QUANTITY DETERMINATION OF AVAILABLE HYDROXYL GROUPS WITH C.I. REACTIVE BLUE 19

This paper suggests establishing a practical, analytical method of determining optimal cotton pretreatment parameters thus assuring increase of sorption properties, which will be dependent of available hydroxyl groups. However, number of available hydroxyl groups will depend on pretreatment process. This is especially emphasized in treatments with caustic soda (merecrization), when structure of cellulose fibre changes, significantly influencing availability of hydroxyl groups. In this, cellulose I converts to cellulose II under alkaline conditions. When compared usually accepted unit cell for cellulose I has following dimensions: a = 8,35 Å; b = 10,3 Å (fibre axis); c = 7,90 Å; β = 84°, while monoclinic unit cell in cellulose II has following dimensions: a = 8,14 Å; b = 10,3 Å (fibre axis); c = 9,14 Å; β = 62°. Within completely arranged structural elements of cellulose, a portion of free hydroxyl groups, on second, third and sixth atom of carbon is not equal and decreases in following order: 2-, 6-, 3- (Fig.1).

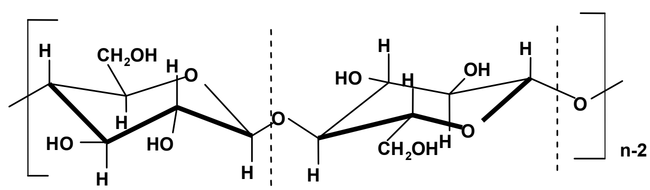

Figure 1. Perspective cellulose formulae

Unlike mercerization, bleaching causes increased fibre cristallinity, which causes the amount of overall available hydroxyl groups to decrease. In order of quantifying the number of available hydroxyl groups a monofunctional C.I. Reactive Blue 19 (Fig.2) dyestuff was set as an appropriate indicator, which can, according to its chemical structure react with only one cellulose molecule.

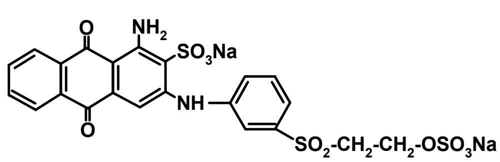

Figure 2. C.I. Reactive Blue 19

In addition, selected dyestuff reacts according to a mechanism of nucleophilic addition, which assures establishing covalent bonds among available hydroxyl groups of cotton and dyestuff at low process temperatures. However, before nucleophilic addition can occur alkaline 1,2-elimination of the precursor grouping is necessary in order of releasing the reactive vinylsulphone system. This implies polarization of carbon-carbon double bond by the electron-attracting sulphone group. Positive character is conferred on the terminal carbon atom as a result of polarization, favouring nucleophilic addition of either a cellulosate anion or a hydroxide ion, which leads to either fixation or hydrolysis (Fig. 3).

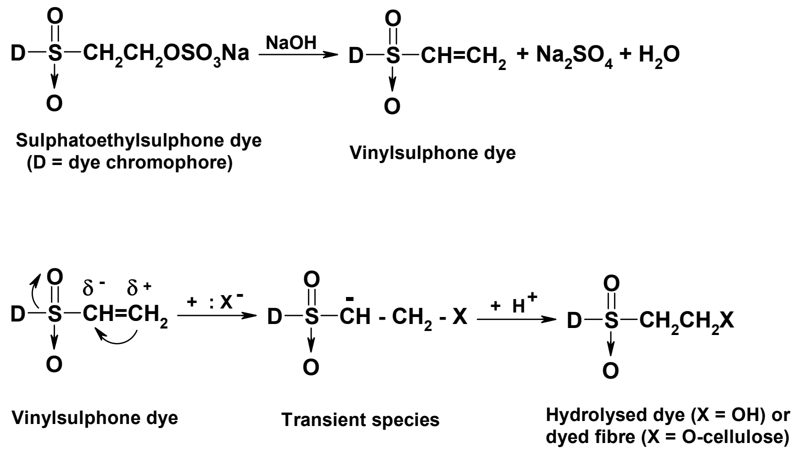

Figure 3. Mechanism of nucleophilic addition

Relatively high amount of dyestuff was used (4%) in order of assuring all available hydroxyl groups to enter the reaction, disregarding unwanted dyestuff hydrolysis. Disregarding the reaction of nucleophilic addition, dyestuff was bonded by concomitant weak bonds, such as van der Waals and hydrogen. Therefore, of all non covalently bonded dyestuff was extracted, while it is not a valid indicator of available hydroxyl groups. Substantively bonded dyestuff was extracted by NaH_2PO_4 (0,06 mol/l) in alkaline media (0,02 mol/l NaOH), making it possible to spectrophotometrically determine the amount of covalently bonded dyestuff from the difference established between overall and substantively bonded dyestuff. Considering this, amount of mmol dyestuff bonded onto the fibre will correlate with the amount of available (free) hydroxyl groups of cotton material (results are given for the amount of 10 g of cotton). Obtained results (Fig. 4) are in correlation with changes occurring with cotton pretreatment processes.

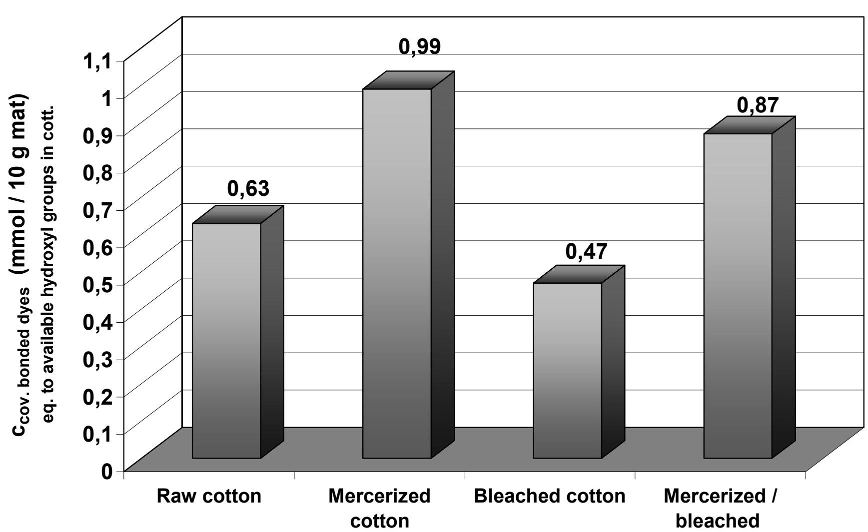

Figure 4. Amount of covalently bonded dyestuff depending on pretreatment process

Results confirm how this analytical method can quantify available hydroxyl groups, which will determine sorptive properties of cotton fibre. In the future, this analytical method could be used in order of optimizing cotton pretreatment conditions.

* *List of publications on this and related topics is included in candidates CV.*