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Color Fastness to Crocking Improvement of Indigo and Sulphur Dyed Cellulosic Fibres

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Abstract: *Commercial polymer chemicals are provided as auxiliaries for improving the color fastness to crocking of dyed fabrics. Indigo and sulphur dyes, the principal class of dyestuffs used to produce jeans, were used. The dyed fabrics present low dry-wet crocking fastness. Application of polyacrylic and polyourethane polymers to the dyed fabrics by aftertreatment process results in the fastness to crocking improvement of Indigo and CI Sulphur Black 1 dyed cellulosic fabric, whilst retain its other desirable properties. Stiffness, colour changes, and tear resistance measurements of the dyed fabrics were carried. Polyacrylates raised most the stiffness and hardness of the fabrics, compared to aliphatic polyurethanes. Tear resistance of the dyed fabrics was not significantly affected by the auxiliaries' application. Finally aftertreatment with the above finishing agents affected colour change in different ways.*

Keywords: *Indigo; Sulphur dyes, Crocking fastness, Polyacrylic Polymers, Polyurethane polymer.*

1. INTRODUCTION

Until 1856 when William Perkins discovered Mauveine, the best substantive colour-fast dye in commercial use was Indigo (CI Vat Blue 1, **Figure 1**). Many chemical

examinations of mummy cloths from ancient Egypt have shown that the blue patterns on them were coloured by Indigo [1]. Natural Indigo was obtained from plants of the genus *Indigofera (isatis tinctoria, indigofera tictoria)*, a name derived from its main country of origin, India [2]. Its synthesis, followed by its marketing was achieved in 1897, in order to satisfy the global demand, as the quantity of plant cultivation and the quality of the extracted Indigo was insufficient. Nowadays, production levels are reported to be around 17000 tons per year [3], establishing Indigo as one of the most demanding colorants throughout history.

Sulphur dyes remain one of the most popular dye classes for cellulosic fibres and their blends. They are widely used to produce economical black, blue, brown, olive, yellow and green shades in medium to heavy depths. It is estimated that about one half of the volume of dye used for cellulosic fibres is due to sulphur dyes (80,000 tonnes annually in 90's), in which case about 80% is the CI Sulphur Black 1 [4]. Although the structure of CI Sulphur Black 1 has been investigated by number of workers, it has not yet been established, assuming to be a mixture of different structures (**Figure 2**). Structures I-III have been proposed for CI Leuco Sulphur Black 1 [5].

Vat and sulphur are the two types of dyes involving a reduction/oxidation mechanism. The purpose of the reduction step is to change the dyestuff from a water-insoluble form, using a suitable reducing agent with an alkali, to a water-soluble form. The oxidation step then converts the soluble dye back to the insoluble form thereby fixing the dye to the dyed material [6, 7]. Until now in most industrial processes, vat dyes especially Indigo are reduced by sodium dithionite $Na_2S_2O_4$. When the leuco-Indigo is achieved, the textile is dipped with the reduced dye, following by exposure to air to re-oxidize the dye. These two steps (dipping/exposing) would be repeated many times to obtain the desired shade (**Figure 3a**). Likewise, the conventional method of application of sulphur dyes is from a dye-bath containing sodium sulphide or thiourea dioxide as a reducing agent [7, 8] (**Figure 3b**).

This process called "ring dyeing", creates a fabric subject to considerable and persistent wash-down or loss of color during extended use, as the outer layer of the yarn is dyed while the inner remains white [9]. The “ring dyeing” effect results in low abrasion and washing resistance giving the potential to garments producers to process them in so many ways that they succeed in producing multiple units staring from one pair of pants. The heavier the depth of shade the lower the crocking fastness rating. They present much lower crocking fastness at the same applied concentration compared for example to direct and reactive dyes. Especially ratings of fastness to wet crocking are unacceptable in the official crocking test scale. Many chemicals are used as finishing products to give to fabrics special properties, hoping as a side effect to improve the colour fastness to crocking of vat dyed fabrics. But, due to the fact that vat dyes are not chemical-bonded to the yarn, any emulsifier acts like a solvent for the dye increasing its thermomigration and staining of the adjacent yarns (bleeding). The crock fastness and wash fastness of the fabric decrease as dyes migrate to the fabric surface. Chemical finishing can be defined as the use of chemicals to achieve a desired fabrics property. It has always been an important component of textile processing, but in recent years the trend to “high tech” products has increased the interest and use of chemical finishes [10]. About 40% of textile auxiliaries are used in finishing, the largest percentage usage of all textile chemicals. Among them softeners are clearly the most important individual product group **(Table 1)**.

