



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

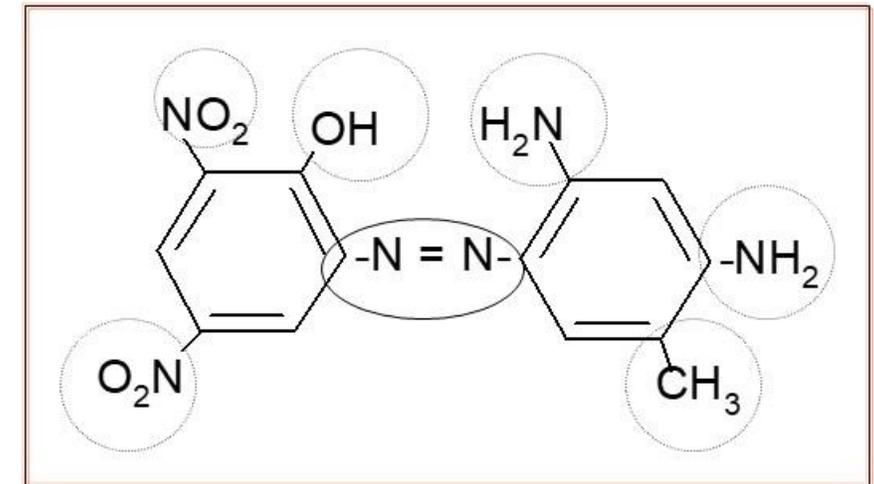
The course is developed under Erasmus+ Program Key Action 2:
Cooperation for innovation and the exchange of good practices Knowledge Alliance

ICT IN TEXTILE AND CLOTHING HIGHER EDUCATION AND BUSINESS

Project Nr. 612248-EPP-1-2019-1-BG-EPPKA2-KA

□ DYES

- ✓ **Dyes** are coloured, mostly organic, **water soluble** chemical compounds which absorb light in visible spectrum.
- ✓ **Dyes** have certain affinity towards textile fibre and bond chemically with textile fiber over functional groups, giving a certain colour to textile.
- ✓ The one who was the first to connect the chemical constitution of one compound with coloration was Otto Nicolaus Witt. In 1876., Witt put forward the first theory of coloration - The Theory of Chromophores and Auxochromes. He believes that unsaturated groups such as nitro (-NO₂), nitroso (NO), azo (NN) and carbonyl (CO) are potential carriers of colour. He called them **chromophores** (Greek: chroma phorein - the bearer of colour). He further states that in order for one coloured substance to be a dye, the molecule must additionally contain groups: amino (NH₂), hydroxide (OH), sulfo (SO₃H) or carboxylic (COOH), which he called **auxochromes** (Greek: auxein-chroma).

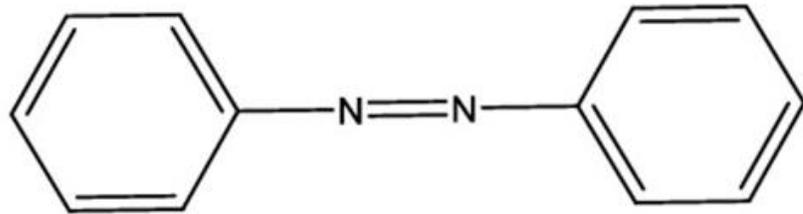


Presentation of a single dye molecule

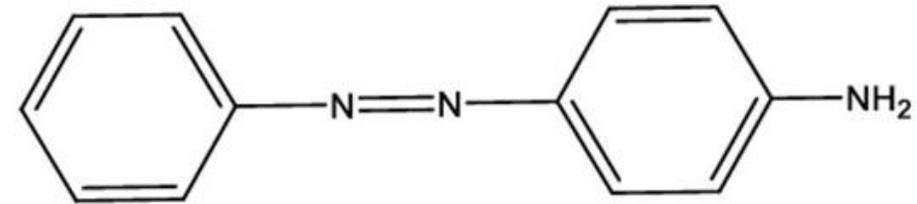
auxochrome + chromophore =
chromogen



- ✓ **Auxochromes** form hydrogen bonds with certain fibre groups: -OH from cellulose or NH_2 from wool or silk.



Azobenzene containing -N=N- chromophore
(Not serving as dye)



p-Aminoazobenzene containing -NH₂ auxochrome
(A disperse dye)

- ✓ Since the auxochromes are capable of forming salts either with a basic or acidic groups, their presence also convert a coloured compound (devoid of salt forming groups) into a dye which must fix permanently to the fiber, i.e., it must be fast to water, light, soap and laundering, when fixed to the fiber. The permanent fixing of dye to the fiber is generally due to the formation of chemical bond between the fiber and the auxochrome.

□ Basic dyestuff groups for given fibres:

FIBERS	DYESTUFF Groups
CELLULOSE fibers (cotton, flax, hemp, as well as cellulose regenerates - viscose)	Recative, Direct, Vat
PROTEIN fibers (wool, silk)	Acid, Basic (Cationic), Metal complex 1:1, Metal complex 1:2, Recative
SYNTHETIC fibres (PA)	Disperse + Acid, Basic (Cationic), Metal complex 1:1, Metal complex 1:2, Recative
SYNTHETIC fibres (PAN)	Disperse + Basic (Cationic)
SYNTHETIC fibres (PES)	Disperse

