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THE pH EFFECTS ON THE AFFINITY OF DIFFERENT FORMS OF LEUCO IN INDIGO DYEING OF COTTON DENIM WARP YARN

Franco Corbani

TRC - Tessitura Robecchetto Candiani SpA - Dyeing Department

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1. INTRODUCTION

Indigo is one of the oldest known textile dyes in the world. In fact this was the firts naturally dye occurring blue colorant discovered by primitive man.

Today, the indigo used in commercial dyeing of denim yarn is no longer of natural origin. In 1880 Adolf von Baeyer (Nobel 1905) discovered the structural formula of indigo and a method of laboratory synthesis and in 1897 BASF (K. Heumann synthesis) introduced on the market the first commercial form of synthetic indigo which gradually replaced the natural dye.

Characteristics of indigo

Is a vat dye (C.I. Vat Blue 1), which in its solid blue pigment form is practically insoluble in water, with non substantivity for cellulosic fibres. To enable cellulosic dyeing, indigo is reduced to acid leuco indigo form, slightly soluble in water and has limited substantivity for cellulosic fibers.

Adding alkali we obtain alkaline leuco indigo (C.I. Reduced Vat Blue 1), which is soluble in water and it is the effective dyeing agent, having low substantivity for cellulosic fibers.

The warp yarn is wetted or predyed with sulfur dyes and, after passed through squeezing rollers, it enters into the firts dyeing dyebath compartment, at 38°-40°C for a short contact time. After squeezing the leuco indigo adsorbed in the fibers it is oxidized "*in situ*", by exposing the yarn to the oxygen of the air, into its original insoluble blue pigment form.

Due to the low substantivity of leuco indigo for cellulosic fibers, the yarn is dyed through successive dye bath compartments in indigo range, whose number can be six or more separate dye bath compartments, to achieve the required shade.

Yarn denim is dyed in two types of continuous dyeing plant: Rope and Slasher Dyeing.

Figure 1

Example of Indigo Slasher Plant*
(Figure 1 and 2)

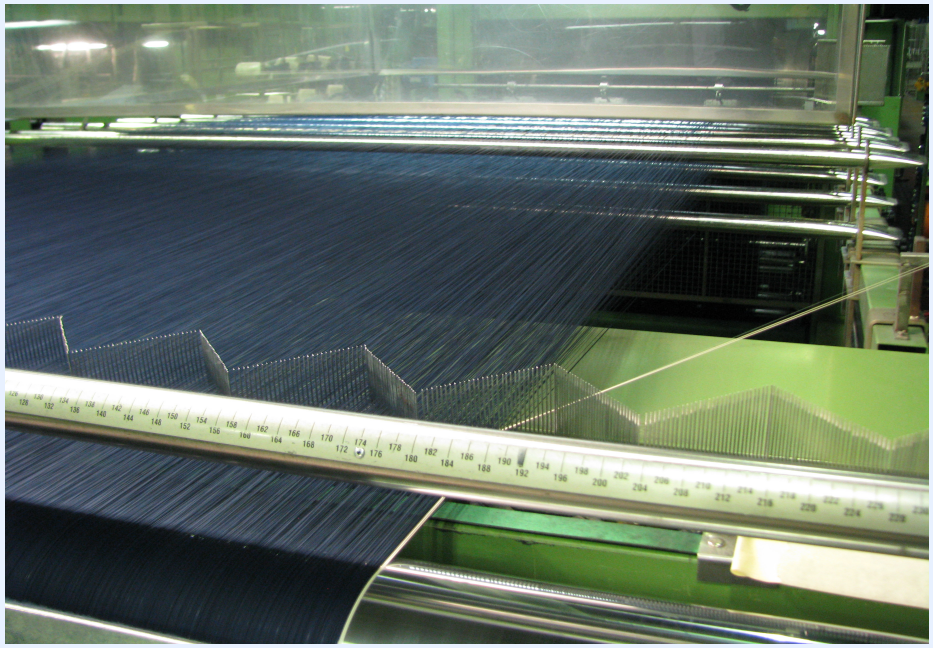


Figure 2

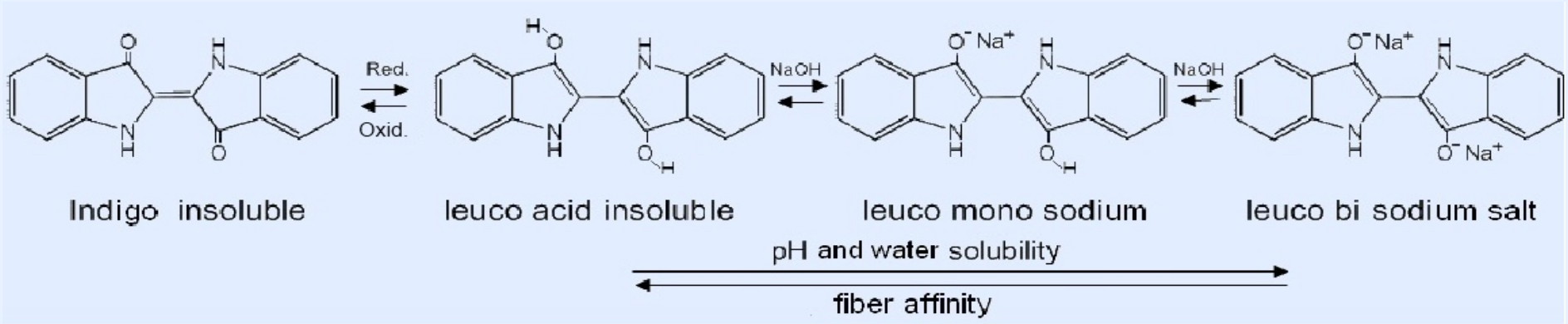
Indigo dye warp yarn

* MASTER – Macherio (Mi) - Italy

IN MY PRESENTATION I WISH TO SHOW YOU HOW STARTING FROM THE EQUILIBRIUM DISSOCIATION OF THE INDIGO REDUCED FORM, WE CAN CALCULATE THE RESPECTIVE UNIT FRACTIONS; ADJUSTING THE pH, IT IS POSSIBLE TO DERIVE THREE CURVES OF THE LEUCO DERIVATIVES, WHICH REPRESENT THE DYEING PHENOMENON AND CONTROL THE CORTICAL/ PENETRATION OF THE DYE IN THE CROSS-SECTION OF THE YARN.

Importance of pH in the behavior of the leuco

Indigo can exist in four forms, one of these is insoluble in water (blue oxidized form), whereas the three others reduced forms: leuco acid, mono sodium and bi sodium leuco indigo salts, are in dynamic equilibrium with each other and have different solubility (yellow form):

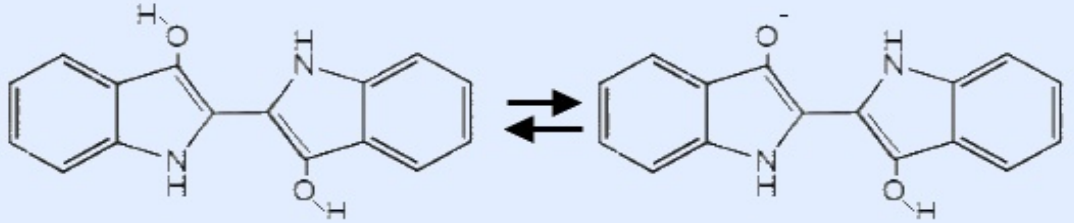


The three reduced forms are the subject of this work.