Table1. *Auxiliaries used in textile finishing*

Finishing product group	Chemicals included	Production Amount (%)
Softeners	Silicones, Cationics, Anionics, Nonionics, Polymers	22,1
Coating products	Polymers	18,4
Remainders	Optical Brightness	14
Flame retardants	THPC-Urea	13,9
Easy care products	DMDHEU	13,5
Hand builders	Acrylic, Polyurethane Polymers	10
Repellents	Fluorocarbons	4,1
Antistatic agents	Cationics	2,3

A number of these chemicals are used in the field of denim fabrics as finishing chemicals, mainly for improving the softness, the appearance and the touch-feel of the fabric. Reasonably, a conversion of the fabric surface to another more waterproof and flat will improve the crocking fastness of the fabric. The most popular commercially categories that could achieve this, without causing big changes on the other techno-commercial features such as stiffness, tear strength and colour loss are shown in **Figure 4**. In this paper, the so-called “hand builders” acrylic and polyurethanes are applied as finishing agents, at high and low add-on concentrations, and their effect on colour fastness to crocking is examined.

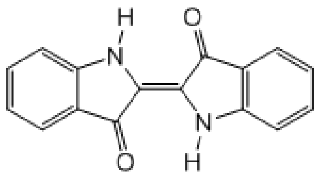

