to remove impurities, such as fixing accelerators, softeners or antistatic agents). In this case, any treatment process carried out at a temperature above 140 °C can lead to the migration of dye to unprinted parts. Even if high-temperature after-treatment processes are not carried out, the application of hot air in the process of making garments or other PES printed fabric items or end-use by the user may lead to dye migration, if all auxiliaries used in PES pre-treatment processes were not removed in detail before printing.
- Two significant criteria for the choice of dye in PES printing are durability during sublimation and behavior during subsequent washing. Given the fixing conditions, which for PES are superheated steam at 180 °C or hot air at 210 °C (thermo-fixing), it is important to choose a thermostable dye resistant to such fixing conditions, to avoid sublimation to unprinted parts of the material.
- **Thickeners** with a high dry matter content (crystal gum (vegetable gum), British gum (heat-treated starches), carob flour ethers) are recommended. Typical PES printing paste recipe contains: thickener, disperse dye, pH regulator (mild acidic pH required, sodium dihydrogen phosphate compatible with alginates as thickeners recommended), oxidizing agent to prevent destruction dyes by reduction that may occur under fixing conditions (sodium chlorate or sodium 3-nitrobenzenesulfonate is recommended), and, if the fixing conditions require, a fixing accelerator or carrier is added.

- If the classic **steam fixation** is performed at 100 °C, a carrier is necessary because optimal dye fixation will not occur. The recommended amount of carrier would be 30 - 60 g/kg of paste, and the fixing time should be 20 - 40 minutes. Dyes suitable for this method of fixing with the addition of carriers are the following disperse dyes (according to the Color Index): CI Disperse Yellow 54, 93 and 184; Orange 25 and 66; Rows 60, 82, 206 and 343; Violet 28; Blue 56, 60, 81 and 287; Brown 4 and 13 and Black.
- After fixing, it is necessary to completely remove the carrier, by washing at temp. above 160 °C. If **superheated steam fixation under pressure** is applied, it is possible to use a much wider range of disperse dyes and achieve optimal colors in deeper tones. Conditions of superheated steam (pressure 0.35 - 0.40 MPa with appropriate temperature; time 20 - 30 min). Disperse dyes suitable for such fixing processes are dyes of the following chemical constitution according to the Color Index: CI Disperse Yellow 93, 126 and 184; Orange 25, 29 and 66; Rows 60, 82, 106, 177 and 343; Violet 28 and 40; Blue 56, 60, 81, 154 and 287; Brown 4 and 13; Black.
- The process of **thermofixation** (as another way of fixing the dye on PES) is carried out at high temperatures of 200 - 220 °C, in a time of 40 to 50 seconds. However, the use of fixing accelerators or carriers is also recommended, because without them the utilization of dyes is only 50-70%. Textured PES materials are not suitable for thermofixation, as specific surface structure is lost during exposure to high temperatures. Such materials are fixed under superheated steam conditions.

- ❑ Fixation is followed by washing in which the excess thickener and unbound disperse dye is removed. After washing, first in cold then in warm water, treatment in an alkaline bath at 40 to 50 ºC is performed. Under these conditions, most of the unbound dye is reduced (destroyed), after which it is washed in a hot and then in a cold bath.
- ❑ Softeners or antistatic agents can be used in the final wash or applied by the impregnation process before the final drying. Drying must not be carried out at a temperature higher than 120 ºC.

✓ **Polyester disperse printing**

✓ POLYACRYLONITRILE (PAN) Printing with DISPERSE DYES

- ❑ Disperse dyes in the printing of acrylic materials - give more pastel colors and achieve limited usage properties and wet resistance. Base dyes in the printing of acrylic materials give brilliant colors and optimal resistance to washing and light.
- ❑ Fixing of the printed base dye on the acrylic fiber takes place according to the same mechanism as in the dyeing processes. Adsorption to the fiber occurs due to the high affinity of the dye cation to the negatively charged surface functional groups of the acrylic fiber. But diffusion from the surface to the interior of the fiber is relatively slow. Thus, the surface of the fiber is always saturated with dye, and the rate of diffusion of dye into the fiber does not depend on the concentration of dye in the printing paste. Base dyes standardized for printing come in liquid or dry granular form.
- ❑ In liquid form they already contain an agent for increasing the solubility of dyes, while a typical recipe with a base dye in powder form involves pre-dissolving the dye with solubilizers (eg glycols) with the addition of acetic acid and hot water (80 to 90 ºC). Dye is added to the thickener. Finally, the addition of a fixing accelerator is recommended. It is necessary to maintain an acidic pH during the entire drying and fixing phase.
- ❑ Of the thickeners, carboxymethyl cellulose or another anionic thickener is recommended.

- ❑ Base dyes of the following chemical constitution are recommended for the printing of acrylic fibers (according to the Color Index): CI Basic Yellow 28, 29, 51 and 63; Orange 27, 28, 30, 37, 42 and 43; Rows 14, 18, 22, 24 and 110; Violet 7, 16 and 20; Blue 1, 3, 147 and 159; Green 4 and Black.
- ❑ Base dyes are fixed exclusively with steam. The best conditions are achieved in conditions of saturated steam under pressure of 0.1 to 0.2 MPa, for 20 to 30 minutes or in conditions of superheated steam (temp. 108 to 110 ºC, under pressure of 0.14 - 0.15 MPa). Fixation is followed by rinsing and soaping at 50 ºC with heating to 70 ºC with 2g/l anionic detergent.

✓ POLYAMIDE (PA) Direct Printing

- ❑ Inks suitable for PA printing are **acid**, **metal complex** and **base**. The use of auxiliaries to increase the solubility of dyes (eg thiodiethylene glycol $C_{12}H_{20}N_2O_4S$), auxiliaries that promote fiber swelling and increase the solubility of dyes (eg thiourea $SC(NH_2)_2$) is recommended. It is recommended to maintain an acidic pH using ammonium sulfate or citric acid.