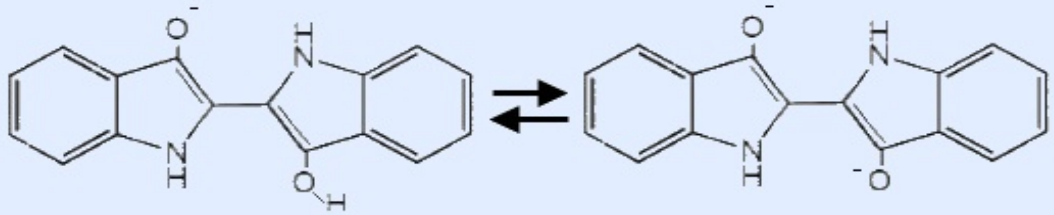
2. CALCULATION OF UNIT FRACTIONS OF THE FORMS: LEUCO ACID (A), MONO SODIUM (M) AND BI SODIUM (B) SALTS.

Regards the three dissociation equilibriums:

- equilibrium dissociation of the leuco acid form to mono dissociated leuco indigo form:

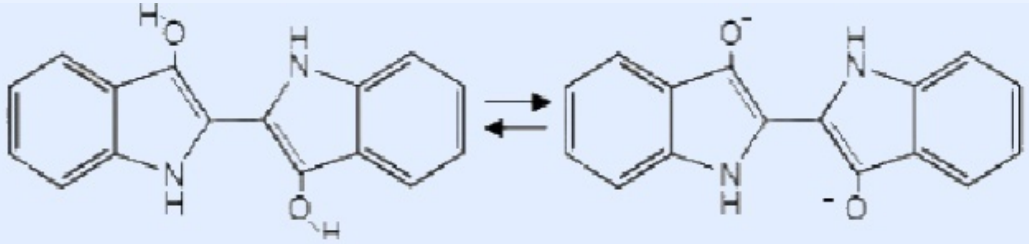
1)  $+ H^+$ $K_1 = [M] . [H^+] / [A]$

- equilibrium dissociation of the leuco mono dissociated form to bi dissociated leuco indigo form:

2)  $+ H^+$ $K_2 = [B] . [H^+] / [M]$

The equilibrium dissociation of the acid leuco form to the bi dissociated leuco indigo form:

3)



leuco acid

leuco bi sodium

$+ 2H^+$

$K_1 . K_2 = [B] . [H^+]^2 / [A]$

The unit fractions of each species of the three forms of leucoindigo (A, M, B).

The fractional amount of leuco acid (A), mono sodium (M) and bi sodium form (B) salts, that are present at a given pH, can be calculated using the pK_a values of each form (pK_a is the negative logarithm of the equilibrium ionization constants and pK_1 , pK_2 represent respectively the firts and second ionization step from acid leuco indigo to the mono e bi sodium forms).

The fractional amount of leuco acid (A) is: $[A] / [A] + [M] + [B]$

The fractional amount of mono sodium leuco salt (M) is: $[M] / [A] + [M] + [B]$

The fractional amount of bi sodium leuco salt (B) is: $[B] / [A] + [M] + [B]$

(Where [A], [M] and [B] indicate the concentrations (mol/l) of the three leuco forms and their sum is equal to 1)

Applying the equilibriums 1), 2) and 3) to the fractional amount indicated above, we optain the equations of the three leuco indigo forms, using the pK_1 and pK_2 values, over the alkaline pH range:

$$\frac{1}{1 + 10^{(pH - pK_1)} + 10^{(2pH - pK_1 - pK_2)}} = \text{fractional amount of leuco indigo acid form}$$

$$\frac{1}{1 + 10^{(pK_1 - pH)} + 10^{(pH - pK_2)}} = \text{fractional amount of leuco indigo mono sodium form}$$

$$\frac{1}{1 + 10^{(pK_1 + pK_2 - 2pH)} + 10^{(pK_2 - pH)}} = \text{fractional amount of leuco indigo bi sodium form}$$

Calculation of the fractional value of each reduced species of indigo found in dye bath as a function of pH

Knowing the values of:

$pK_1 = -\log K_1 = 7{,}97^*$ and

$pK_2 = -\log K_2 = 12{,}68^*$

we calculate the values of the fraction of each leuco indigo specie in relation to the changes in the dyebath pH (see Table 1 and Fgure 3).

Table 1

pH	Leuco acid	Leuco monosodium	Leuco bisodium
7	1	0	0
7,25	0,99	0,01	0
7,5	0,99	0,01	0
7,75	0,98	0,02	0
8	0,97	0,03	0
8,25	0,95	0,05	0
8,5	0,91	0,09	0
8,75	0,85	0,15	0
9	0,76	0,24	0
9,25	0,64	0,36	0
9,5	0,5	0,5	0
9,75	0,36	0,64	0
10	0,24	0,76	0
10,25	0,15	0,85	0
10,5	0,09	0,9	0,01
10,75	0,05	0,94	0,01
11	0,03	0,95	0,02
11,25	0,02	0,95	0,03
11,5	0,01	0,93	0,06
11,75	0,01	0,89	0,1
12	0	0,83	0,17
12,25	0	0,74	0,26
12,5	0	0,61	0,39
12,75	0	0,47	0,53
13	0	0,33	0,67
13,25	0	0,22	0,78
13,5	0	0,14	0,86
13,75	0	0,08	0,92
14	0	0,05	0,95

* J. N. Etters, J.S.D.C., **109** (1993) 251
* Richard S. Blackburn, Thomas Bechtold, Philip John, J.S.D.C., Color Technol. **125** (2009) 193-207