Figure1. *Chemical structure of Indigo*

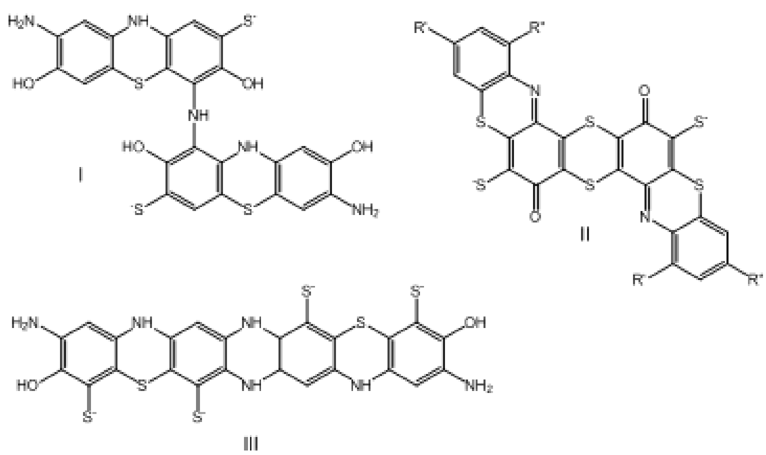

Figure2. *Proposed structures for CI Leuco Sulphur Black 1*

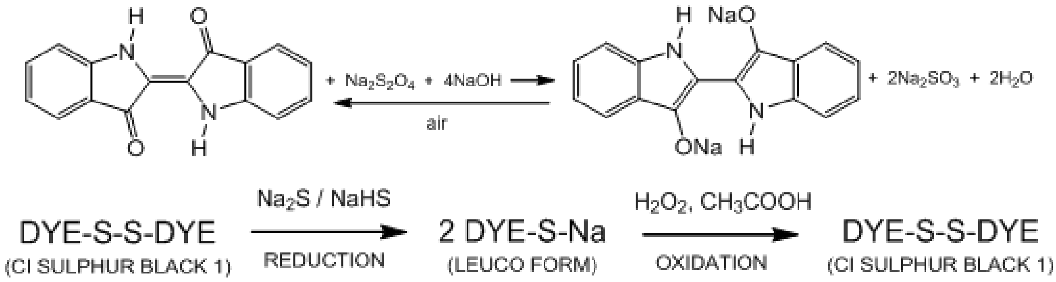

Figure3a,b. *Reduction/oxidation mechanism of a: indigo, b: sulphur dyes*

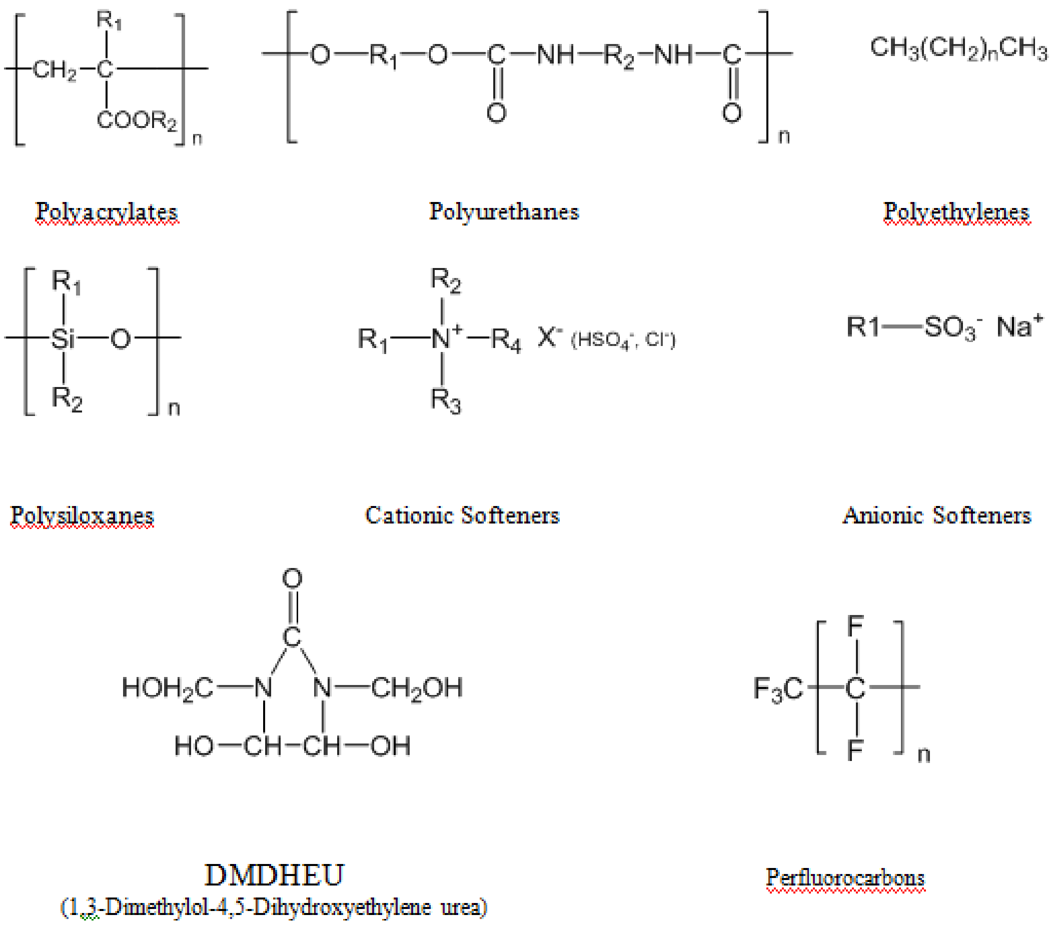

Figure4. *Popular commercially categories of finishing chemicals*

2. Materials & Methods

Three representative dyeings have been chosen in heavy depths with Indigo, CI Sulphur Black 1, and a combination of two which are:

a) Indigo dyeing 6% o.w.y (on weight of yarn)

b) CI Sulphur Black 15% o.w.y

c) Predyeing with CI Sulphur Black 1,5% o.w.y. and dyeing with Indigo 4% o.w.y.

Polyacrylate and polyurethane commercially available finishing products of an initial 40% solid concentration, diluted furthermore to water in different high and low concentrations, were applied on each of the three different dyed fabrics mentioned before with the next sequence:

1) Untreated dyed fabric (blank)
2) Acrylic copolymer, 60g/l active solid (Resacril M/Conc)
3) Acrylic copolymer 12g/l
4) Acrylic copolymer 60g/l with melamine catalyst 10g/l (Catalizzatore PA/Z)