- ❑ Typical composition of PA printing paste: dye (acid or metal complex), thickener (with a higher dry matter content - 8 to 14%), urea, thiodiethylene glycol, ammonium sulfate, anti-foaming agent, water. Thickeners based on plant gums are recommended. For most inks used for PA printing, it is recommended to fix with saturated steam (100 to 103 ºC) for 20 to 30 minutes. Pressure steamers (35 to 105 kPa) can also be used. In **rare cases**, thermofixation is performed in PA.
- ❑ In the final rinsing, it is necessary to reduce the high affinity of acid dyes to PA fiber, so that, during rinsing, the dye does not bind to unprinted parts of the fabric. Therefore, washing is carried out in a slightly alkaline solution (1 g/l Na_2CO_3), at a temperature of 40 ºC with heating to 60 ºC and 1.5 g/l of cationic auxiliary which will bind the washed anionic dye and keep it in the washing bath.
- ❑ The best choice of PA dyes for printing: CI Acid Yellow 49,79 and 222; Orange 95; Red 274, 276, 337 and 360; Violet 42 and 103; Blue 113, 205, 220, 221, 264 and 313; Green 81 and 84; Black. Suitable metal complex dyes are: CI Acid Yellow 232; Orange 107 and 166; Red 279 and 414; Blue 199 and 335; Brown 413 and 415; Green 91; Black 140 and 220.

✓ Direct Printing of PROTEINE FIBERS

- ☐ **Protein fibers include**: sheep wool, mohair (angora goat wool), alpaca (llama wool), cashmere (cashmere goat wool), camel hair, silk. In printing, as in dyeing, the amphoteric character of protein fibers is important, as a result of which protein fibers can be dyed and printed with a wide range of dye groups (**acid, base, metal complex, reactive and direct**).
- ☐ **Acid dyes are mostly used**. **Acid dyes** must be chosen which, in addition to the satisfactory brilliance of the print, also achieve the optimal properties of wet fastness and light fastness. **Base dyes** give brilliant colors, but do not show adequate durability. Urea or thiourea must be used as auxiliaries in protein fiber printing pastes as dye solubility enhancers, glycols and hot water. **Thickeners based on vegetable gums** as well as **gums obtained by heating dry starches (British gum)**, **with a high dry matter content**, are recommended.
- ☐ It is also important to maintain an acidic pH that is conducive to dye fixation. This is achieved by the addition of: ammonium sulphate $(NH_4)_2SO_4$), ammonium tartrate (tartaric acid $C_4H_6O_6$), oxalates, in some cases acetic acid (CH_3COOH) or glycolic acid ($C_2H_4O_3$).Sodium chlorate ($NaClO_3$) is used as an adjuvant when using dye-sensitive dyes. Among other auxiliaries, anti-foaming agents are used, as well as the addition of various oils to achieve smooth, uniform prints, sharp contours.

- **Fixing:** steam for 30 to 60 minutes (when using acid dyes on wool or silk). The most brilliant and stable prints are achieved by the process of fixing with saturated steam at a temp of 100 – 102 ºC. Fixation is followed by a final wash to remove excess unbound dye and thickener. During the final wash, post-treatment with polycondensates of aromatic sulfonic acids (Mesitol HWS, Erional NWS) can be carried out. Treatment with such agents increases the wet resistance of printed wool, carried out at 60 ºC, for 20 min, during the final washing process.
- With **metal complex dyes 1:1** and **1:2**, better fastness is achieved compared to acid dyes in wool printing, especially light fastness, but the color they give is darker (color brilliance is not achieved as with acid dyes).The method of application of these dyes is practically no different from the use of acid dyes, except that these dyes do not require the addition of acid as an pH regulators. The process of dye dissolution, the choice of thickener, the choice of fixing method and the method of subsequent, final washing, is the same as with acid dyes. Therefore, it is possible to mix acid and metal-complex dyes in the same printing paste, but then no acid is added. The disadvantage of these dyes is that at lower pH (in more pronounced acidic conditions) there is a decrease in the stability of the printing paste, and dye aggregation can occur.

- **Reactive dyes** form chemical bonds via SH, NH or NH_2 groups in the polypeptide chain, in an acidic pH environment (pH 3 - 5) at 80 to 100 ºC. With reactive dyes, good durability and brilliant colors are achieved. The process of preparing the printing paste and printing is the same as with acid dyes. The fixation time can be shorter, 10 to 20 min under saturated steam conditions at 100 to 102 ºC. In the process of final washing, it is necessary to completely remove the excess unbound dye, because it depends on achieving optimal durability. Therefore, washing is carried out with the addition of soap, in several successive baths with a gradual increase in temperature (40 - 60 – 80 ºC), with the addition of sodium hydrogen phosphate (Na_2HPO_4), ammonia to maintain alkaline pH 9 and anionic detergent. This washing procedure is carried out only with reactive dyes and only on chlorinated wool (treated against leaks).

❑DIRECT Printing with PIGMENTS

❑ Precisely due to the principle of mechanical bonding of pigments to textiles, pigment printing is applicable to all types of textile materials, from natural, synthetic to various fiber mixtures, which is its great advantage.

❑ In addition to these and some other advantages, pigment printing has some disadvantages. The biggest disadvantages of pigment printing are open problems related to touch and durability. These problems can be solved to some extent by a good choice of binder, suitable softeners and crosslinkers, thus ensuring quality production and use stability.