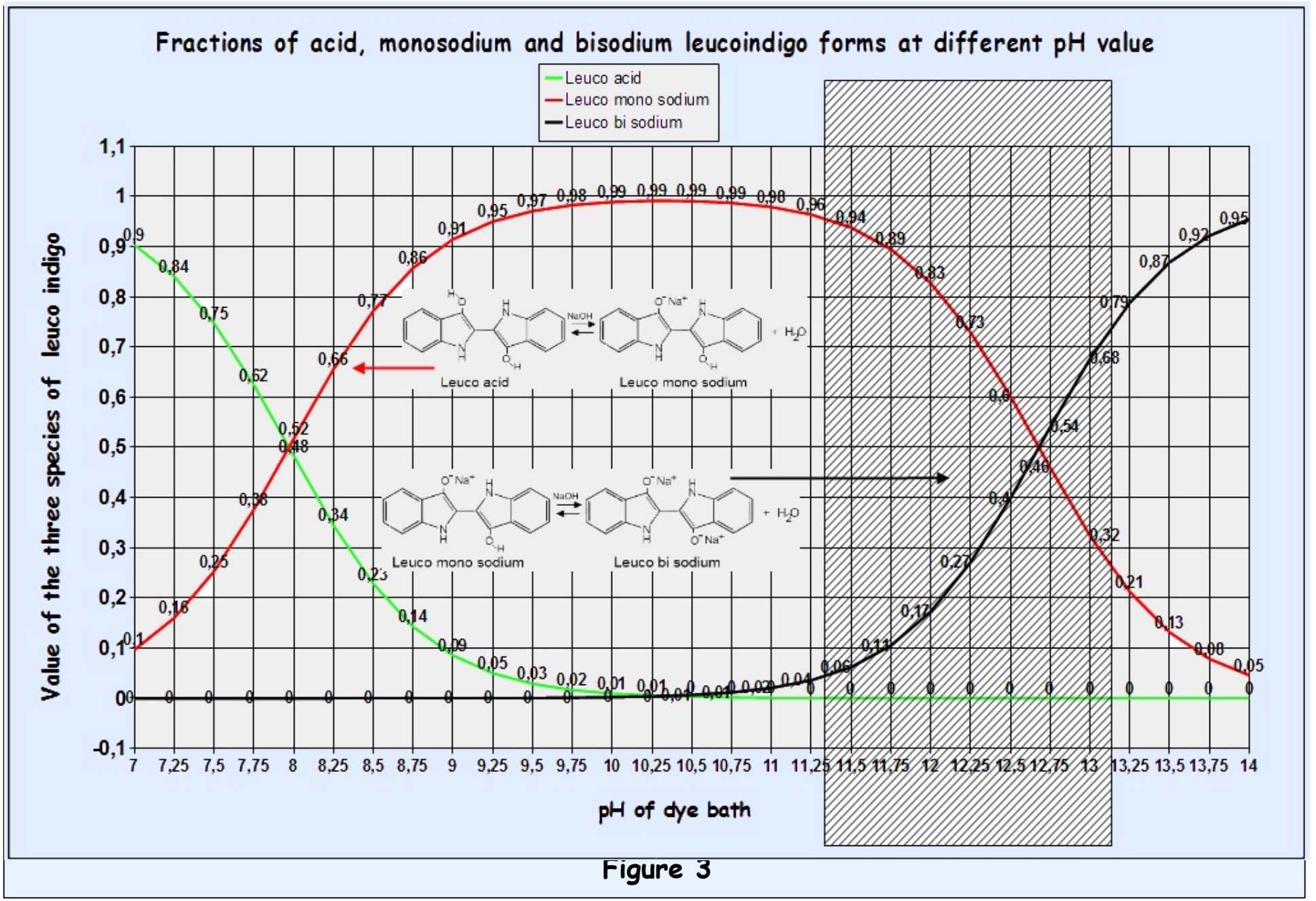

Fractions of acid, monosodium and bisodium leucoindigo forms at different pH value
Leuco acid
Leuco mono sodium
Leuco bi sodium
Value of the three species of leuco indigo
pH of dye bath
Leuco acid
Leuco mono sodium
Leuco mono sodium
Leuco bi sodium

Figure 3

And now see more of the optimum pH range.

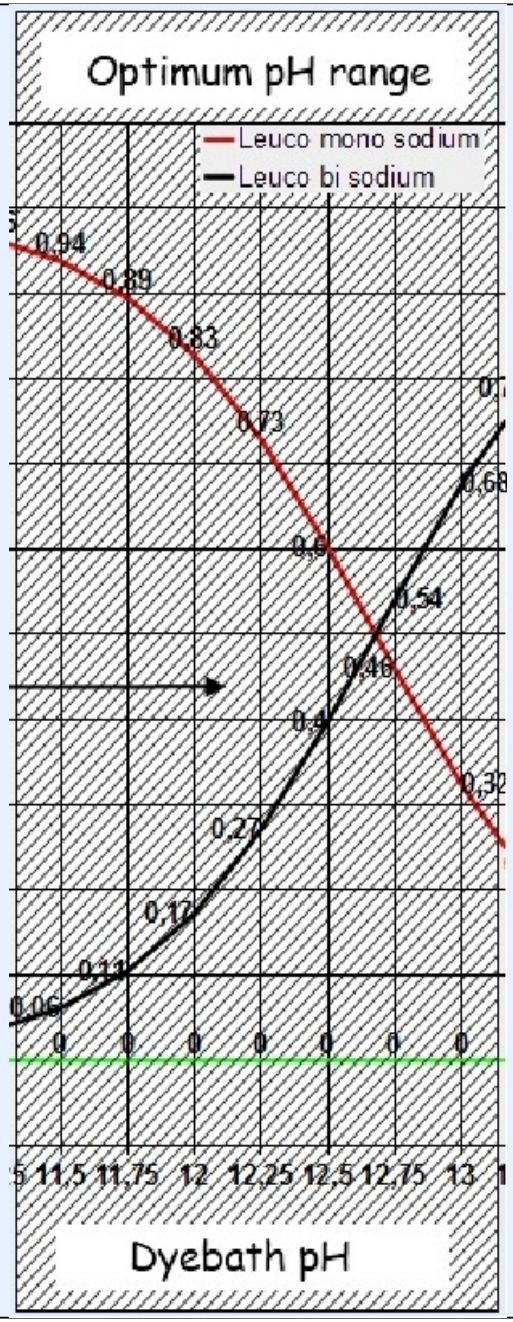


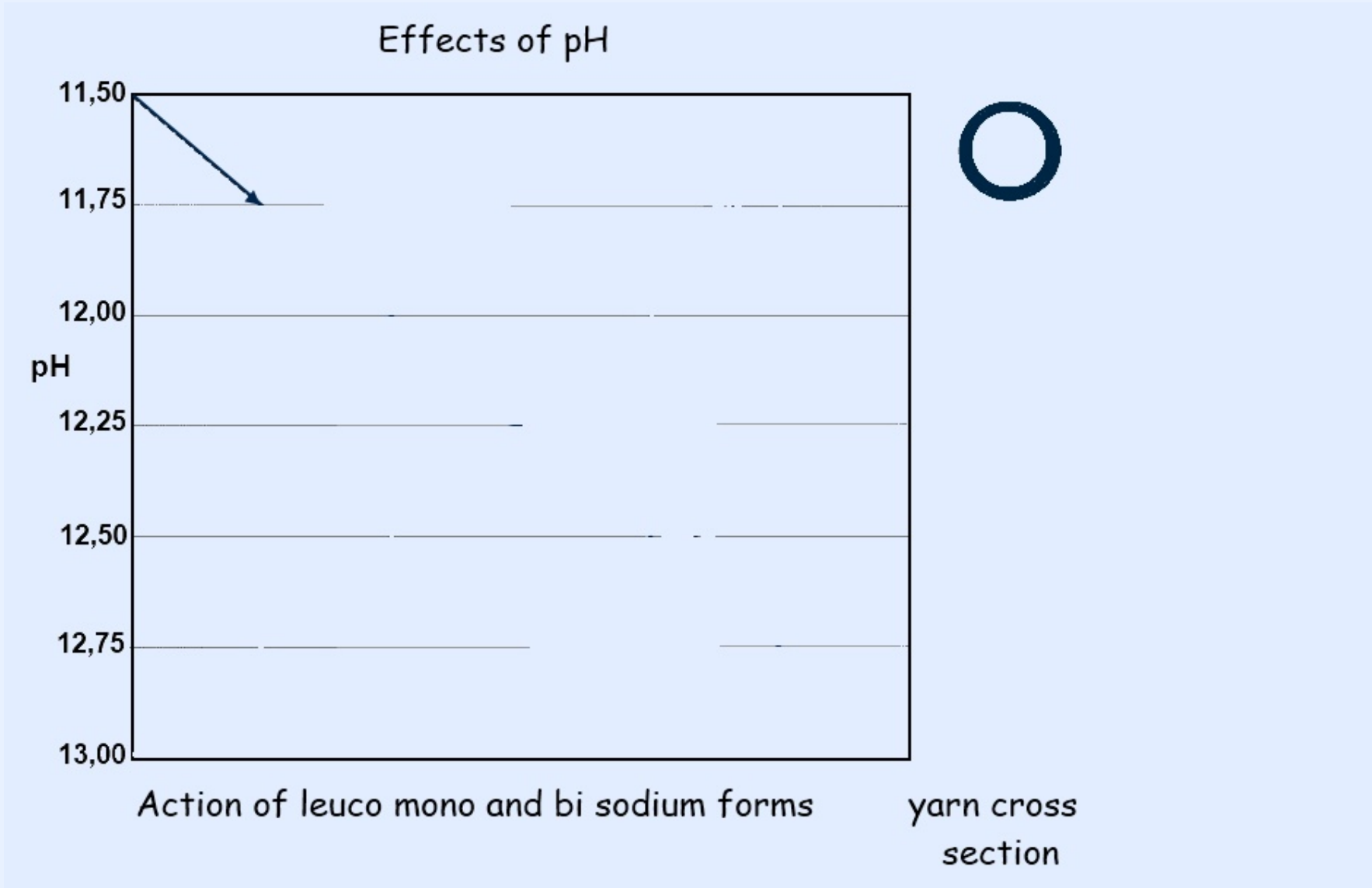
Figure 4 - Fractions of mono sodium and bi sodium leuco indigo forms in the range between 11,5-13 pH.