5) Acrylic copolymer 12g/l with melamine catalyst 2g/l
6) Acrylic copolymer 60g/l with polyisocyanate catalyst 6g/l (Catalizzatore PU)
7) Acrylic copolymer 12g/l with polyisocyanate catalyst 1,2g/l (Catalizzatore PU)
8) Aliphatic polyurethane 20g/l (Politex PU/38)
9) Aliphatic polyurethane 10g/l
10) Aliphatic polyurethane 20g/l with melamine catalyst 2,5g/l
11) Aliphatic polyurethane 10g/l with melamine catalyst 1,3g/l
12) Aliphatic polyurethane 20g/l with polyisocyanate catalyst 2g/l
13) Aliphatic polyurethane 10g/l with polyisocyanate catalyst 1g/l

All chemicals were supplied by Prochimica Novarese S.p.A and Kyke Hellas S.A.

2.1. Apparatus

A.A.T.C.C Crockmeter Model CM1 S/N/ 8457 from SDL ATLAS TEXTILE TESTING SOLUTIONS was used for colorfastness to crocking measurement. Chatillon Digital Force Gauge Pneumatic Fab-Stiffness Tester Model DFGS50-PFST S/N 25117 from J.A.KING & COMPANY GREENSBORO N.C. WEIGHTING SCALES SYSTEMS was used for stiffness measurement. Heavy Duty Elmendorf from TWING ALBERT’S INSTRUMENT COMPANY PHILADELPHIA USA was used for Tear resistance measurement. Dual-beam d/8^o Spectrophotometer Model 600 from DATACOLOR was used for colour measurement. Labcoater type LTE-S from MATHIS AG was used for polymer thermofixation.

2.2. Dyeing

Dyeings were made industrially in continuous process. Yarns passed through 8 vats, each followed by an air passage for oxidation. The processing speed was 20m/min with an immersion time of 25 seconds in each vat and oxidation time of 2:30 minutes followed by a final rinse. Fabrics, after have been produced in looms department, were impregnated in laboratory equipment with chemicals listed above by padding, in two different concentrations (high/low) proposed by suppliers, with a 65% o.w.f. (on weight of fabric) pick-up, followed by a drying and thermo fixation in a tender at 160^{o}C for 1 minute.

2.3. Measurement Tests

In order to examine the durability of the chemicals, the series of tests were done in two stages separately. One stage is after the application and the other after a washing, according to “AATCC Test Method 96-1997, Dimensional Changes in Commercial Laundering of Woven and Knitted Fabrics except Wool”. This washing is made by garment industries to approach the domestic laundering. The tests are:

a) AATCC 8. Colorfastness to Crocking
b) ASTM D4032. Stiffness Measurement of Fabrics
c) ASTM D1424. Tear Resistance of Textile Fabrics
d) DE_{CMC} Total Color Difference

3. RESULTS AND DISCUSSION

3.1. Colorfastness to Crocking

Figures 5 and 6 show the dry-wet crocking fastness of Indigo and Sulphur Black 1 dyed fabrics respectively before and after one washing while **Figure 7** shows the dry-wet crocking fastness of CI Sulphur Black 1 and Indigo combination.

1 unit of the grey scale rating (1-5) for improvement in dry crocking fastness before washing was observed (Fig. 4) for indigo dyeings aftertreated with the polyurethane finishing agents 8-13 while slight improvement was observed for the samples aftertreated with the acrylic finishing agents 2-7 compared to the untreated dyed fabric 1 (reference sample). The effect of all 12 different trials of finishing agents on dry crocking fastness after washing was slighter high compared to that before

washing given that crocking fastness of the untreated sample after washing is higher. As the rubbing force for the wet testing procedure is about double the rubbing force for dry rubbing [11], wet crocking ratings of indigo and sulphur black dyed fabrics at heavy depths of shade, cannot overcome the level of 1-2 on the grey scale for staining according to AATCC 8. None of any applied chemical combination had a worth noticing improvement on wet crocking fastness of dyed fabrics. Especially on fabrics dyed with CI Sulphur Black 1 (Fig. 5) had no influence at both wet-dry crocking fastness. Similar results were obtained with the dyeings with CI Sulphur Black 1 and Indigo combination (Fig. 6). In general the fabrics appear good fastness at dry but unacceptable poor at wet crocking, regardless the different applied concentration of the finishing chemicals.

