DENIM ACADEMY BOOKS

# INDIGO

Denim is a firm, durable, twilled fabric that is produced by cross-weaving of coloured warp and white weft yarns. The most important feature of denim fabric is the vintage look created by abrasion or different kinds of finishing applications. The mere reason for this special look is magical ‘’Indigo’’ which the warp yarns are dyed with.

# DYE STUFFS

## Reactive Dyes

RDS are highly soluble in water. Under certain  conditions, it has tendency to react with the fibre to dye. The medium must be alkaline for dyeing process. After dyeing process, steam fixation is crucial so that dyestuff and fibre can be fixed together.  The typical characteristics of RDS are having a wide range of color spectrum, bright shades and good fastness properties.

DENIM ACADEMY

## Indathren Dyes

These dyes are insoluble in water and have very poor affinity to fibre. Some chemical reactions should take place in order that the dyestuff can become activated. The reaction, called as ‘’Reduction’’, between dyestuff and hydrosulfite occurs in alkaline medium. After dyeing process, dyestuff should be oxidized in order to be fixed on the fibre. Because of this feature, indanthren dyes are classified as vat dye. Most important characteristic of indanthren dyes is having very good fastness properties.

## Sulphur Dyes

Has high molecular structures and contains sulphur inside. As a principle, these are similar to vat dyes. With a reducing agent, it converts to soluble form and then with an oxidizing agent it returns to initial insoluble form.  Dyestuff is fixed on the yarn or fabric with steam application.

**Fastness:** The resistance of fabric to the action of external influences, such as light, washing, crocking, perspiration, acids, alkalies, etc.
**Vat Dye:** These dyes are insoluble in water. They need to be reduced to be able to dye.

## Fastness Comparison of Dyestuffs

| | WASHING | LIGHT | PERSPIRATION | CROCKING |
|---|---|---|---|---|
| INDANTHREN | Good | Very Good | Good | Good |
| SULPHUR | Fair | Good | Good | Poor |
| REACTIVE | Good | Good | Good | Good |
| INDIGO | Poor | Fair | Good | Poor |

**Table 1. Fastness Comparison**





# Indigo DyeStuff

## Indigo Plant

Indigo plant, named as ‘’Indigofera tinctoria‘’ , is discovered around 1600s (B.C.). Indigo dyestuff, extracted from its leaves, had been used in various primitive dyeing processes for years. In 1880’s, the first synthetical (unnatural) indigo dye was developed by German chemist Adolf von Baeyer. He has identified the chemical structure of indigo. After 1900s, synthetic indigo was marketed. This has triggered off the indigo dyeing developments as a result of improvement in denimwear.

In ancient years, indigo dyestuff was fermantated in wooden vats. This process which’s called as ‘’vatting’’, is supposed to be the origin of vat dyes.

**Picture 1. Indigo Plant/ Indigo Tinctoria**

## PROPERTIES OF INDIGO DYESTUFF

Indigo dyestuff which is classified as vat dye, is insoluble in water and has no affinity to the fibre. They have poor washing fastness which lets the color of denim fabric to change naturally. Indigo creates living colours on fabrics.

Indigo dyestuff can never fully penetrate into the fibre since its molecule is so big and it only adheres to the surface and remains at outer surface of the fibre. The inside stays white. It abrades or fades continually. This character of indigo lets denim fabric to have its final look with different types of washing and finishing applications. It enables denim fabric to response to finishing applications that gives a real life to the fabric.

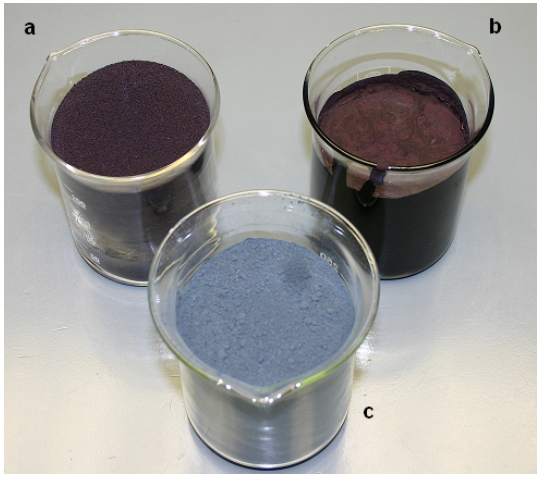
Indigo dyestuff should be classified into two different chemical forms :