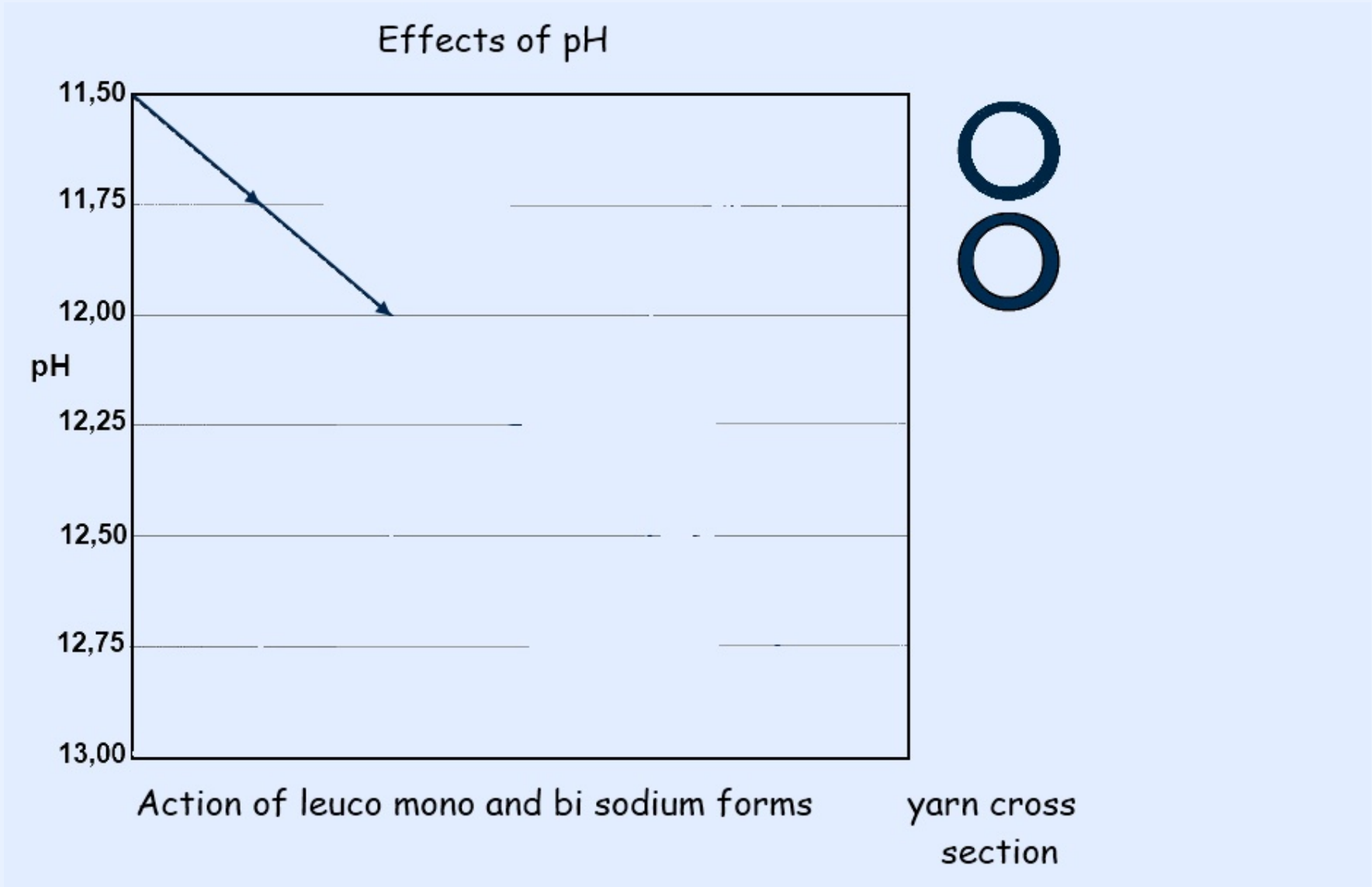
3. AFFINITY OF THE MONO SODIUM AND BI SODIUM LEUCO INDIGO FORMS

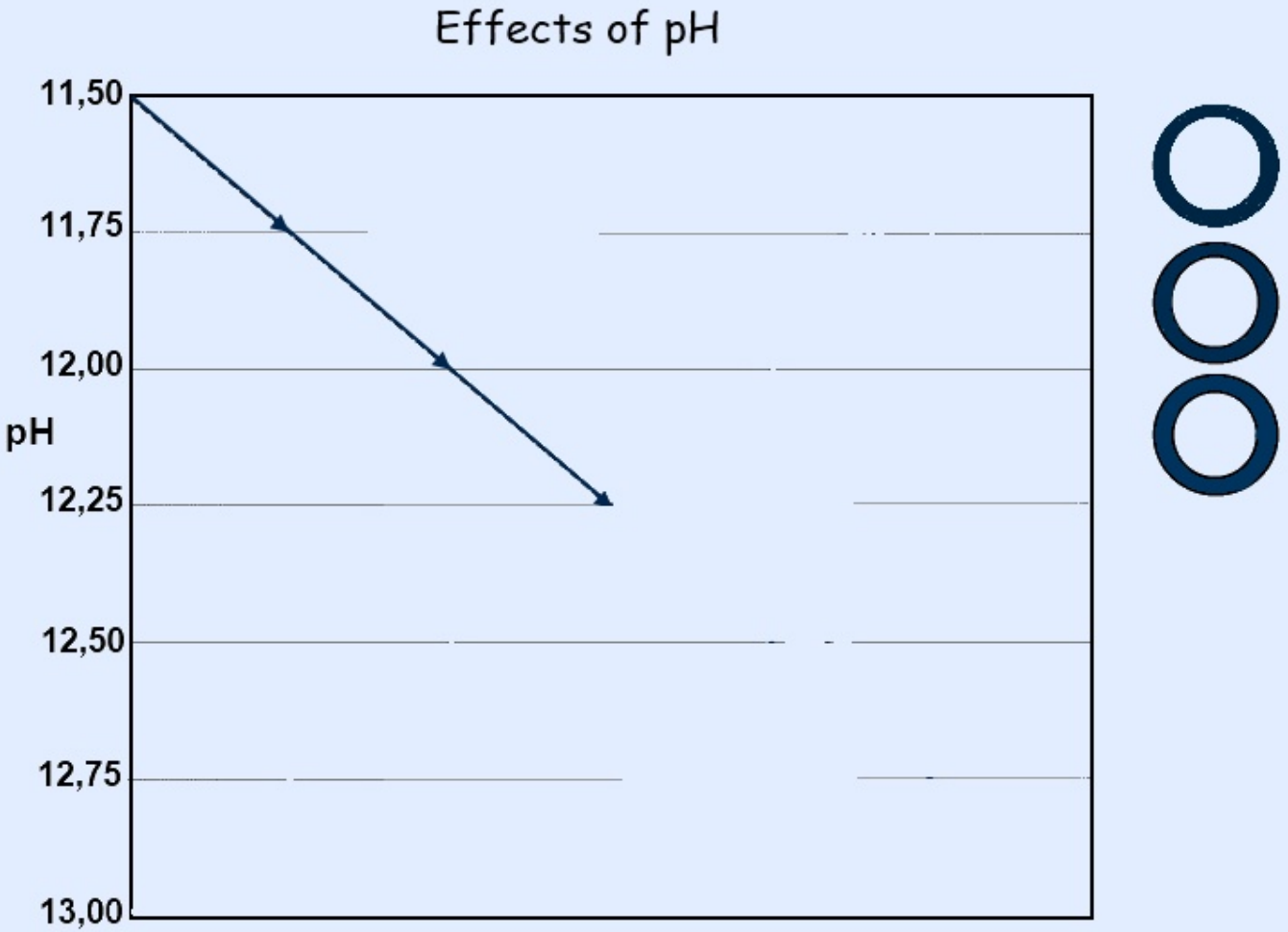
The leuco mono sodium form of leuco indigo has much higher affinity for cellulose fiber than bi sodium form. Therefore, depending of the value of pH in the optimum range, we