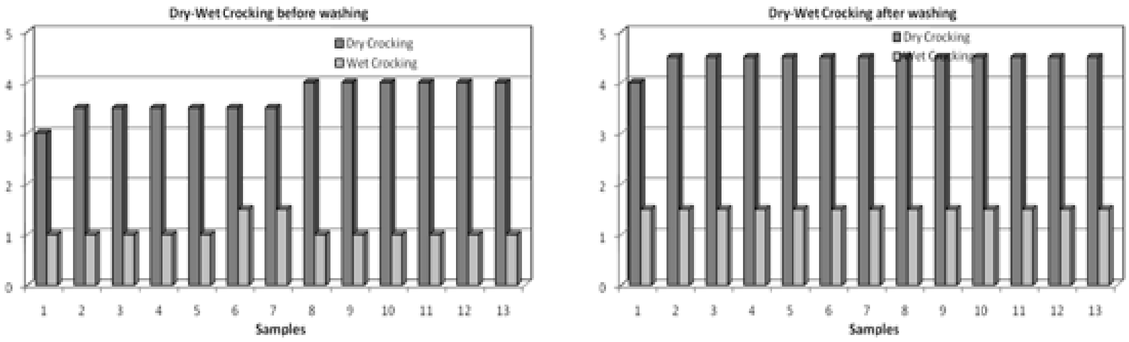

Figure5. *Crocking Fastness of 6% o.w.y. Indigo Dyeing*

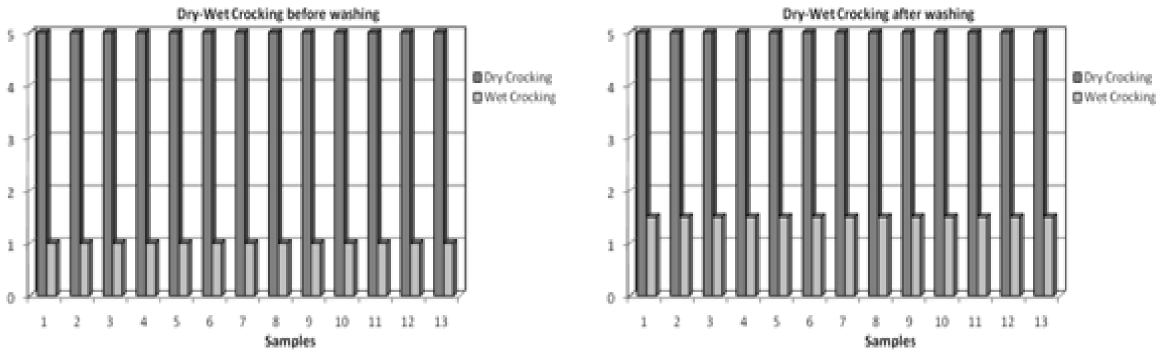

Figure6. *Crocking Fastness of 15% o.w.y. CI Sulphur Black 1*

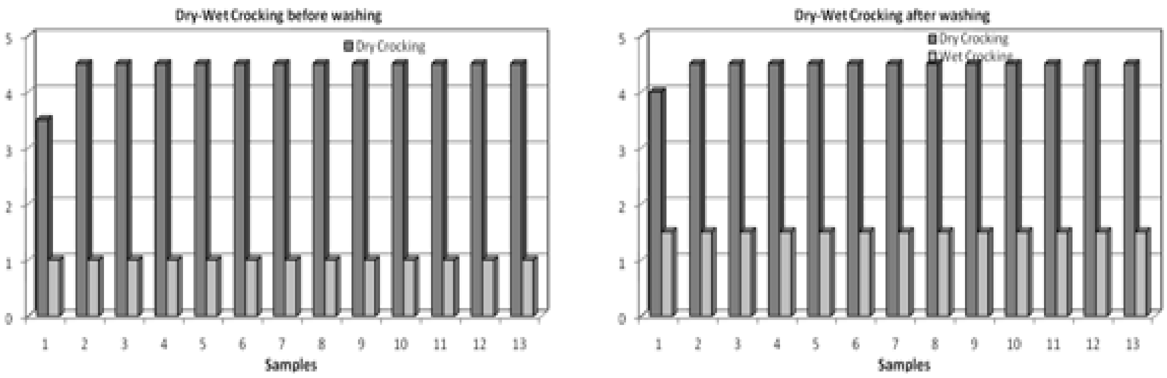

Figure7. *Crocking Fastness of CI Sulphur Black 1 and Indigo combination*

3.2. Stiffness Measurement

Figures 8, 9, 10 illustrate how chemicals affect the stiffness of fabrics. As expected, polyacrylates are the category of polymers which raise most the stiffness and hardness of a fabric, compared to aliphatic polyurethanes, retaining the effect and after washing (Fig. 7,8). In the aggregate, polyurethanes lie almost on the same level, without a remarkable difference compared to untreated fabric (Fig. 9). Furthermore raising the applied concentration of polyacrylates on fabric, results in higher stiffness.