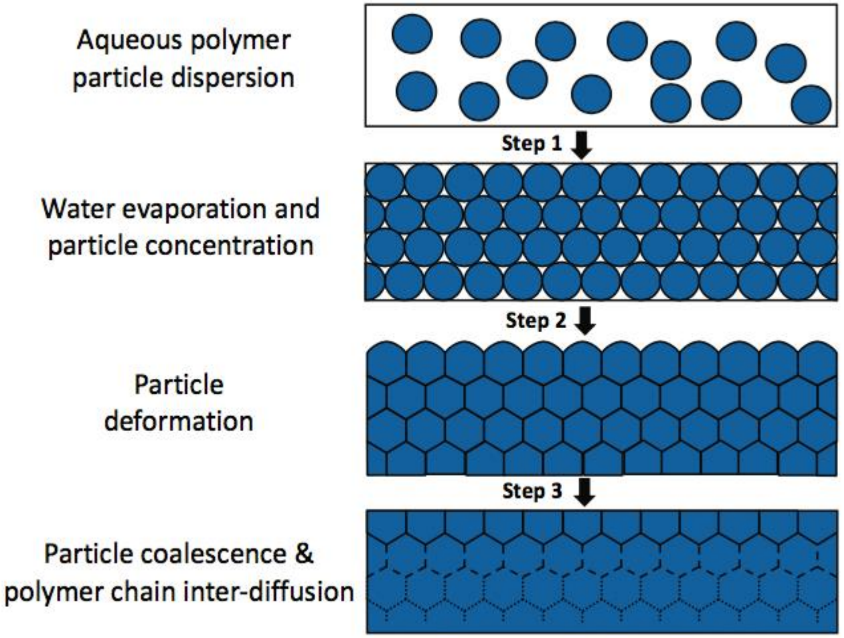
❑ A prerequisite for good print quality is a quality composition of the printing paste. Modern pigment printing is based on the choice of quality pigment dispersion, thickening system, binder and additives primarily softeners, crosslinkers and emulsifiers.

- For more than 3000 years, the use of mineral pigments has been known, which in addition to natural binders (various oils, viscous aqueous solutions of albumin, vegetable gums, etc.) have been used for patterning and decoration of textiles. But despite the fact that **pigment printing is the oldest method of printing**, it did not play a significant role in industrial production until II. World War. The reasons are that satisfactory color brilliance could not be achieved, the use of binders that significantly changed the properties of softness, flexibility and elasticity of textiles and poor resistance to wear and washing.

✓ BINDERS

- **The polymer film formed by the binder** in pigment printing is a **three-dimensional structure of long chains of macromolecules**, which, when applied to textiles together with pigment dyes, **create a three-dimensional cross-linked structure**. Such a cross-linked structure is formed in the phase of fixing the prints, which is usually carried out in hot air in pigment printing, whereby the so-called self-crosslinking or to reaction with suitable crosslinkers which, as auxiliaries, are added to the printing paste. **Crosslinkers ensure elasticity and optimal film adhesion**.

- **In the fixing phase**, through the drying process, a polymer film of binder is formed. The formation of the polymer film takes place in two phases: **flocculation** (**or coagulation**) and **coalescence**. During the first phase of film formation, water and surfactants are removed from the binder by absorption and evaporation. Dispersed solid binder particles coagulate and form a gel layer of tightly packed particles, which have poor strength and adhesive properties. During the second phase of the drying process, the gel particles bind (“coalesce”) to form a continuous film.



- The lowest temperature at which the film is formed depends on the chemical constitution of the binder, but generally for pigment printing ranges from 120 ºC. The rate of film formation depends on the particle size of the binder.
- The reaction between the binder and the cellulosic material can be represented as follows:

$$\text{Binder-CH}_2\text{-OR + HO-Cellulose}$$

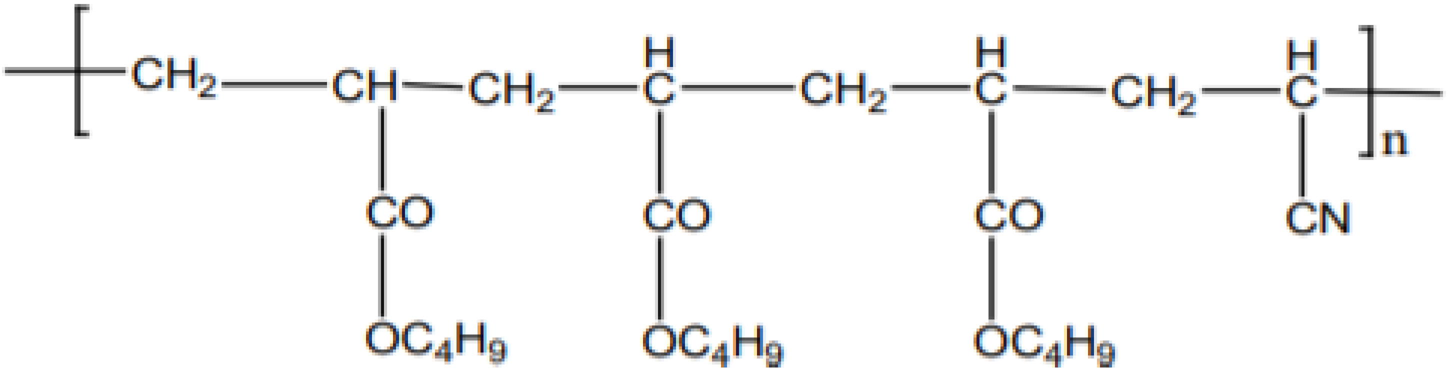
$$\leftrightarrow$$

$$\text{Binder-CH}_2\text{-O-Cellulose + ROH}$$

$$\text{(R is CH}_3\text{ or H)}$$

- **The choice of binder** always depends on the requirements for durability as well as the economic aspects of production. The choice of binder for a given pigment dye is a complex but key aspect of the development of a printing paste recipe that will ensure the required characteristics of the print. Depending on the final expected characteristics of the product (printed textile material), different polymers can be selected that will ensure the achievement of the required characteristics.