have various degrees of ring dyeing of the denim cross-section yarn.

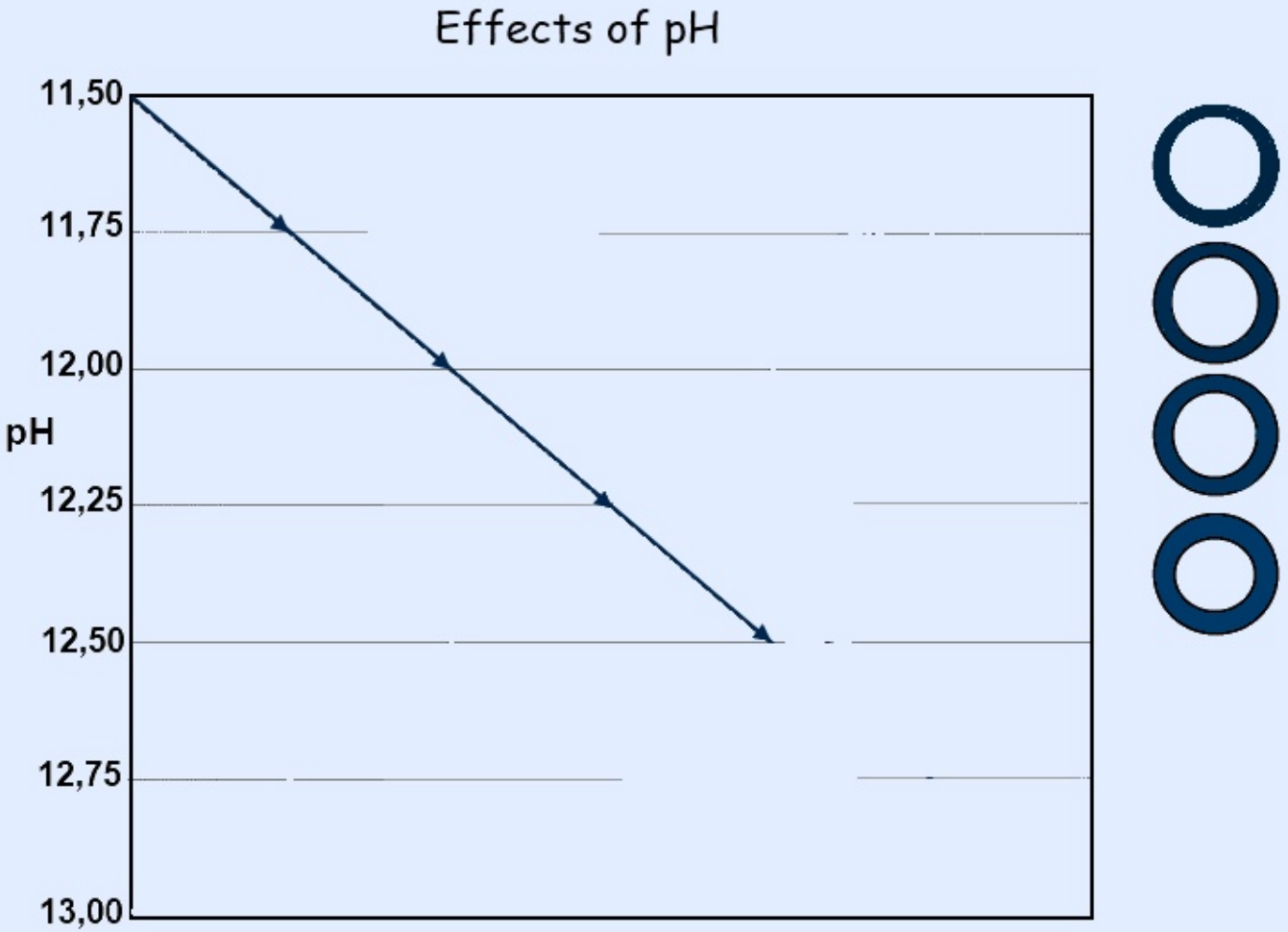
The colour yield, expressed as the depth of shade obtained for a given amount of fixed dye, is much greater for a dyeing conduced a pH 11,5 than a pH 13. In the latter pH the dye have more penetration.