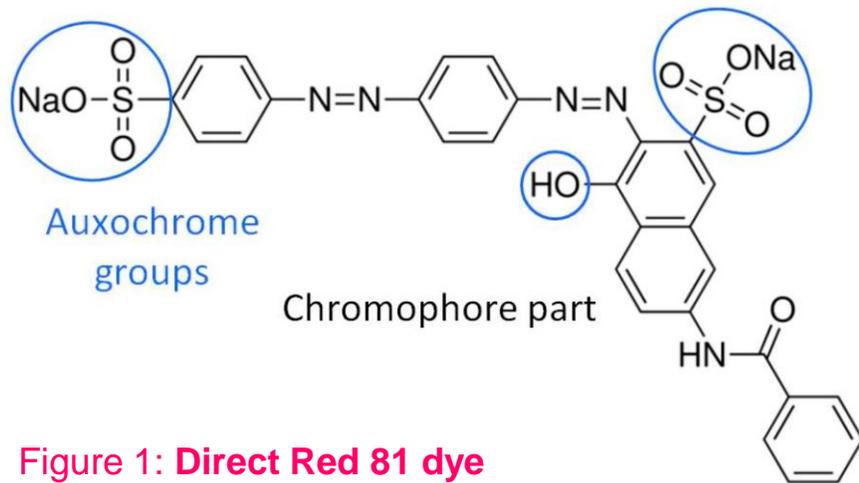


Figure 1: Direct Red 81 dye

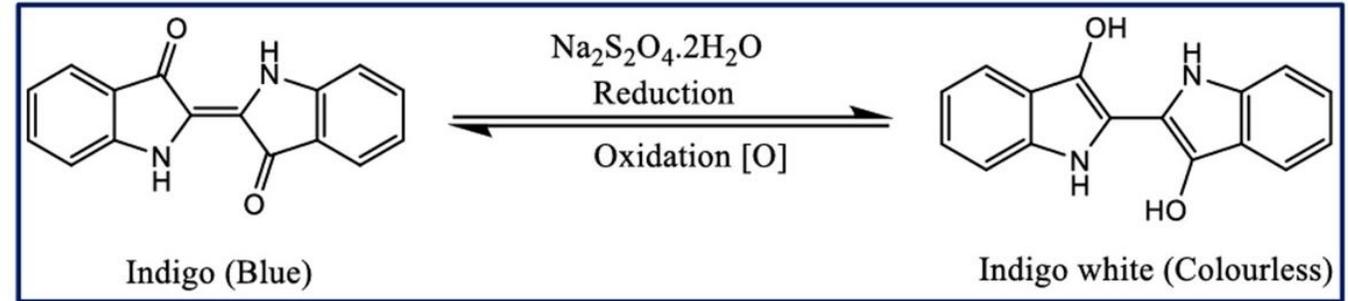


Figure 2: The reduction of Indigo dye

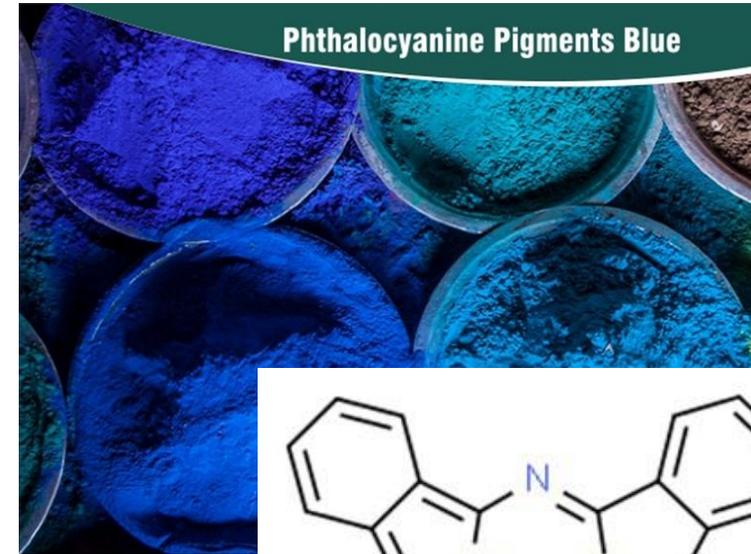
- ❑ The figure 1 is showing the chemical structure of Direct Red 81 dye, containing azo-group. They usually contain at least one azo group and some sulfonic acid groups thus making them soluble.
- ❑ One of the very common groups of dye in printing of cellulosic materials is the group of **vat** dyes. These are water-insoluble dyes, which are converted into a soluble form through the reduction process during printing, and after printing, they are returned to an insoluble form during the oxidation process, which is why they provide excellent fastness properties. For the reduction of vat dyes, mostly the Sodium hydrosulphite is used ($\text{Na}_2\text{S}_2\text{O}_4$). **Figure 2** is showing the reduction and oxidation process of Indigo dyes (the most well known vat dye of natural origin. Today only synthetic indigo dyes are used).

- ❑ Printing can be defined as a controlled form of localized dyeing, and, in principle, all dyes used in textile dyeing processes can also be used in printing processes. The mechanism of dye fixation, both in dyeing and in printing, is the same, but the solubility property of dye in printing processes is a much more critical parameter than in dyeing processes. Namely, the amount of water in the printing paste is strictly limited, and in the fixing phase, the ink must be dissolved again in a small volume of condensed steam.
- ❑ Another reason for careful selection of dyes for printing, is the fact that the dye in the printing process, diffuses through the layer (film) of the thickener before adsorption on, and diffusion into the fiber. If the dye does not have a high diffusion rate, the fixation time must be extended. Therefore, a choice of lower molecular weight dyes with satisfactory durability properties is preferred.
- ❑ Although the same dyes can be used in both dyeing processes and processes, there are still some differences in the standardization of the same dyes for dyeing and printing. For example, in the case of dyes that require the presence of electrolytes, a lower amount of electrolytes is preferred in printing processes, especially if electrolyte-sensitive thickeners are used.



□ PIGMENTS

- ✓ **Pigments** are colored, insoluble chemical compounds that also have the property of absorbing light in the visible spectrum, but have no affinity for textile material and bind mechanically with the help of binders.
- ✓ According to their chemical structure, they belong to the groups of azo dyes, anthraquinone, indigoid and phthalocyanine dyes. The size of the pigment particles thus obtained ranges from 0.05 to 1 μm , or even more than 100 μm for special pigments. The pigment must have good resistance to light and a certain resistance to temperature. Friction resistance is somewhat weaker and depends on the binder.