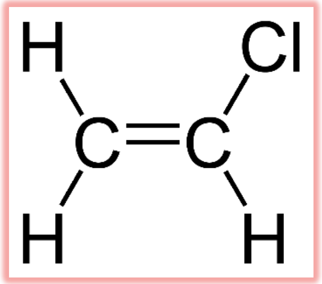
- Most binders used in pigment textile printing are polymer products whose general structure can be shown by the following scheme:



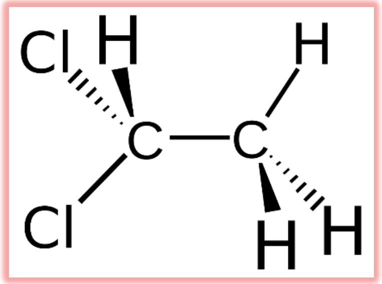
$$-\left[CH_2-\underset{\substack{|\\CO\\|\\OC_4H_9}}{CH}-CH_2-\underset{\substack{|\\CO\\|\\OC_4H_9}}{\overset{H}{C}}-CH_2-\underset{\substack{|\\CO\\|\\OC_4H_9}}{\overset{H}{C}}-CH_2-\underset{\substack{|\\CN}}{\overset{H}{C}}\right]_n-$$

General structure of acrylate polymer

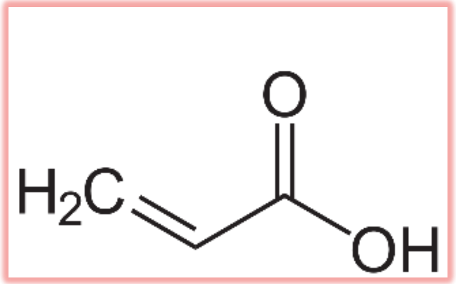
- Depending on the required characteristics of the finished product and the requirements for softness, elasticity, durability of the pigment and polymer film layer, binders can be so-called "Custom-made" or can be produced by targeted selection of a monomeric base. Unsaturated monomers such as vinyl chloride, dichloroethane, acrylic acid, acrylonitrile, esters and ethers of acrylic acid are most commonly used. The binders most commonly used in pigment printing processes are styrene-butadiene, styrene-acrylate or vinyl acetate-acrylate copolymers.