1. Natural form, insoluble in water (cannot dye the fibre)
2. Leuco form, soluble in water (can dye the fibre)

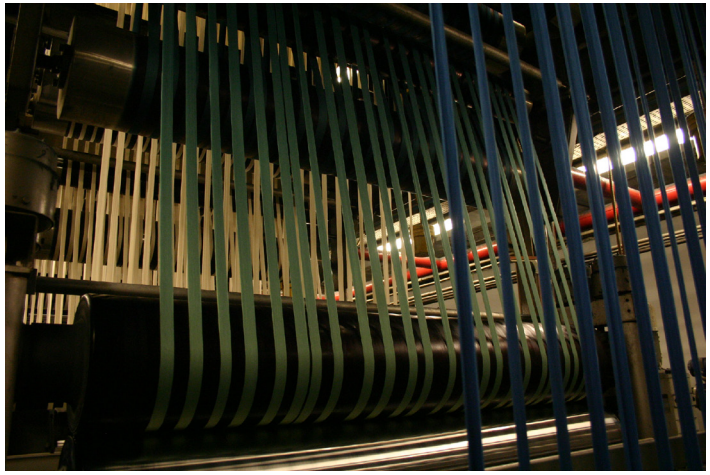
DENIM ACADEMY ORTA ANADOLU DENIM EDUCATION PROGRAM

In natural form, indigo dyestuff has a color of blue but after reduced to leuco form, the color of the solution turns to yellow.






**Picture 2. Indigo forms: (a)Synthetic indigo granules (b)- Liquid indigo (c) Natural indigo**



**Picture 3. Indigo changing colour when exposed to air**

## What is reduction-oxidation?

In order that indigo is able to dye the fibre, it needs to be activated (leuco-form). In other words, indigo should be converted into soluble form and the affinity to fibre should be increased. Some chemical reactions are necessary for converting indigo to leuco form. These reactions are called ‘’ reduction’’. Reduction takes place in certain conditions with the presence of hydrosulfite in alkaline medium. To keep the solution alkaline ( basic), caustic ( NaOH ) is used. After reducing and dyeing, dyed ropes have to be aerated so that the dye and fibre can be fixed together. This process is called ‘’ oxidation’’.

CHEMICAL REACTIONS

Reduction in indigo dye pad :

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| C16H10O2N2 | + | Na2SO4 | + | NaOH | = | C16H10O2N2Na2 | + | NaSO3 | + | 2H2O |
| Indigo | | Hydro | | Caustic | | Indigo | | Leuco | | |

Oxidation with aeration :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C16H10O2N2Na2 | + | ½ O2 | + | H2O | = | C16H10O2N2 | + | 2 NaOH |
| Indigo leuco | | Aera-tion | | | | Indigo | | Caustic |

Ancak indirgenmiş, leuco formdaki indigo’nun dahi, elyafa karşı **afinitesi** düşüktür. Bu nedenle boyama fazla sayıda tekneye daldırma ve boyama işleminin tekrarlanması ile mümkün olabilir. İndigo boyama prosesinin özelliği de buradan gelmektedir.

**Vatting**: It’s the chemical reduction process which is the origin of vat dyes.
**Penetrasyon:** It’s the ability of dyestuff to diffuse or get into fibre.
**Affinity:** The attraction or force between dyestuff and fibre that causes them to combine.

# DYEING PROCESSES

# Pad Dry Pad Steam

This process can be performed with reactive, indanthren and pigment dyestuff and has 4 main steps. At first step, dyestuff and auxilary chemicals are fed into the dye pad and fabric picks up the dyestuff on itself. Second step is drying. After drying, fabric goes into the chemical pad at third step. Finally, dyestuff gets fixed on the fabric at the steamer. The amount of feeding and auxilary chemicals might be changed according to the dyestuff used.

# Pad Steam

This process is performed with sulphur dye. “Pad – Steam” which’s a part of PDPS dyeing method is used for this process. Fabric picks up chemicals and dyestuff from the same pad and goes to the steamer for fixation.

DENIM ACADEMY

# Indigo Dyeing Process

## Indigo dyeing methods

Indigo dyeing is built on “continuous warp dying”. Basically there are 2 main methods of indigo dyeing.