Phthalocyanine BLUE pigment chemical constitution



- **Natural pigments (inorganic):**

- ✓ Iron oxides and hydroxides present in nature have been used as pigments since prehistoric times. They were used as dyes by the Egyptians, Greeks and Romans. Hue range - yellow to brown.
- ✓ Of the natural pigments of iron oxide, hematite has achieved significant economic importance as a red pigment, goethite as a yellow and umber as a brown pigment. Chromium oxide pigments (Cr_2O_3) are used in the dye and pigment industry to obtain quality green pigment dyes. Titanium dioxide (TiO_2) is used exclusively as a white pigment in textile printing.
- ✓ Zinc oxide (ZnO) is of better quality than titanium dioxide, but due to its price, it is only used in painting.
- ✓ Soot is used exclusively for the preparation of black pigment.

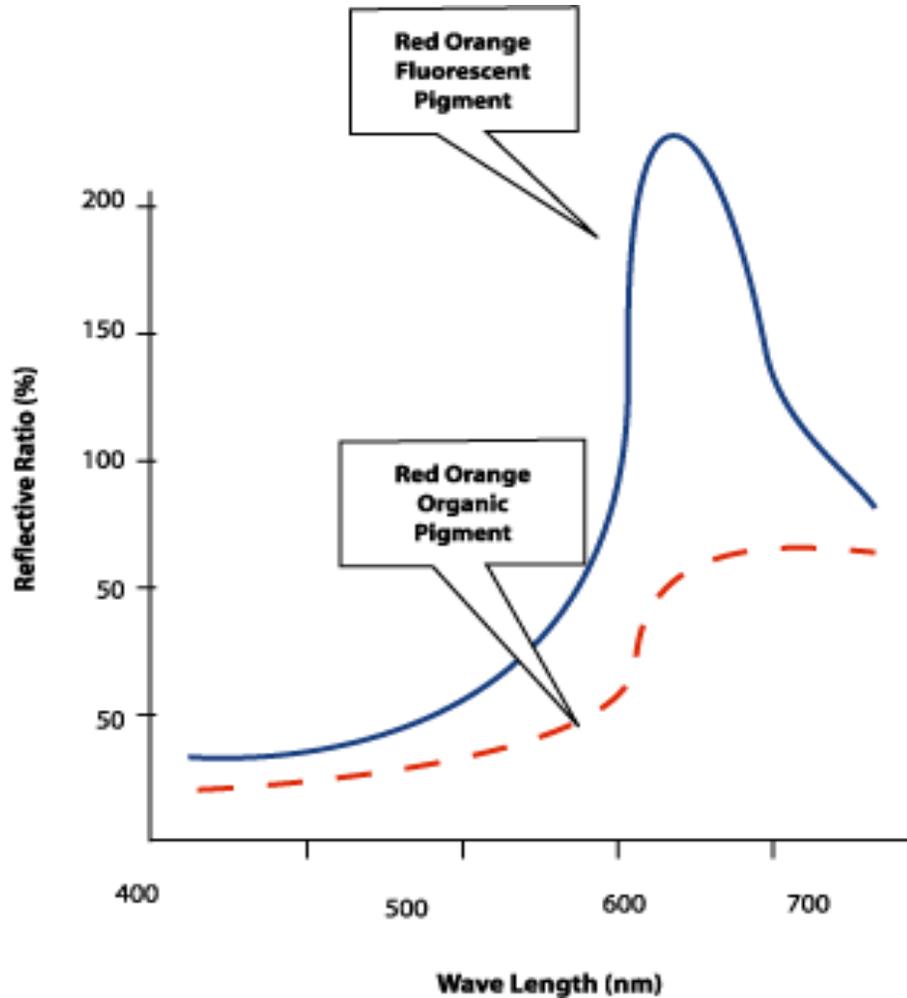
- **Synthetic pigments (organic):**

- ✓ Organic pigments are products synthesized under strictly defined conditions. They are chemically cleaner and therefore have a higher gloss than natural pigments. Organic pigments are produced in all hues and shades.