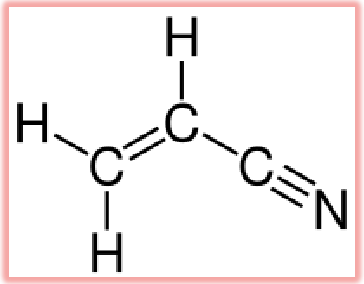
Vinyl chloride



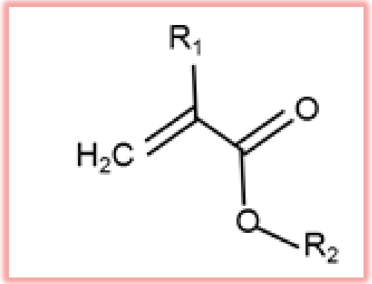
Dichloroethane



Acrylic acid



Acrylonitrile

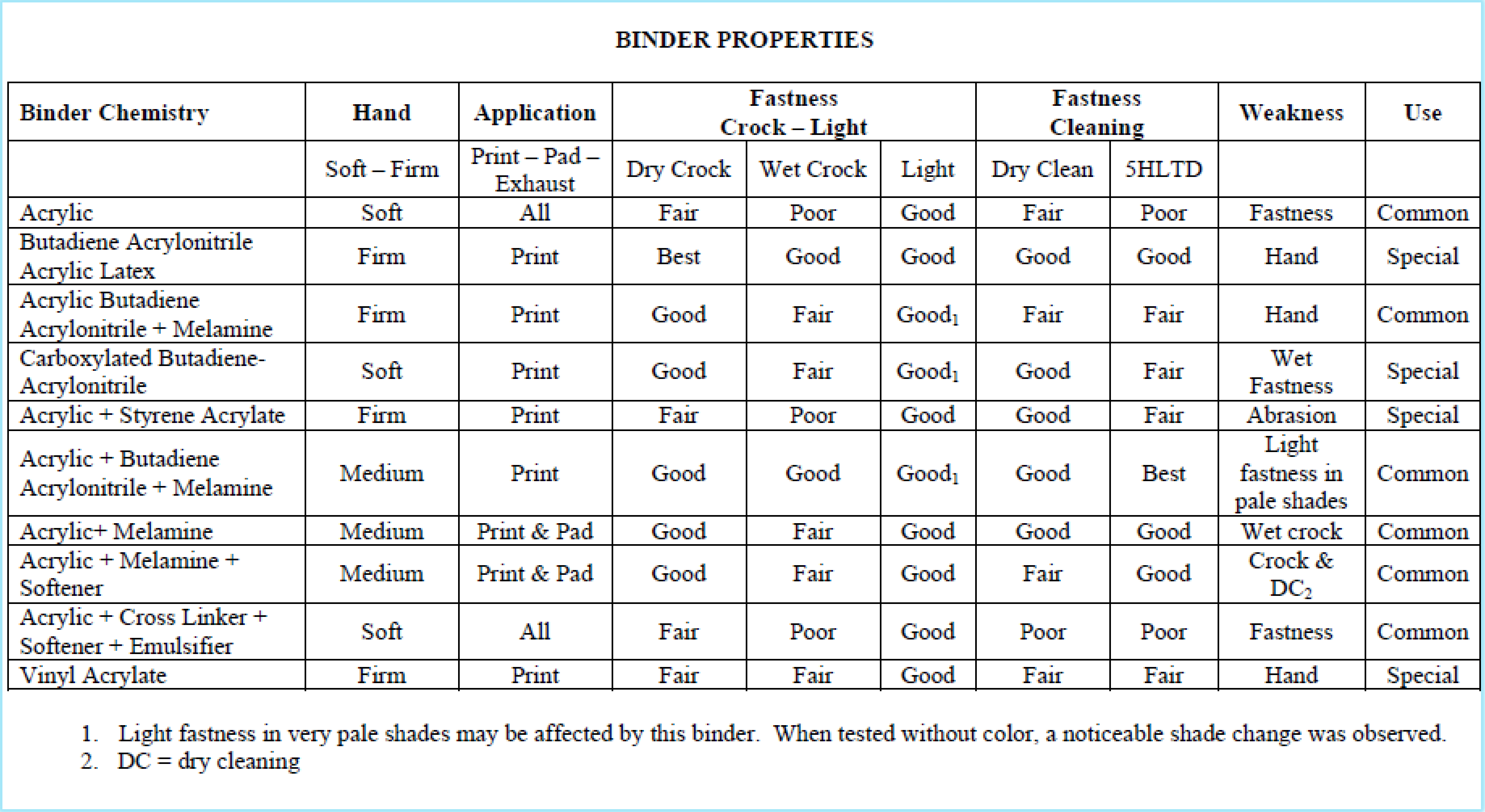


Acrylic acid ester

- ❑ Monomers used for the production of binders can be classified into 3 groups:
  - ✓ **Soft monomers** - characterized by a lower Tg (glass transition temperature) value, these are long-chain alkyl acrylates, low solubility in water. Examples: butyl acrylate, ethyl acrylate, methyl acrylate, iso-octyl acrylate. These monomers contribute to the flexibility and elasticity of the polymer film.
  - ✓ **Hard monomers** - they are characterized by a higher Tg value. Examples: styrene, methyl methacrylate, acrylonitrile. These monomers contribute to structural strength, usability, washing resistance.
  - ✓ **Functional monomers** - monomers with different functional groups, such as carboxyl or hydroxyl, which are characterized by very good solubility in water. Examples: acrylic acid and hydroxyethyl acrylate.

- ❑ The choice of monomer can affect the properties of the film, ie the degree of crosslinking, which must be somewhat controlled, and must not lead to the formation of too strong layer of crosslinked macromolecules. The monomers are dispersed by suitably selected surfactants, wetting agents, emulsifiers, dispersants, etc., and polymerization is initiated by free radicals resulting from a redox reaction between, for example, potassium persulfate ($K_2S_2O_8$) and sodium bisulfite ($NaHSO_3$). The role of these radicals is the accumulation of monomers, in order to form a layer of macromolecular chains.

- ❑ By combining the ratio of radicals involved in polymerization, the growth of macromolecules can be controlled to some extent or by the addition of auxiliaries, the so-called regulators, which regulate the length of the polymer chains, so that the final product has satisfactory properties.
- ❑ The strength of the polymer-textile substrate bond (adhesion forces) and the bond strength of the polymer chains in the polymer film (cohesion forces) must be optimal because it affects the softness, elasticity, thermoplasticity and resistance of the film to organic solvents. Excessive crosslinking results in good moisture resistance, but also in to hard touch. Poor cross-linking results in poorer resistance to moisture, but also softer feel.
- ❑ A good choice of binder can affect the softness of touch. In addition to the glass state temperature, an important requirement when choosing a binder is the relationship between the forces of adhesion and cohesion, which should be approximately equally strong in the polymer film. The resulting polymer film, in addition to the basic property of optimal usability, must also meet the properties of optimal elasticity, cohesion and adhesion to textile substrates, resistance to hydrolysis and the inability to swell in dry cleaning processes.



BINDER PROPERTIES

Binder Chemistry	Hand	Application	Fastness Crock – Light			Fastness Cleaning		Weakness	Use
	Soft – Firm	Print – Pad – Exhaust	Dry Crock	Wet Crock	Light	Dry Clean	5HLTD		
Acrylic	Soft	All	Fair	Poor	Good	Fair	Poor	Fastness	Common
Butadiene Acrylonitrile Acrylic Latex	Firm	Print	Best	Good	Good	Good	Good	Hand	Special
Acrylic Butadiene Acrylonitrile + Melamine	Firm	Print	Good	Fair	Good[1]	Fair	Fair	Hand	Common
Carboxylated Butadiene-Acrylonitrile	Soft	Print	Good	Fair	Good[1]	Good	Fair	Wet Fastness	Special
Acrylic + Styrene Acrylate	Firm	Print	Fair	Poor	Good	Good	Fair	Abrasion	Special
Acrylic + Butadiene Acrylonitrile + Melamine	Medium	Print	Good	Good	Good[1]	Good	Best	Light fastness in pale shades	Common
Acrylic+ Melamine	Medium	Print & Pad	Good	Fair	Good	Good	Good	Wet crock	Common
Acrylic + Melamine + Softener	Medium	Print & Pad	Good	Fair	Good	Fair	Good	Crock & DC[2]	Common
Acrylic + Cross Linker + Softener + Emulsifier	Soft	All	Fair	Poor	Good	Poor	Poor	Fastness	Common
Vinyl Acrylate	Firm	Print	Fair	Fair	Good	Fair	Fair	Hand	Special