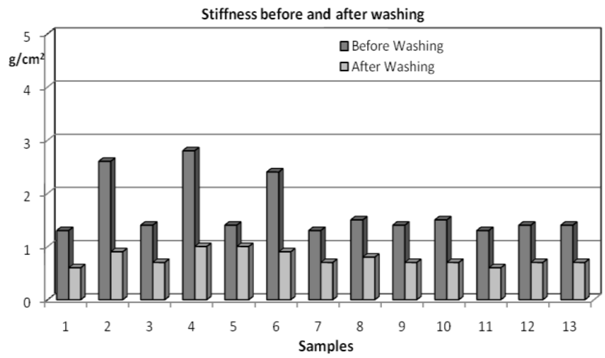

Figure8. *Stiffness of Indigo dyed fabric*

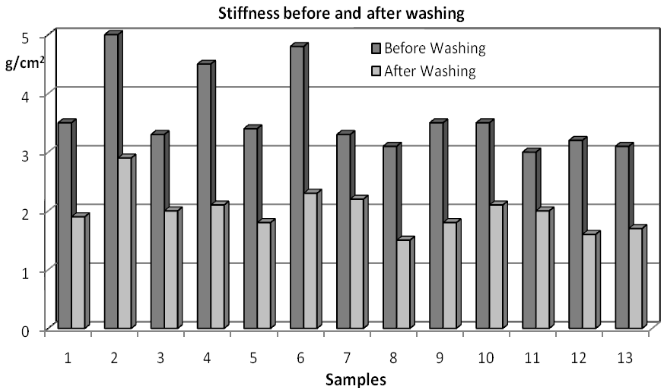

Figure9. *Stiffness of CI Sulphur Black 1 dyed fabric*

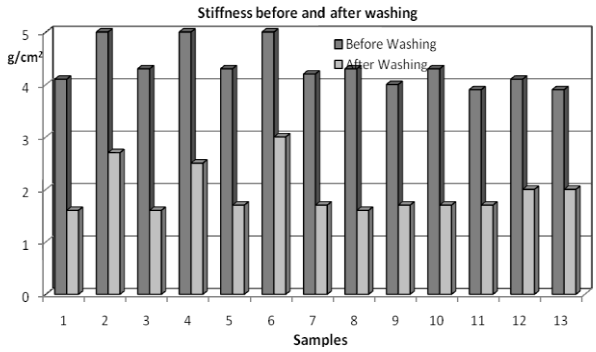

Figure10. *Stiffness of CI Sulphur Black 1 and Indigo combination*

3.3. Tear Resistance

In the field of denim, a warp tear measurement of around 3200 grams (ASTM D1424) is the commercial lower limit accepted from all jeans garment manufacturers. None of any category of applied products, independently of the concentration, influences warp tear in such way that run the risk to approach 3200 grams of tear strength **(Figures 11, 12, 13).**