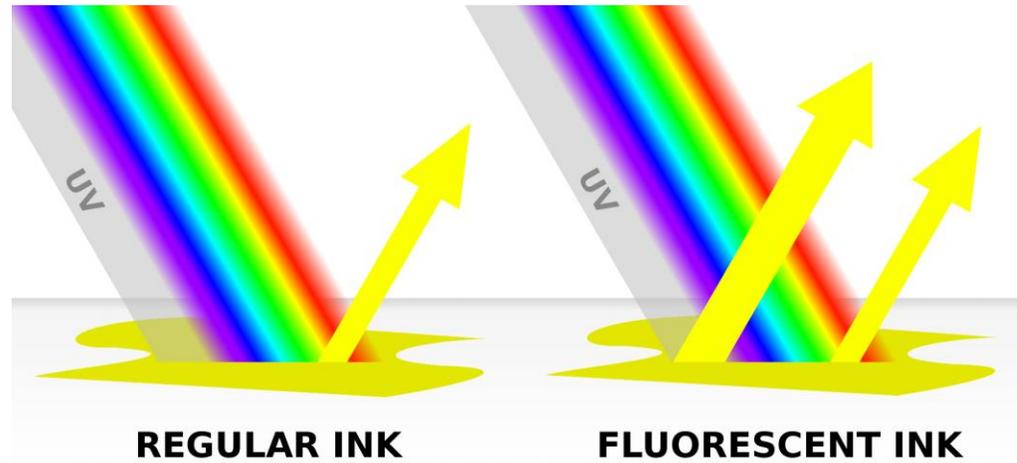
□ *Pigments with Special Effects*

Fluorescent, phosphorescent, Pearl, Metal pigments

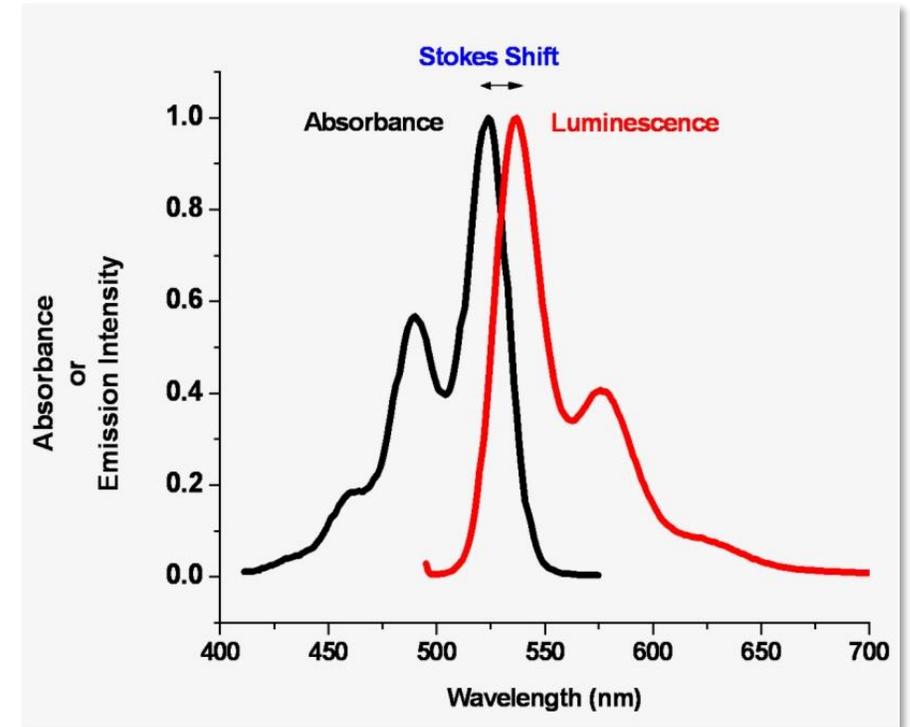
□ **Fluorescent pigments**



- ✓ Fluorescent dyes/pigments have the ability to absorb and emit at the same time, absorbing shorter wavelengths (absorb in the UV region or VIS region bounded by UV) and emit longer wavelengths of the visible spectrum. In other words, they are characterized by the so-called. Stokes shift (Sir George Gabriel Stokes, 1819-1903, founder of the concept of fluorescence).
- ✓ They are characterized by exceptional intensity and brilliance with a high proportion of reflection (Figure).



Stokes shift → 50 to 70 nm. Due to Stokes shift between absorption and emission, fluorescent hues will be characterized by a reflection of analog shade, for example, a dye that absorbs about 430 nm will emit in the range 480 to 500 nm, meaning visually the color hue will be yellow with yellow-green fluorescence.



Fluorescent pigments are chemically different from conventional textile pigments. These are actually fluorescent dyes dissolved in a transparent, colorless solid polymer in the form of finely dispersed particles. The solid thus obtained is ground into a powder of very fine particles and used in textile printing by the method of the classical pigment printing process.



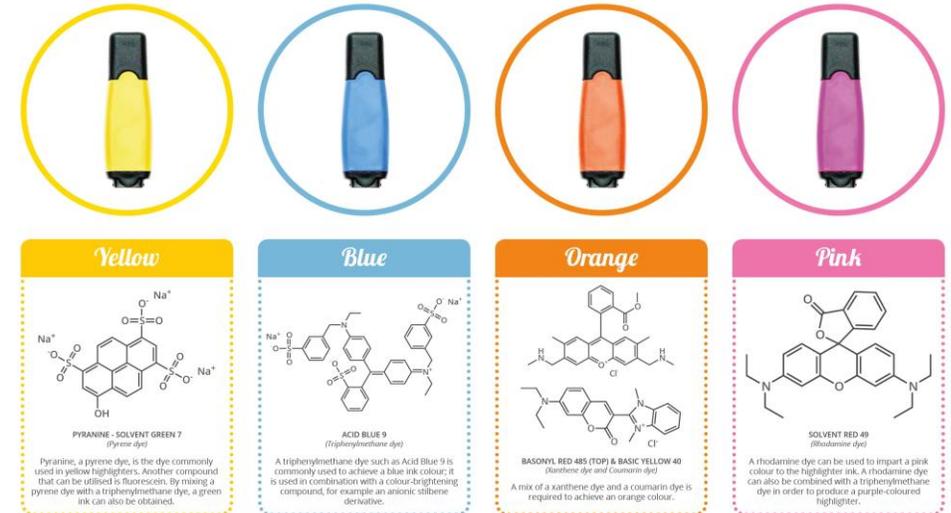
❑ Polymers in which fluorescent dyes form a solid solution have a key influence on the subsequent properties of the pigment. They must be good solvents for dyes and ensure high resistance to other solvents and thermal stability. Traditionally, the polymer matrix for pigments that are fluorescent in daylight, has been based on the toluene-sulfonamide-melamine-formaldehyde thermoset. However, due to the toxicity of formaldehyde compounds and their abandonment in production and use, more and more producers are switching to thermoplastic polymers based on polyurethane, polyamide or polyester.

❑ Azo dyes, certainly the most important group of dyes for use in textiles, do not have the property of fluorescence. The most important fluorescent dyes for textiles contain a carbonyl group as a chromophore.