1. **Classic method**: beaming, dyeing the warp yarns in rope form, rebeaming and sizing
2. **Open-width method**: Warp yarns are dyed and sized respectively

## Indigo dyeing technologies.

1. **Rope dyeing:** This is the oldest way to dye warp yarns (ropes) and does not have any risk concerning “side to side” problem. Moreover, dyestuff absorption is almost the same since that all the ropes have the same tension during the process.

2. **Loop Dyeing:** Warp yarns are dipped into the unique pad many times.

3. **Slasher Dyeing:** Warp yarns are dyed as open-width form and dyeing, drying, sizing processes are performed in the same machine continously.

**Advantage of Rope Dyeing against Slasher Dyeing**:

- Large quantities can be dyed continuously
- In rope dyeing, ropes are dipped into the dye pads with identical tension and angle, therefore there's not any risk of "side to side" problem.
- Dyeing machine does not have to stop while feeding new dyeing parties which means energy saving.
- Yarn wastage is not that much.

Orta Anadolu uses "Rope Dyeing" process.



## Indigo Dyeing Machinery

There are 4 continuous rope dyeing machines in Orta Anadolu. Additionally, there is a sample dyeing machine designed by Morrison exclusively for Orta .

Average capacity of indigo dyeing machines are 40000 – 50,000 mts/day

## Dyeing Process

1. Bottom Dyeing: Pre-process pads are used as dye-pads which "Bottom Dyestuff" can be reactive, sulphur or indanthren. This process needs different equipments.
2. Pure indigo dyeing: According to the desired color, number of the dye pads can be adjusted.
3. Sulphur Dyeing
4. Reactive Dyeing

5. Indanthren Dyeing
6. Topping Dyeing: As soon as ropes dip into indigo dye pads, they are sunk into another dye pad, which can be reactive, sulphur or indanthren.

Indigo Dyeing Machine has 3 main parts:

1. Pre-Process pads
2. Dyeing Pads
3. Washing Pads

## Indigo dyeing process flow

**1. Pre-Processes: (Pre-process pads)**

According to the desired final look and dyeing properties, pre-wetting, bottom dyeing or washing can be achieved as a pre-process. Pre-Wetting helps to increase the affinity of the warp yarn to the dyestuff . Bottom dyeing is needed to get different casts using reactive, indanthren or sulphur dyestuffs. Washing After bottom dyeing process, ropes should be washed in order to remove excess dyestuff unfixed from the warp (rope). This is crucial for optimum crocking values. Pre-wetted ropes are ready to be dipped into dye pads. Dipping and aerating (oxidizing) are repeated until required cast is achieved.

**2. Dyeing Process (Dye pads)**

Affinity of indigo dyestuff is still not sufficient after reduction. Thus, indigo dyeing process is based on repeated dipping and aeration. Dyeing machines are designed taking this point into consideration. That's why they have more than one dye pad. Basically, ropes continously take the dyestuff from the pads and are fixed thanks to air reaction.

Indigo dyeing has 3 important parameters :

- Indigo
- Hydrosulfite ( used as reduction agent )
- Caustic ( to keep the pH of the bath as alkaline)

These chemicals must be fed at sufficient ratio consistently. Dye pads are supported by an internal circulation system.

The amount of chemicals to be fed must be constant during the process in order to avoid indigo - hydro concentration and pH value differences. This circulation system eliminates possible shade differences on fabric.

**What's ring dyeing?**

As already known, indigo dyed ropes (warp yarns) have an ecru core and its outer layer is dyed. This is called "ring-dyeing". The ring-dyeing property of a rope is determined by pH value and hydro concentration. The penetration of dyestuff into fibre in a dye bath having 11.5 pH is not good. When pH value shifts towards 13.0, in other words increases, penetration gets better; dyestuff can better penetrate into fibre core, that's to say, ring dyeing efficiency drops. This drastic drop affects fabric-washing properties.

Efficiently ring - dyed fabrics would respond washing (finishing) better and faster. These parameters have been adjusted according to end-product properties.

The rope turns yellow-green colour when first dipped into indigo bath. It turns to magic indigo blue as soon as it reacts with air. This legendary colour change is really worthwhile.