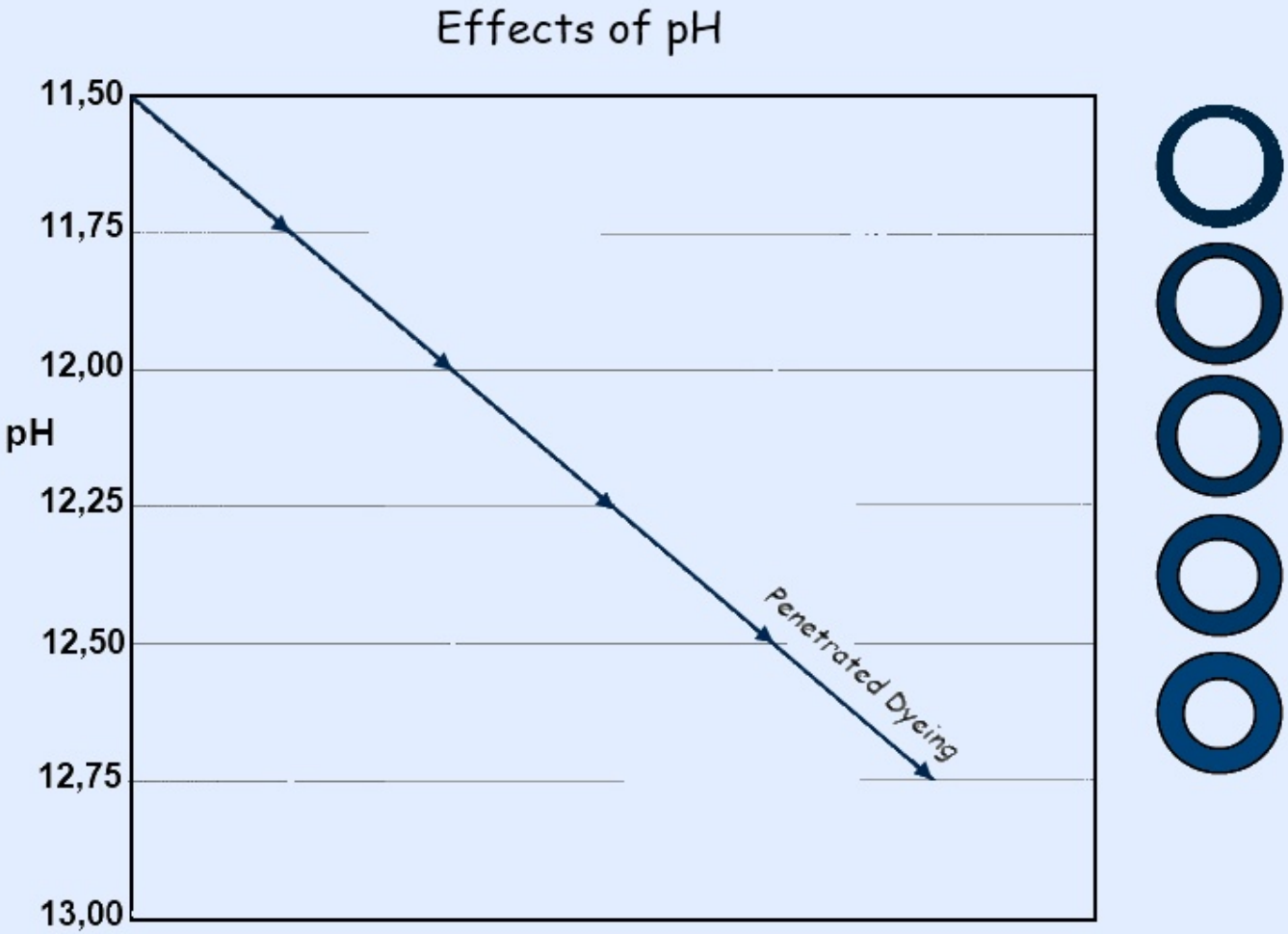
By varying the pH, we can get dyes with different distribution of the dye (cortical or penetrated) in the cross section of the yarn, as seen in the sequence shown here:

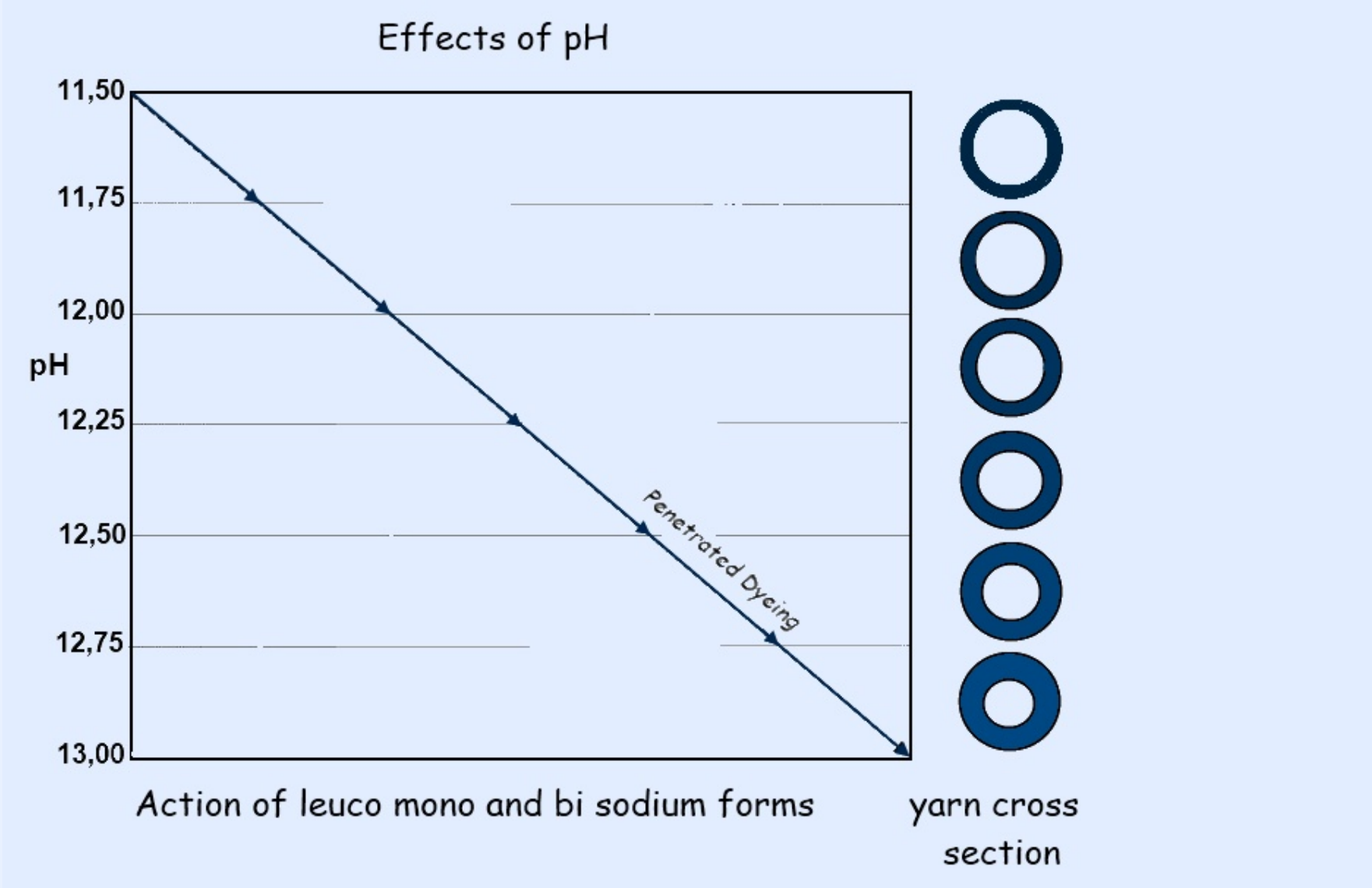

Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Action of leuco mono and bi sodium forms
yarn cross section


Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Action of leuco mono and bi sodium forms
yarn cross section

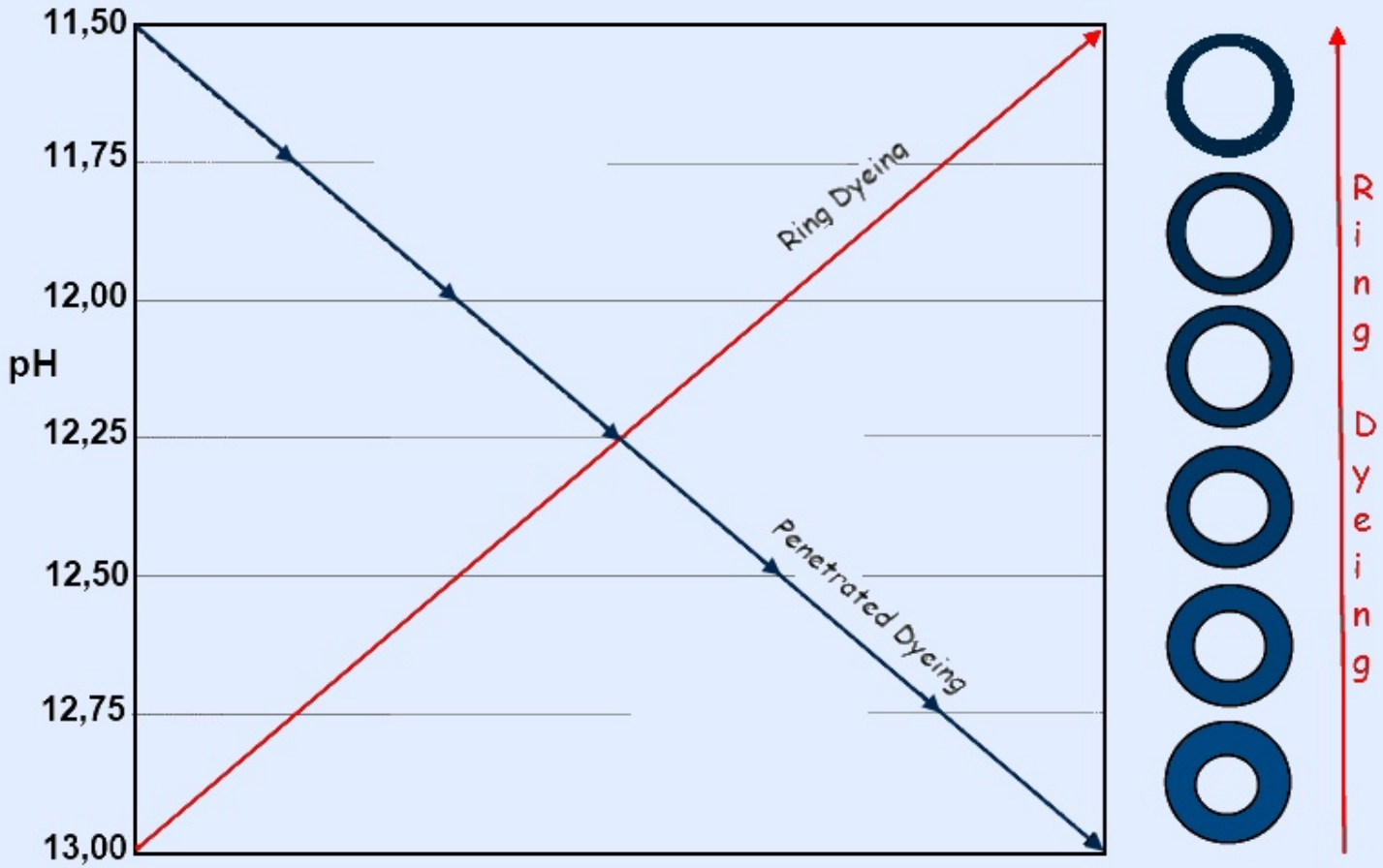

Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Action of leuco mono and bi sodium forms
yarn cross section


Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Action of leuco mono and bi sodium forms
yarn cross section


Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Penetrated Dyeing
Action of leuco mono and bi sodium forms
yarn cross section