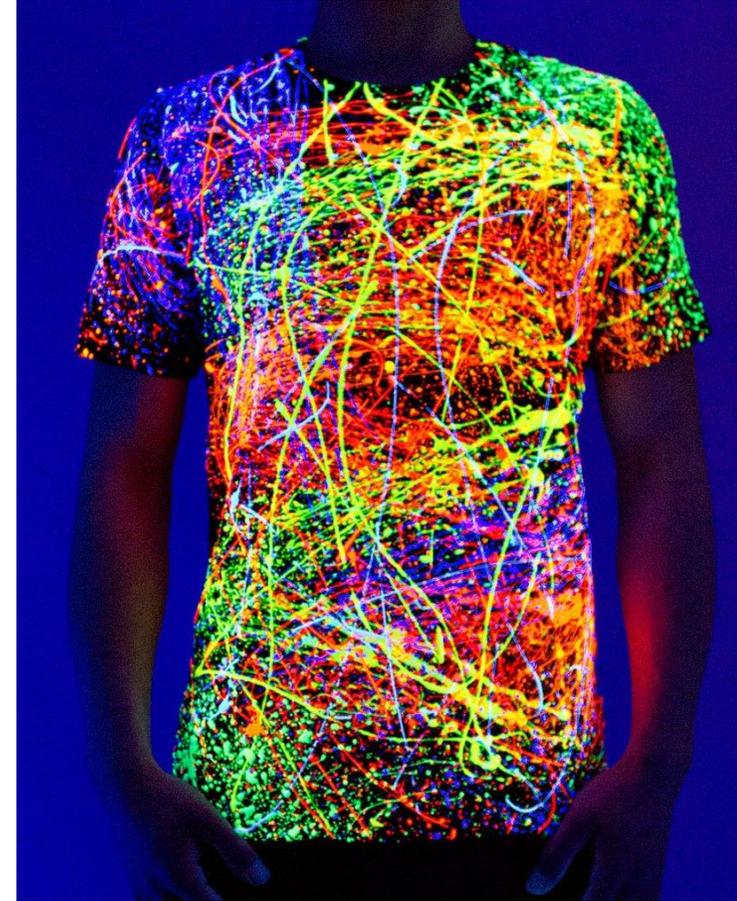
THE CHEMISTRY OF HIGHLIGHTER COLOURS

HIGHLIGHTERS COME IN A RANGE OF COLOURS. THIS GRAPHIC SHOWS A SELECTION OF COMPOUNDS THAT CAN BE USED TO IMPART THESE COLOURS TO THE INK.





**Print with fluorescent pigments under
standard lighting conditions.**

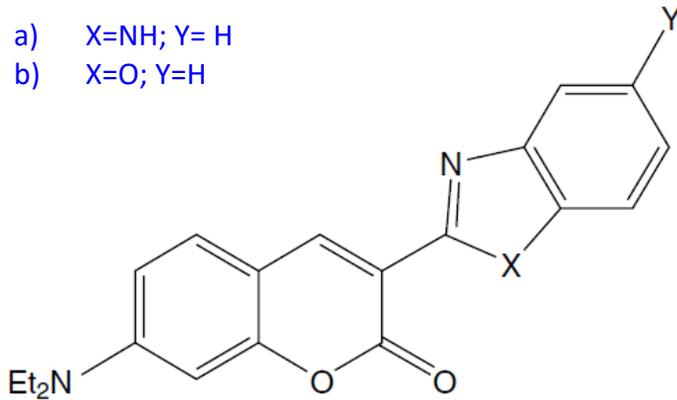


**Print with fluorescent pigments under
UV lighting conditions.**

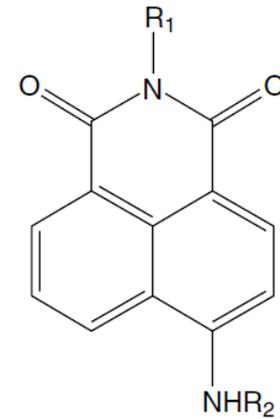


Coumarin derivatives are the most important industrial fluorescent dyes, of which benzazoly-coumarin-based dyes are most commonly used for yellow shades (**benzimidazolyl** (a)), (**benzoxazolyl** (b)); **aminonaphthalimides**; based on **rhodamine** for red to purple shades; for blue and green shades **copper phthalocyanines** are mainly used.

- a) X=NH; Y=H
b) X=O; Y=H

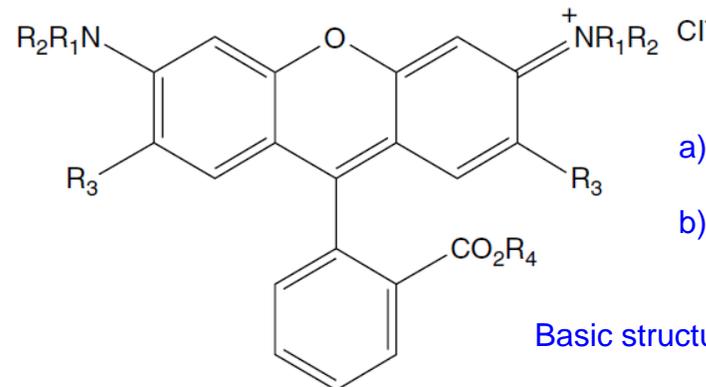


Basic structure of coumarin-based fluorescent dye



- a) R₁ = 2,4-dimethylphenyl; R₂ = H
b) R₁ = R₂ = (CH₂)₃CH₃

Basic structure of aminonaphthalimide fluorescent dye



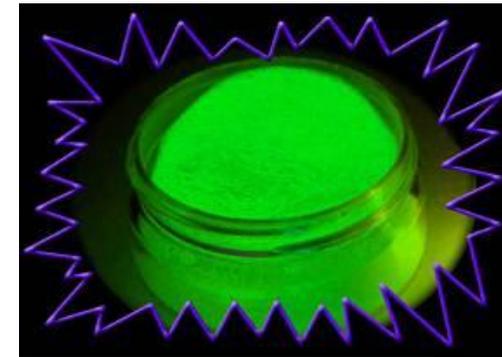
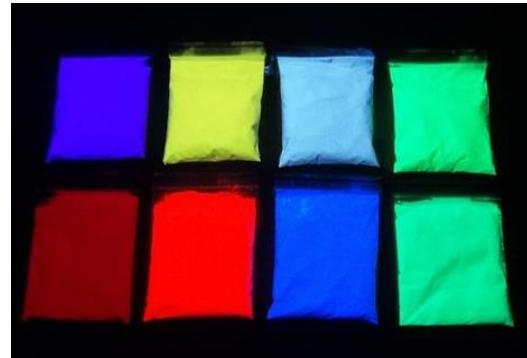
- a) R₁ = R₂ = C₂H₅; R₃ = R₄ = H
b) R₁ = H; R₂ = R₄ = C₂H₅; R₃ = C₃

Basic structure of rhodamine-based fluorescent dye



□ UV pigments

- Also fluorescent dyes/pigments, but unlike fluorescent pigments that fluoresce under UV and VIS light, UV pigments in their chemical constitution contain inorganic luminescent compounds that absorb only UV radiation of long and short wavelengths and then emit absorbed energy in the form of intense fluorescing coloring. While they are not in the excited state, ie under daylight, they have a very weak, pastel color or are even colorless.