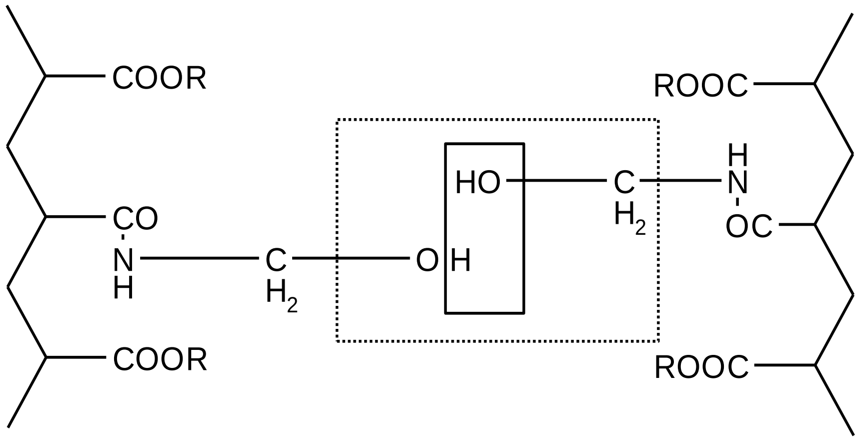
1. Light fastness in very pale shades may be affected by this binder. When tested without color, a noticeable shade change was observed.
2. DC = dry cleaning

- ❑ The requirements to be met by a quality binder are:
  - ✓ resistance to solvents, water, high and low temperature
  - ✓ polymer film must have high mechanical resistance
  - ✓ it must not be a substrate for the development of bacteria, molds and fungi
  - ✓ resistance to washing and abrasionas
  - ✓ little impact on the feel of the material
  - ✓ resistance to aging
  - ✓ it must not change color
  - ✓ must be easily removed from machine parts, etc.

✓ CROSSLINKING

- ❑ Elasticity and improved adhesion of the polymer film to the textile substrate is also achieved by adding a crosslinker to the composition of the printing paste. The crosslinking reaction must result in covalent bonds that are not sensitive to hydrolyzing agents and liquids (detergents, body sweat, etc.). The crosslinking reaction must be initiated exclusively during fixation. Under storage conditions, crosslinkers must be stable and must not induce crosslinking reactions outside the fixation conditions.
- ❑ The simplest crosslinking reaction is the condensation reaction of carboxyl with hydroxyl groups of macromolecules that form a polymer film. The disadvantage of this crosslinking process is the requirement for a very high fixing temperature at which yellowing of the textile can occur, and an ester bond is formed which is relatively sensitive to hydrolysis.
- ❑ Crosslinkers increase the resistance of the prints to breakage, washing and dry cleaning, but have a negative impact on touch. If the binder molecules do not have self-crosslinking groups, crosslinkers are added to the binder, which may be: urea, formaldehyde or melamine formaldehyde condensate, methylated urethane compounds, etc., which have at least two reactive groups in the molecule.

- ❑ In textile printing, N-methylol acrylamide-based crosslinkers are the most common. N-methylol groups with the help of catalysts react with each other at the fixation temperature, or methylol groups react with hydroxyl groups which are also present in the binder copolymer. The equilibrium reaction requires the removal of water from the reaction system, so a suitable fixing temperature of 120 ºC.

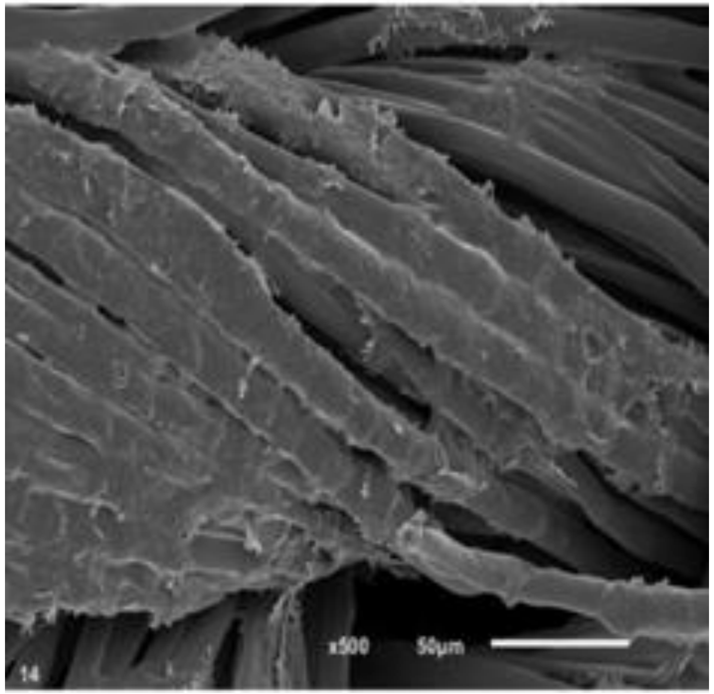


This type of water-based poly N-methylol crosslinker first appeared in 1955.

- ❑ Today, a polymerization system (coupling monomers such as methyl acrylic amide, methylol methacrylamide or more stable methyl ethers) with monomers of acrylic acid ester, acrylonitrile or butadiene monomers is more common, such that the film-forming macromolecule contains 2% N-methylol groups, evenly distributed along the chain. A higher proportion of methylol groups would result in the formation of a too-strong polymer film, which would not have satisfactory resistance to friction and washing.