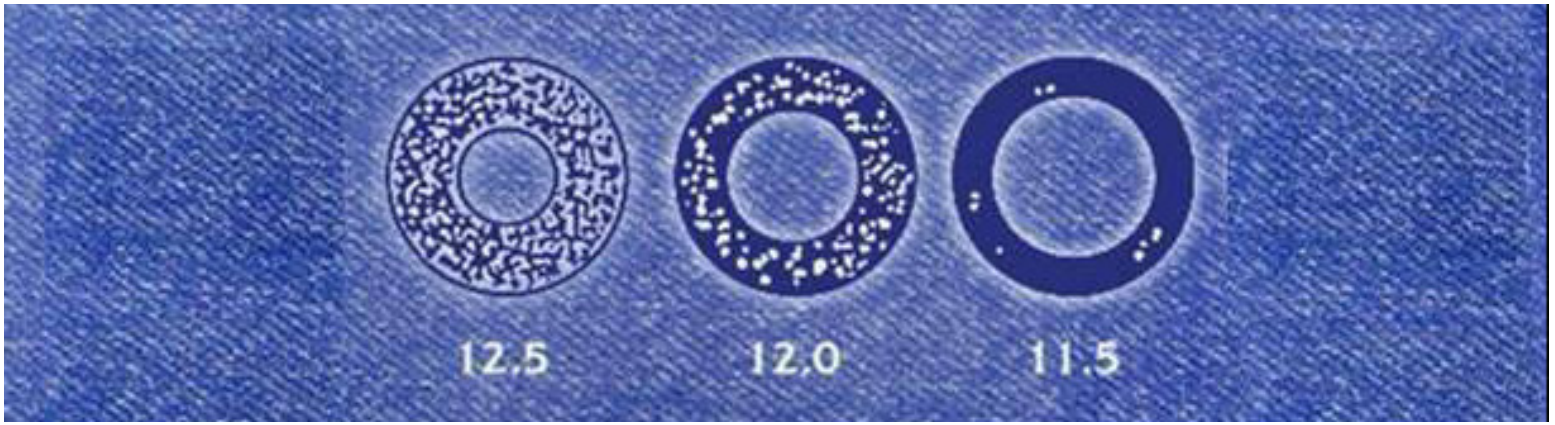
**Washing and Drying of Ropes (Washing pads and drying cylinders)**

After iterative numbers of dipping, ropes follow washing pads in order to remove unfixed indigo dyestuff. Besides, this step has a neutralization effect, as pH value needs to be lowered because of high pH environment during dyeing process.
This step is completed reaching sufficient humidity with the help of steamed drying cylinders. Sufficient humidity ratio is important for the efficiency of re-beaming of ropes after dyeing.

# Main parameters of indigo dyeing

- Reduced indigo concentration: Effective on colour depth and darkness.
- Hydro concentration: It is the chemical that helps reduction of indigo dyestuff. Since reduced indigo has strong decomposition tendency, there must be excess hyro in dye bath. The preservation of reduced form is accomplished by excess hydro. Therefore, the control of hydro concentration in dye bath solution has great importance. The amount of hydro is effective on penetration of indigo dyestuff into fiber.
- pH (the alkality of solution) : The typical feature of indigo dyestuff is that pH should be higher than 11,5. The best dyeing is achieved between 11,5-12,5 pH. The penetration increases when pH is increased, darker and consistent shades can be obtained. Therefore, the response to stone-washing gets more difficult.

- Number of dye pads: is effective on shade depth.
- The speed of machine is effective on following parameters:
    1. Dipping time
    2. Penetration
    3. Oxidation (airing) time
- Pressure (Nip) rollers are effective on below parameters:
    1. The amount of dyestuff picked up
    1. Penetration




**Picture 4. Penetration of indigo dyestuff on different pH levels**

**Below are the important parameters and their effects to get consistent and reproducable dyeing:**

| PARAMETER | VARIATION | EFFECTfv |
|---|---|---|
| The amount of reduced indigo | Increase | Shade depth increases |
| | Decrase | Shade depth decreases |
| Concentration of caustic | Increase | pH increases, dye penetration increases, shade gets reddish, brightness seen. |
| | Decrase | PH decrease, ring effect increases, easy to stone wash, dullness seen |
| Concentration of Hydrosulphite | Increase | Penetration increases, shade getting lighter and bluer, proper dyeing getting harder |
| | Decrase | Insufficient indigo reduction, unfixed dye on surface, shade gets reddish |
| Dipping time | Increase | Penetration and shade depth increases, difficult to stone wash |
| | Decrase | Shade depth decreases, ring effect increases, easy to stone wash. |
| Number of dye pads | Increase | Shade depth increases. |

**Table 2. Effects of the parameters**

# Process Control

## Foxboro Automation System

Foxboro automation is a system used to control various and countless process data in indigo dyeing. The system is designed to check every individual step in process and alert in case of any disorder. The set values are loaded into system according to a certain dyeing recipe. If there's any remarkable difference between preset and present values, system alerts by an alarm signal and necessary precautions are taken.