□ PHOSPHORESCENTE pigments

- ✓ **Phosphorescence** is similar to fluorescence, a phenomenon that occurs when a substance absorbs radiation of a certain wavelength or group of wavelengths and re-emits photons of different wavelengths. The difference is in the emission duration. If the emission stops after removing the excitation source, then the illumination is called fluorescence; if the show continues (so-called "afterglow"), then it is called **phosphorescence**.
- ✓ The best known and oldest phosphorescent pigment is zinc sulfide reinforced (doped) with copper ZnS:Cu, which is characterized by the green color of the emitted light. However, the limitations of sulfide-based phosphorescent pigments are: the size of the pigment particle, which is why it is only applicable for screen printing with flat screens; to achieve optimal phosphorescence it is necessary to apply a very high concentration of pigment in a thick layer of binder; the strength of phosphorescence depends on the particle size (larger particle - stronger emission).



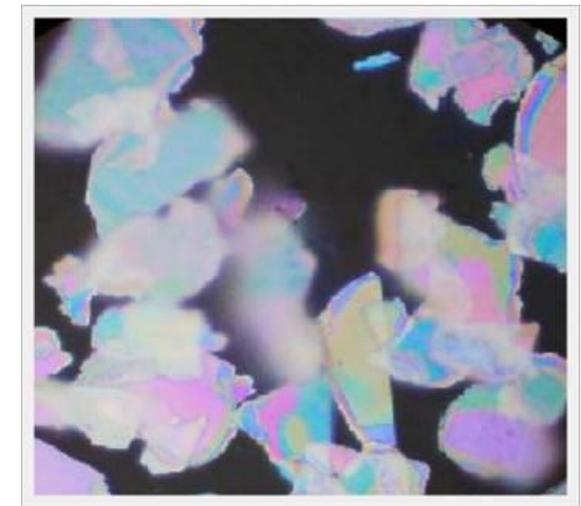


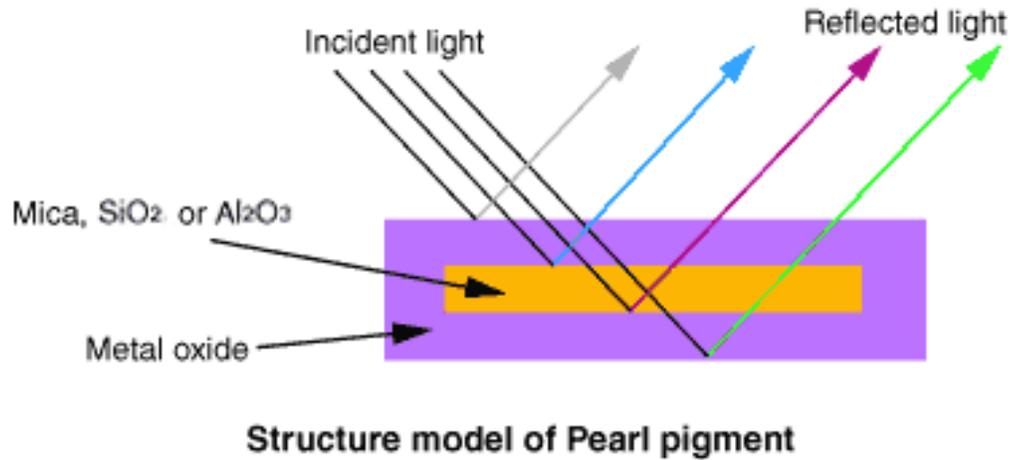
- Therefore, in the 90^s of the 20th century, based on intensive research, a ***new generation of phosphorescent pigments based on alkaline earth metal aluminates*** was synthesized, which have 10x longer emission and 10x higher brilliance and intensity for the same pigment concentration. Aluminates based on calcium, barium or strontium, compared to conventional sulfides, are chemically more stable and are characterized by greater brilliance and much longer subsequent emission without the presence of harmful radiation. In addition to the chemical constitution, the size of the pigments as well as their distribution within the binder affect the print quality and the final appearance of the printed material.



❑ PEARL pigments

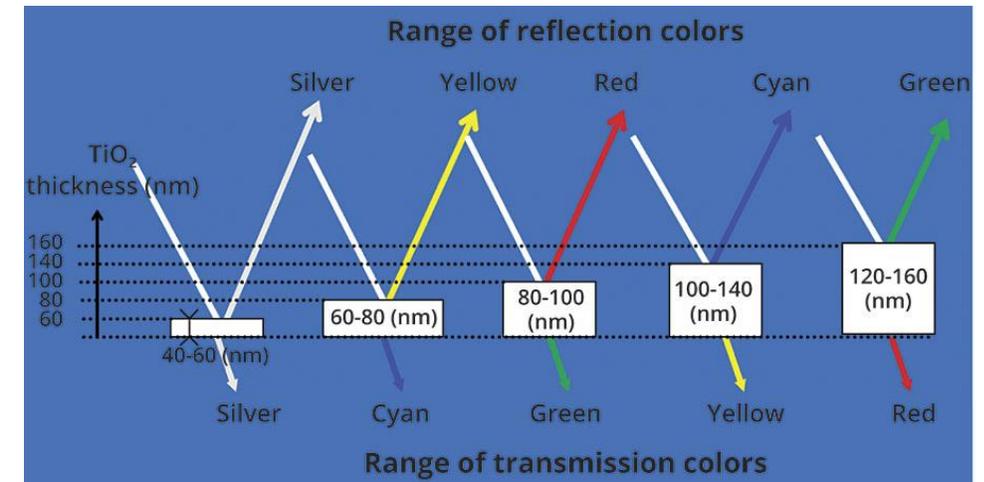
- ❑ The optical properties of *pearl* pigments are defined by their multilayer structure, because the incoming light is reflected and scattered within the boundaries between the layers. The gradual reduction of reflected light leads to a pearly glow - a specific type of glow that seems to grow out of the surface of an object.
- ❑ Also, different layer refractive indices lead to constructive interference - the reason why pearl pigments exhibit goniochromatic properties (a property of significant color change with a change in viewing conditions, such as viewing angle or lighting conditions). Pearl pigments are often defined by their hue of interference - the dominant wavelength of light reflected in the specular angle of incident light. By increasing the angle of illumination in relation to the position of the observer, the dominant wavelength of the reflected light changes, so with the inclination of the material printed with such pigments, the different changes and color transitions are experienced. The range of colors that can be achieved by changing the position of the lighting or the observer primarily depends on the structure of the pigment layers, as well as their arrangement and thickness.