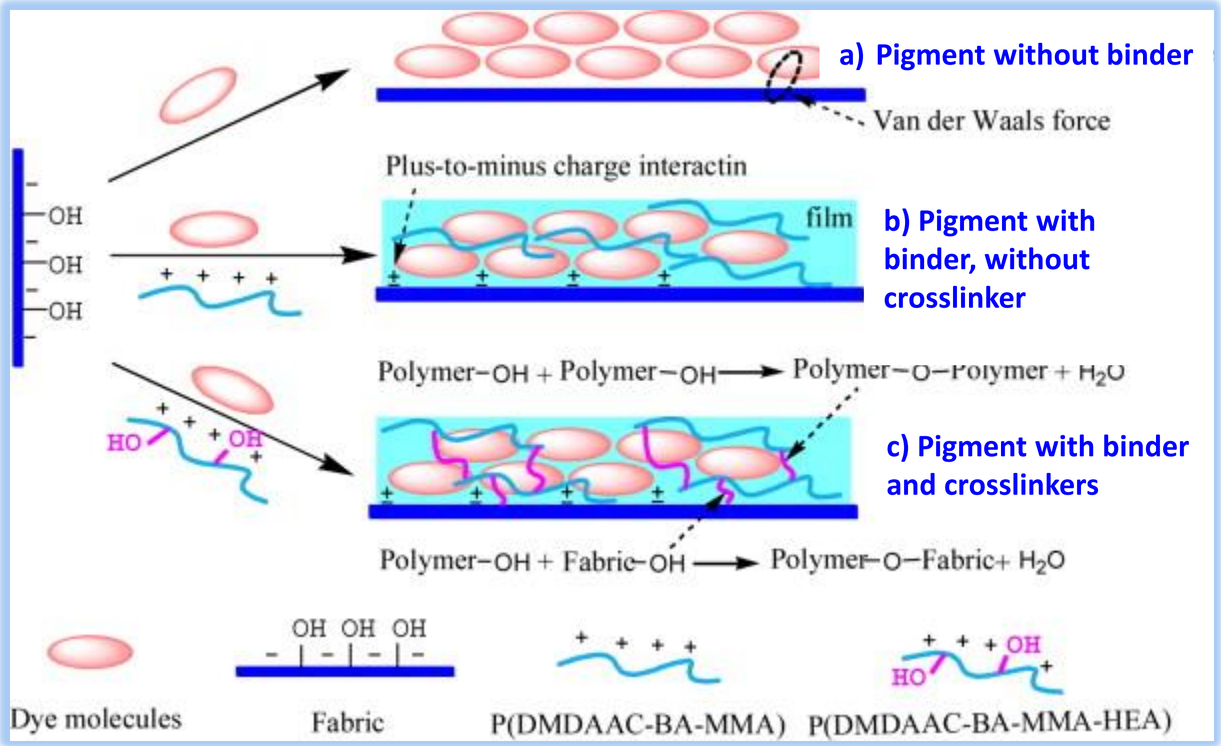
✓ EXTERNAL CROSSLINKING

- Binders containing copolymers with N-methylol groups can be combined with poly-N-methylol compounds as so-called external crosslinkeras. They are especially useful in the printing of hydrophobic materials. For this purpose, water-soluble methyl ethers of tetra- or hexa-methylolamine are recommended.
- They act as an adhesive layer between the binder and the textile, and contribute to the crosslinking on the surface of the polymer film. Their reaction with hydroxyl groups of aqueous thickeners and nonionic dispersants based on polyglycol ethers also reduces the swelling of the film and improves the wet resistance properties of the printed surface. Due to the large proportion of very polar groups, external crosslinkers form very solid films, and it is therefore possible to use significantly smaller amounts of binder in such cases.



SEM image of a polymer film on cotton

- Example of interaction between textile surface and pigment without binder and crosslinker, with binder only and with binder and crosslinker additive.



- Binders can be anionic (older generation, conventional use in printing) and cationic (new generation).
- The diagram shows the mechanism of the ratio of pigment and textile substrate without binder (a), with a cationic binder based on a mixture of monomers Dialyl dimethyl ammonium chloride (DMDAAC), N-butyl acrylate (BA), Methyl methacrylate (MMA) (b), and in in the third case (c) with the addition of the crosslinking monomer Hydroxyethyl acrylate (HEA).

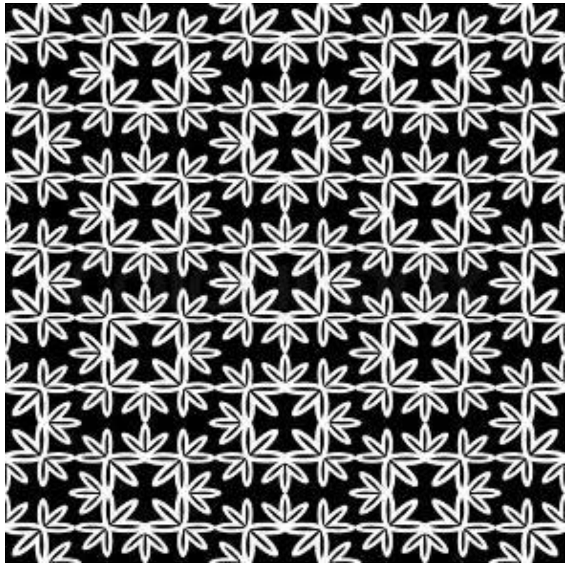
- The diagram shows that between the pigment and the textile material, in the case (a), application of the pigment without binder, there are no forces other than weak Van der Waals forces that cannot bind the pigment to the surface of the material. The binder creates a transparent polymer film on the surface of the textile material and thus binds the optimal amount of pigment, showing (b) application of pigment with the binder. In the case of (c) application of a pigment with a binder with the addition of a crosslinking monomer, since it is a binder based on cationic monomers, due to the positive charge there is an electrostatic interaction with a negatively charged textile surface and the amount of bound pigment increases.
- Also, cationic crosslinking monomers can form chemical bonds with the hydroxyl groups of the textile material, thereby contributing to the bond strength of the polymer film and the material as well as the strength of the pigment fixation to the material. This further contributes to better resistance to dry and wet friction.
- Another important component in the printing pigment paste with the binder is the fixative. Fixers are substances that have functional groups, so at elevated temperatures they react with the plastic mass or with itself to form a cross-linked structure. Newer binders, such as polymer dispersions, contain self-fixing reactive groups (-$CONH_2$, -OH, -COOH) which crosslink even at relatively low temperatures and form a film with good adhesion forces on the textile surface. Such binders do not require the addition of a fixative.