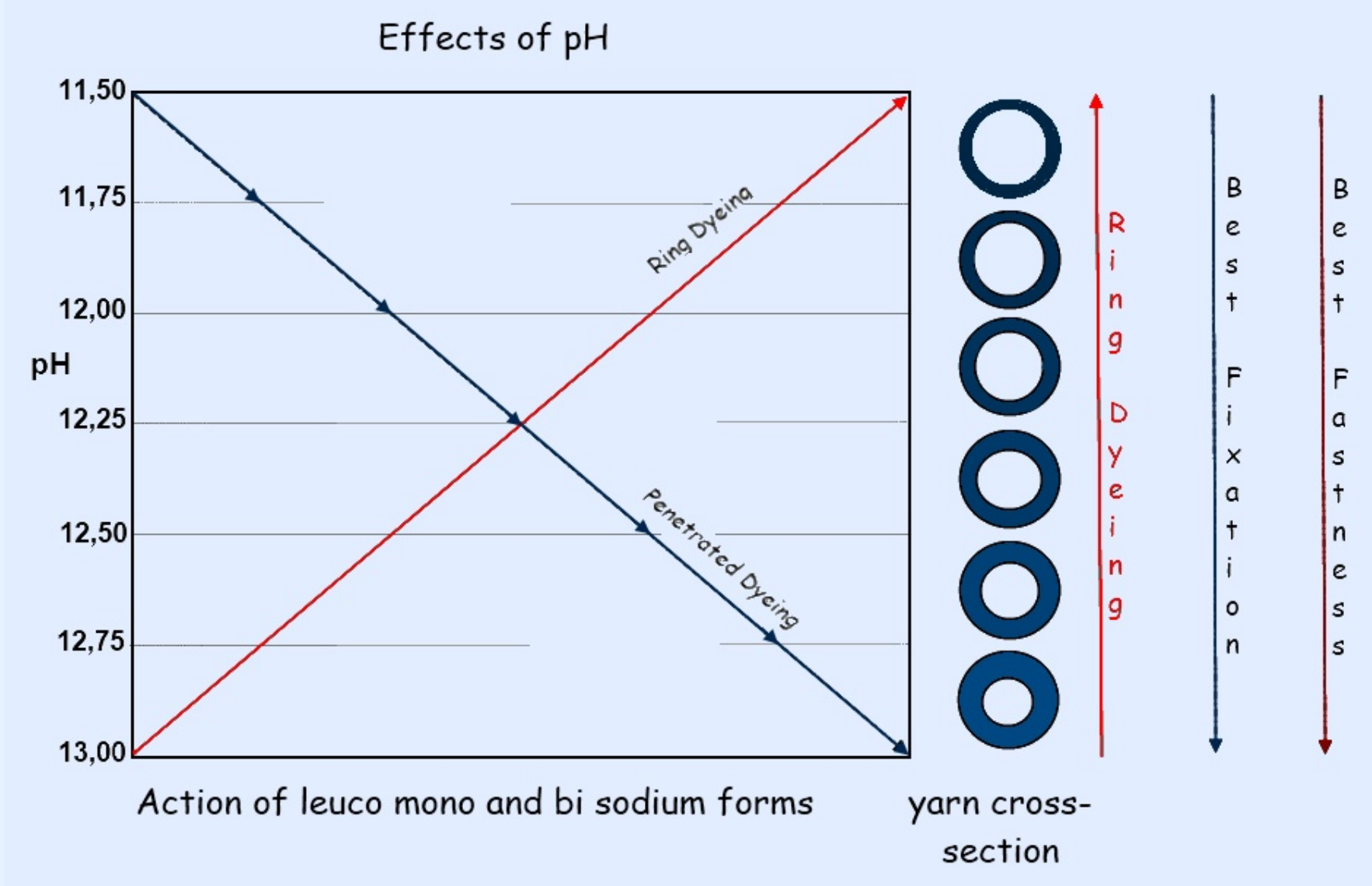

Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Penetrated Dyeing
Action of leuco mono and bi sodium forms
yarn cross section

Effects of pH



Action of leuco mono and bi sodium forms

yarn cross-section


Effects of pH
11,50
11,75
12,00
pH
12,25
12,50
12,75
13,00
Ring Dyeing
Penetrated Dyeing
Ring Dyeing
Best Fixation
Best Fastness
Action of leuco mono and bi sodium forms
yarn cross-section

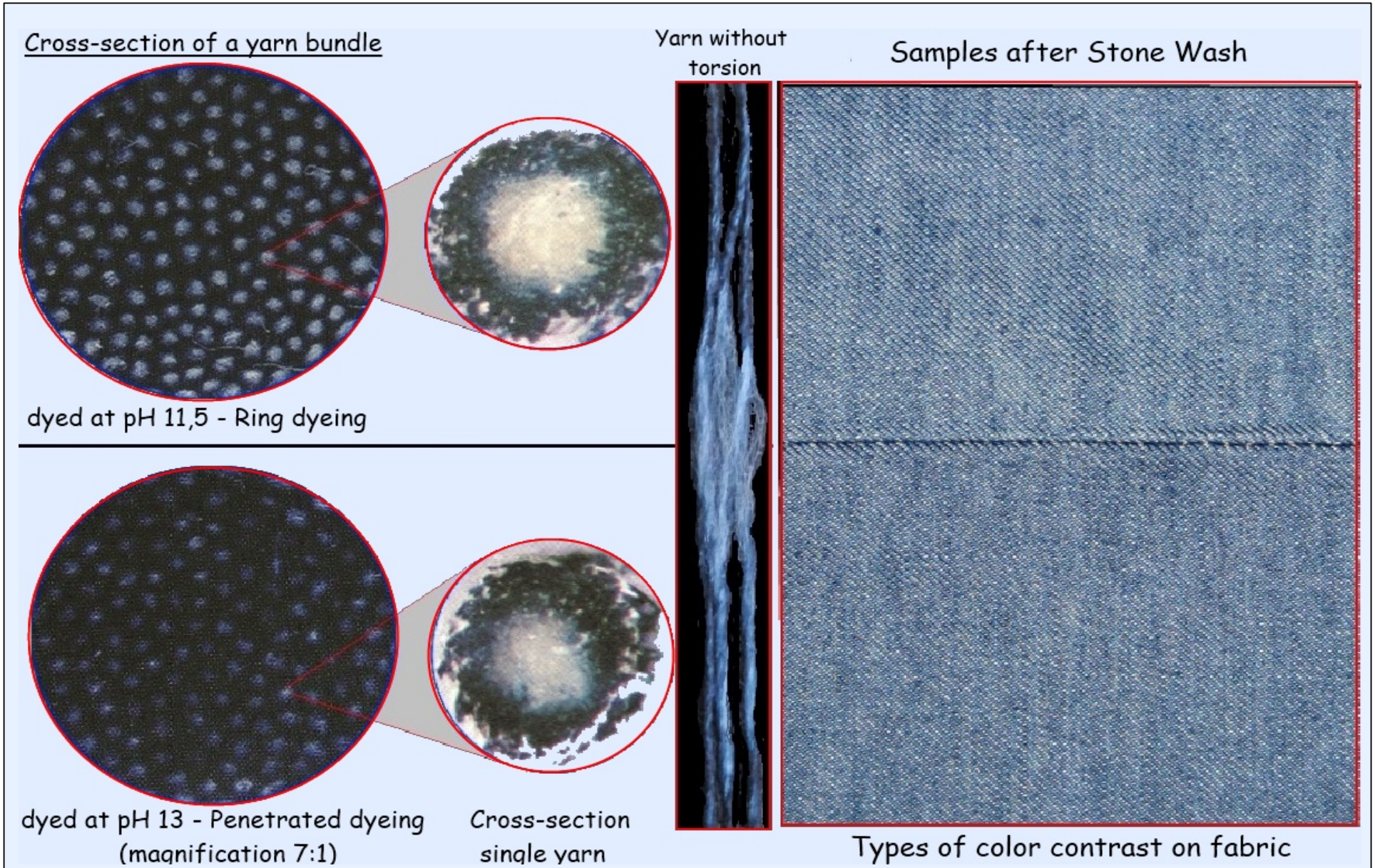


Figure 5. Distribution of the indigo in the yarn cross-section depending on the pH and contrast effects on the fabric after stone wash

4. CONCLUSIONS

Into the range of pH between 11,5 and 13 we have a major change of the fractions of leuco mono sodium and bi sodium. At pH 11.5, 94% of the leuco form is present in the mono sodium form (with greater affinity for the fiber) and 6% in the bi sodium form, while at pH 13 is 32% of leuco mono sodium compared with 68% of bi sodium.

Thus it appears that at pH 11,5 there will be relatively more cortical dyeing than that obtained at pH 13. It is also noted how due to the slope of the two curves, a small change in pH (in this interval), cause an important change in the relationship between the two forms (mono sodium and bi sodium) and consequently the degree of penetration of dye. In some cases we may want to use the buffer solutions to adjust the dyebath pH.

It is also noted how:

- The electrolytic bath charge does not change the unit fractions value of the leuco forms, although contributes to aggregate the dye and push it through the yarn.

- The dry crocking fastness grades of laboratory dyes*, carried out under different conditions of indigo concentration in the bath and pH variations, show how these values worsen with the cortical dye and contains some of the dye deposited outside the yarn.

- Indigo dyes of cotton have poor fastness, especially to crocking and the chlorine and this is responsible for the attractive blue color that develops after repeat laundering of denim clothings.

* J. N. Etters, J.S.D.C., AATCC, *Text. Chem. Color.*, **21** (12) (1989) 25.

THANK YOU FOR YOUR ATTENTION