Example: Feeding valves are opened/closed, amount increased/decreased etc.

## Tests

It's vital to control amount of dyestuff and chemicals in dye pads during dyeing process. Especially, the most important parameters which are indigo-hydro concentration and pH value are hourly tested by sampling. In case of any remarkable change, necessary precautions are taken. Thus, the differentiation of process parameters and potential head-tail problem are minimised.



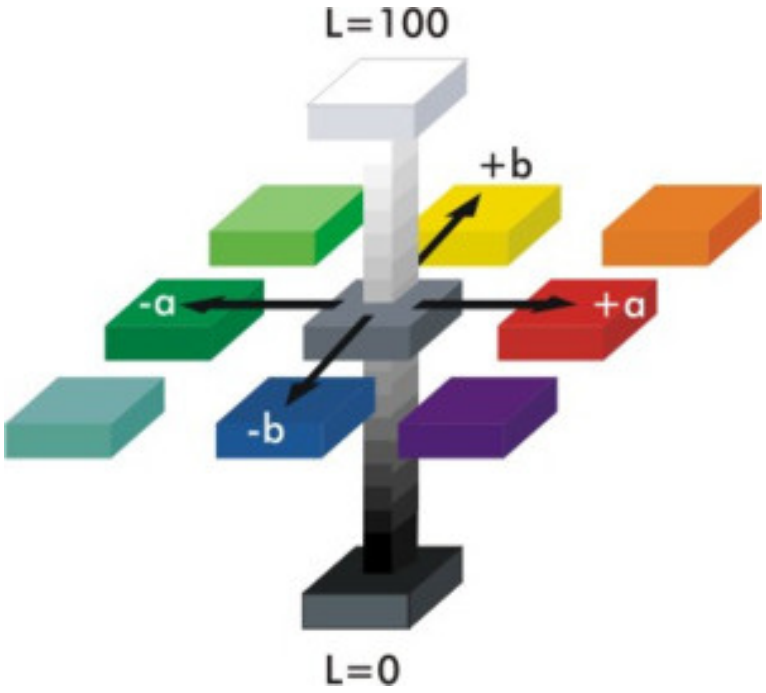
# Shadeband

The raw material of denim fabric is mostly cotton or cotton blends where cotton is a natural fibre.Natural fibres are impacted by various external factors like climate and contaminations which will directly cause different maturity levels and relatively a slight colour range by means of whiteness and yellowness.
Maturity differences generate variation in dye absorption capabilities and therefore shade differences. This in combination with the generic process parameter variation throughout the fabric manufacturing process generates a shadeband.

Hunter Lab is a computer supported system, which defines color mathematically in an oversensitive way .

Colour is characterized by three parameters in space ; **L,a,b**.

**L : lightness – darkness**
**a : greenness – redness**
**b : blueness – grayness ( brightness – dullness )**




**Picture 5. Hunter Lab Renk Diagram**

Master colour is defined as 555 with these 3 parameters. Since ”a” value is negligible in indigo dyeing, 55 system is taken into consideration.

Master colour of an article can be defined as the target colour representing the production best which's approved and agreed upon by the costumer.  In Orta Anadolu, 90 % of any production lot must be in an acceptable shade range.

Important points about shadeband :

- It is impossible that all production lots can be shade 55 pratically. Each production has an acceptable shade band.
- Each and every Orta quality has a standart shipment recipe. Shade is evaluated based on this recipe both for control of shipment and production.
- Each shipment lot is evaluted seperately. Any roll that belongs to a certain shade group may be denominated as another shade group in a different shipment. If shipment recipe changes, the shadeband has completely changed.

DENIM ACADEMY

# Pre-Blanket / Production Control

The difficulty in indigo dyeing process is that the final look can be seen after fabric washing/stoning. Thus, it is hard to determine the colour on ropes.

In order to control the production;

- Each weaving beam is sampled.
- A blanket including master roll swatch is sewn and washed with the recipe of relevant article. It is called pre-blanket.
- After washing, the samples are measured in Hunter Lab, compared to master roll.
- Furthermore, rolls are evaluated visually. Precautions are taken, if needed.

DENIM ACADEMY

ORTA ANADOLU DENIM EDUCATION PROGRAM