✓ EXPANSIVE PRINTING

- Pigment printing in which an agent (usually vinylidene chloride or other) is added to the printing paste, which has the ability to decompose at a temperature of 130-150 ° C and create gases that cause swelling of the printing paste. The height of swelling depends on the amount of pigment in the printing paste (higher amount of pigment dye - lower relief).
- The pigment itself contirbutes to the weight of the basic printing paste in which the swelling component is contained, and there cannot be pronounced relief of the print if a larger amount of pigment is present.
- Fixation temperature must be carefully adjusted (if the temperature is too high, there may be a sudden expansion and cracking of the film).

✓ COVER PRINTING

- Used for printing darker (deeper) colored surfaces. Dyes and pigments are opaque in themselves and therefore cannot be printed on already dyed fabrics, especially if there are darker, deeper colourations. Therefore, the so-called **cover printing** is applied, in which the image is first printed only with white pigment, ie printing paste containing white pigment, most often titanium dioxide TiO2, which is the only pigment that has the property of covering any color of the substrate.
- After printing with white pigment, the pattern is printed over it with a conventional pigment printing paste containing pigments of the desired colors.



✓ THICKENERS for PIGMENT PRINTING

- ❑ Conventional polysaccharide-based thickeners, such as starches, cellulose ethers, alginates or rubbers, although applicable to a wide range of dyes in textile printing processes, and certainly the oldest, **are not applicable to pigment printing**. **Their rheological properties are not suitable for pigment printing**, and the film they form on textile material is too thin and brittle and is not suitable for bonding pigments.
- ❑ For pigment pastes, the pseudo plastic property characteristic is extremely important. Due to that property, the pigment paste easily adheres to the textile material, but the depth of its diffusion is limited.
- ❑ Pseudo plastic flow is characteristic of heterogeneous, coarsely dispersed systems. Under the influence of a certain shear force, the flow property appears, but as soon as the action of the force stops, the paste returns to the consistency of the solid on the surface of the textile. Pigment pastes cannot penetrate deep into the structure of textiles due to their rheological - pseudo plastic properties. Because they remain on the surface of the textile material, pigment pastes provide more brilliant, shiny colors and sharp prints.
- ❑ Thickeners suitable for pigment printing nowadays, given the above pseudo plastic properties, are synthetic emulsion thickeners.

- ❑ In the 1960s, thickeners based on synthetic polymers were developed for pigment printing, with rheological properties similar to emulsion thickeners and a very low dry matter content. These are mainly copolymers of unsaturated organic acids - acrylic acids (polyacrylates) and malic acids, with the addition of some oil component in 4-5% (hydrophobic component which reduces the diffusion of pigment deeper into the printed area and thus provides a more brilliant print).
- ❑ General characteristics and advantages of synthetic thickeners:
  - ✓ Achieve viscosities suitable for printing, even with very small proportions of dry matter (1-2%)
  - ✓ They do not contain oils or heavy gasoline
  - ✓ By their chemical composition are copolymers of acrylic acids (polyacrylates)
  - ✓ They are available in paste form
  - ✓ Optimal viscosity is achieved by mixing the thickener in a certain ratio with water or an alkali such as aqueous ammonia solution
  - ✓ The characteristic recipe of the printing paste based on synthetic thickener for pigment printing contains: binder, water, emulsifier, synthetic thickener with crosslinkers, softener, urea (dispersant), pigment dye and fixative.

- The ratio of the **basic components of the printing paste for pigment printing** depends on the fact that to achieve optimal usage stability, even with small amounts of pigments (up to 1 g of pigment per 1 kg of paste), it is necessary to achieve a polymer film thickness of 5 µm. In general, pigments require binders in an amount 1.5 to 2 times their weight, and for printing on hydrophobic textile materials (including PES/cotton blends), an additional 0.5 to 1% of external crosslinkers are added to the composition of printing pastes, depending on the desired color depth and requirements for usability.

✓ ADVANTAGES of PIGMENT PRINTING

- ❑ Pigment printing is the most economical printing process, which is certainly contributed by the elimination of the phase of subsequent washing and processing, and higher production speeds.
- ❑ If the pigment printing process is carried out with the correct choice of binder and crosslinker for a given material and the characteristics of the pigments to be used, then in pigment printing can be obtained quite satisfactory properties of light fastness and in general, satisfactory usability.
- ❑ Pigment printing is applicable to all types of textile materials, including glass fibers, PVC, artificial leather and the like.
- ❑ From an environmental point of view, synthetic thickener-based pigment printing pastes are more acceptable than any other form of printing paste.

✓ DISADVANTAGES of PIGMENT PRINTING

- ☐ The usability of medium to darker pigment prints on PES, acrylic and wool materials is not satisfactory, and these materials printed with pigment printing are not recommended for garments, but items that will not be exposed to systematic use and wearing.
- ☐ Also, pigment printing on synthetic fiber blends, such as PES/cotton, has poor abrasion resistance and significant color loss due to more frequent use and wear.
- ☐ Pigment printing is not suitable for bulky materials
- ☐ The original surface structure of the textile material is covered with a polymer film formed by a binder, which is aesthetically undesirable.
- ☐ Pigment printing is not completely resistant to dry cleaning, depending on the choice of pigments and binders (which must be standardized as resistant to solvents), however, there may be a loss of brilliance and depth of color.