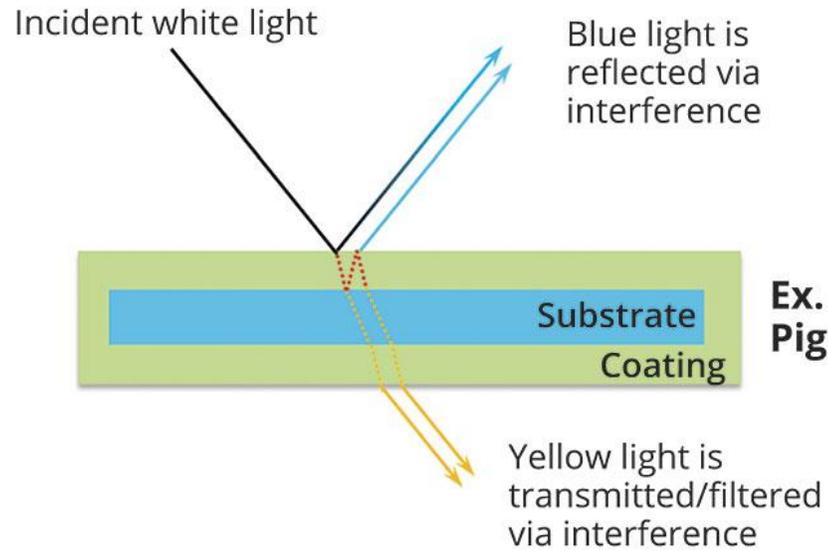




- ✓ The multilayer structure of pearl or pearlescent pigments consists of a carrier layer of lower refractive index, most commonly silicon dioxide (SiO₂), alumina (Al₂O₃) or mica - common name for the group of potassium-aluminum silicate minerals, and a layer of high refractive index such as metal oxides TiO₂ or Fe₂O₃.

- ✓ A layer of higher refractive index and reflection overlays the carrier layer of lower refractive index resulting in a pearl effect and a color overflow effect resulting from light interference. With different thicknesses of the outer layer of metal oxide, the effect of reflection of different colors is obtained, as shown in the figure.





Ex. Blue Pearlescent Pigment



- ✓ Multilayer pearl pigments have the shape of semi-transparent high-smoothness tiles. The smoothness of the surface results in reflection, but due to the property of partial transparency, only part of the light is reflected and part is transmitted through the outer layer to the inner layer from which it is further partially reflected. It is this interaction with the incident light that results in a special pearl and overflow effect.



❑ METAL pigments

❑ They can be **silver**, **gold** and **copper**. Thin lamellas of **golden pigment**, which are obtained from brass (an alloy of copper and zinc characteristic golden colour) are protected by special additives so that the pigment is not sensitive to water and air. The **silver pigment** is obtained from aluminum lamellae on which aggravation is carried out because otherwise they float. Grain fineness is defined by grinding the lamella and is 10 - 20 μm . Silver pigment with a fineness of 200 μm is also called glitter.

❑ Unlike pearl pigment, **metallic pigments** are not transparent and therefore reflect from the total amount of incident light. Due to their great smoothness, they have a mirror effect and reflect almost the entire incident light, in the right direction. Since the regularity and amount of reflection decreases at the edges and corners of the pigment particle, the larger the pigment particle and the larger its central surface, the stronger the reflection and the greater the brilliance and shine.





- ❑ For these special pigments, the fineness of the screen is always chosen in dependence on the fineness of the pigment. It is not recommended to take the screen with a fineness of more than 50 mesh, in order to ensure the maximum coverage of the printed surface with the pigment, and to achieve the desired effect. For coarse pigments - **glitter**, the fineness of the screen is a maximum of 20 mesh.



❑ THERMOCHROMIC dyes

- ❑ The color change of a compound with the effect of temperature is called thermochromism. Thermochromic dyes can be divided into two groups as leuco dyes and liquid crystal dyes. For both types, the active components are usually microencapsulated and applied to the textile substrate like a pigment with a binder. Each microcapsule contains the entire system and has a diameter ranging from a few microns to 20 μm , depending upon the processes used in its manufacture.
- ❑ Leuco dye is a dye that can switch between two chemical forms. One of them is colorless. The thermochromic effect provided by some liquid crystals is quite different from those of leuco dye types. They provide a constantly changing spectrum of colors at a range of temperatures when observed. The thermochromic property of liquid crystals is provided by the selective reflection of light. The wavelength of the reflected light varies according to the refractive index of the liquid crystal and the helical settlement distance of the molecules. Since the distance between molecules changes depending on the temperature, when the temperature changes, the wavelength of the reflected light also changes, so the resulting color differs.



Reversible thermochromic colorants are commercially available with various activation temperatures, from 15 to 65 °C, but most applications are limited to three standard temperature ranges, namely cold (ca. 10 °C), body-heat activated (ca. 31 °C) and warm (ca. 43 °C).

□ LEUCO dyes as THERMOCHROMIC system

- ✓ Leuco-dyes having a thermochromic properties are used in thermochromic formulations that incorporate three-component systems which contain a color former (leuco-dye) and frequently used developers (typically weak acids such as bisphenol A, gallates, phenols, hydroxybenzoates and hydroxycoumarin derivatives) in a low-melting solvent (such as methyl stearate). The melting point of the solvent controls the temperature at which the color of the three-phase composite forms.
- ✓ While several polar solvents have been reported to be suitable for thermochromic changes, alcohols and esters are preferred. When the three-component mixtures outlined above are heated together in the controlled proportions and the color formers and developers are dissolved in the low-melting co-solvent, the solution changes its color when it is cooled. Thus, the stimulation of the thermochromic effect is mainly dependent on the design of the system upon warming and cooling.
- ✓ These types of functional dyes in the solid state undergo a ring-opening reaction and give rise to a striking color change when they come in contact with an acid, and these changes are reversible with the change in temperature.

T.C + Extender	Yellow pigment + extender	Result Color at ambient temperature For 27°C ink	Result Color at ambient temperature For 15°C ink
99 % + 1 %	4 % + 96 %		
75 % + 25 %	4 % + 96 %		
50 % + 50 %	4 % + 96 %		
25 % + 75 %	4 % + 96 %		
10 % + 90 %	4 % + 96 %		
1 % + 99 %	4 % + 96 %		

- ✓ At higher temperature, the co-solvent melts, and the interaction between the co-solvent and the developer becomes dominant. The dye and developer no longer interact strongly so that the composite loses its colour. The melting point of the co-solvent controls the temperature at which decoloration/coloration occurs and is usually denoted by the activation temperature (TA).
- ✓ The colour former and its relation with the electron-accepting colour developer defines the position of the longest wavelength absorption which causes coloration/decoloration. The temperature at which decoloration/coloration occurs is controlled by the melting temperature of the co-solvent.



- ✓ The colour of the composite changes according to the competitive interactions not only between the dye and developer but also the co-solvent and the developer. Initially, at low temperature, the co-solvent is in solid form, leading to strong interaction between colour former and colour developer, which results in the composite being coloured.
- ✓ So these systems involve changes in the phase between colored solid and colorless liquid phases.



<https://etextile-summercamp.org/2017/summerof/wed-designing-and-printing-with-thermochromic-pigments/>

□ LIQUID CRYSTALS as THERMOCHROMIC system

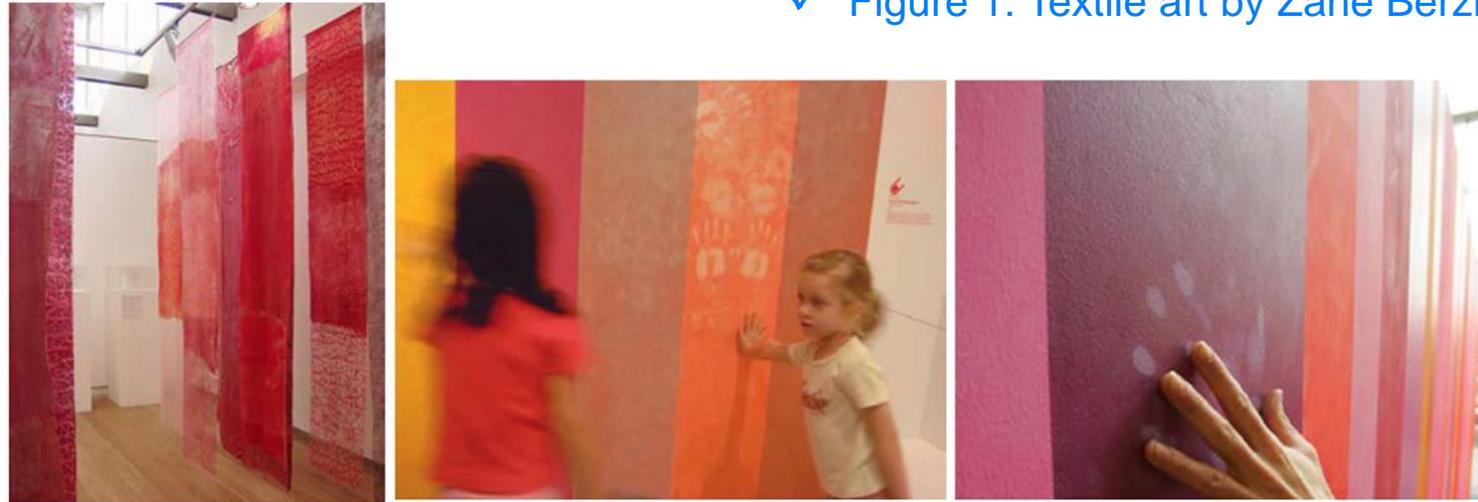
- ✓ Since the application of thermochromic systems based on leuco dyes is much more widespread and the possibilities of application are much more diverse, and the application of thermochromic systems based on leuco dyes is dominant in textiles, for liquid crystals as thermochromic systems is given only a brief overview.
- ✓ Thermochromic liquid crystals (TLC) demonstrate a colour change as the temperature is raised through a continuous colour spectrum of the rainbow. The liquid crystals should preferably be printed on a black background to provide more intense colour reactions. A structural feature of the liquid crystal, referred to as the pitch length, varies in relation to temperature, and causes the colour play to alter when the liquid crystals are heated. The relation between temperature and pitch length is nonlinear, meaning that the time specific colours that are displayed differs as the liquid crystals are heated steadily.
- ✓ Liquid crystals are highly anisotropic fluids that exist between the boundaries of the solid phase and the conventional, isotropic liquid phase.
- ✓ The TLC based temperature visualisation is based on the property of some cholesteric and chiral-nematic liquid crystal materials to reflect definite colours at specific temperatures and viewing angle.



- ✓ The colour change for the TLC ranges from clear at ambient temperature, through red as temperature increases and then to yellow, green, blue and violet before turning colourless (isotropic) again at a higher temperature. They appear colourless above and below the active range.
 - ✓ The colour-temperature play interval depends on the TLC composition. It can be selected for the bands of about 0.5 °C to 20 °C, and working temperature of –30 °C to above 120 °C. These colour changes are repeatable and reversible as long as the TLC's are not physically or chemically damaged. The response time of TLC's equals about 10 ms. It is short enough for typical thermal problems in fluids. Since the colour change is reversible and repeatable, they can be calibrated accurately with a proper care and used in this way as temperature indicators.
- A few examples of using the TLC thermochromic system in textile and design application can be given:
- ✓ Figure 1: Textile art by Zane Berzina „Skin Wallpaper”
 - ✓ Figure 2: Sara Robertson „Textiles printed with liquid crystal”



✓ Figure 1: Textile art by Zane Berzina „Skin Wallpaper”



✓ Figure 2: Sara Robertson „Textiles printed with liquid crystal”