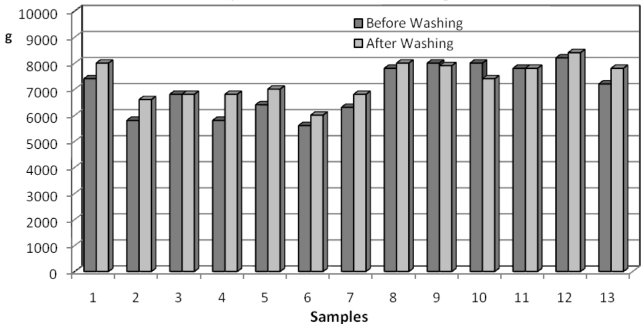

Figure11. *Warp tear of Indigo dyed fabric before*

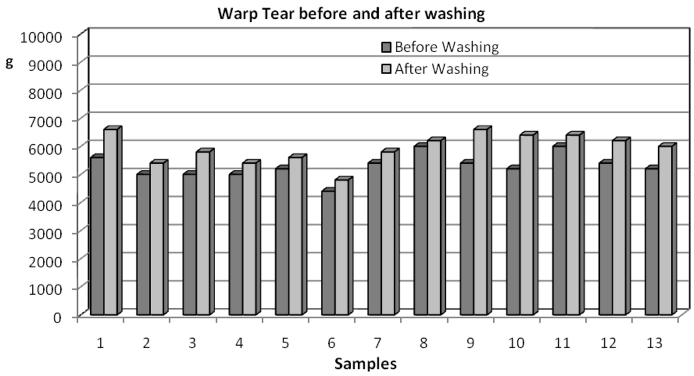

Figure12. *Warp tear of CI Sulphur Black dyed fabric*

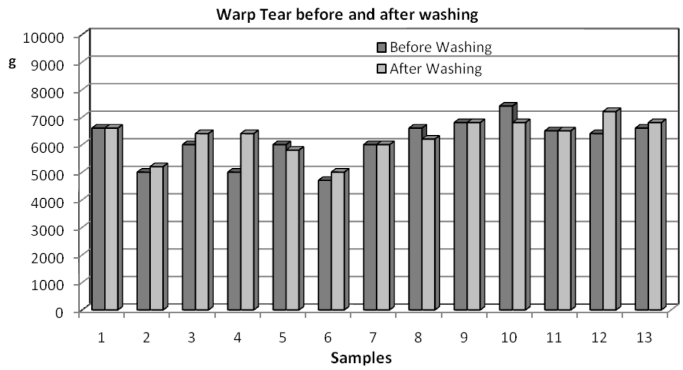

Figure13. *Warp tear of CI Sulphur Black and Indigo combination*

3.4. Color Measurement

Total color difference, expressed as DE_{CMC}, is nowadays the official formula used from industries either to evaluate tolerances or to automate conformity testing (in the textile industry particularly). It is based on CMC method (Color Measurement Committee of the Society of Dyers and Colorists) which is a modification of CIELAB formula minimizing the errors.

$$DE_{CMC} = \left[\left(\frac{\Delta L*}{lS_L} \right)^2 + \left(\frac{\Delta C*}{cS_C} \right)^2 + \left(\frac{\Delta H*}{S_H} \right)^2 \right]^{1/2}$$

In general, a maximum tolerance of $DE_{CMC} = 1$ between the desirable fabric and the hole fabric lots, is the agreement between fabric suppliers and denim garment traders. Value higher than $DE_{CMC} = 1{,}5$ is considered as unacceptable color difference between two fabrics. **Figures 14, 15, 16** reveal that polyacrylate polymers affect color change more than polyurethanes**,** retaining the color difference between treated and blank fabric at high levels. Additionally, the colour difference is increased when an emulsion of higher concentration is applied on fabrics (ex. Fig. 13, sample 2 DE_{CMC}=1.75 at 60g/l, sample 3 DE_{CMC}=0.95 at 12g/l). On the contrary, polyurethanes, either before or after washing exhibit acceptable total color difference compared to the initial untreated fabric.

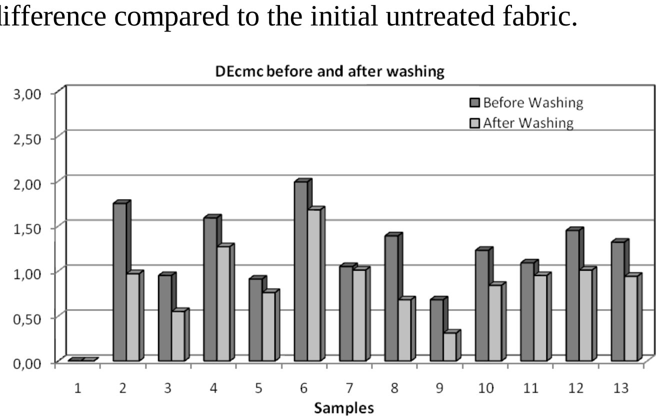

Figure14. *DE_{cmc} of Indigo dyed fabrics*

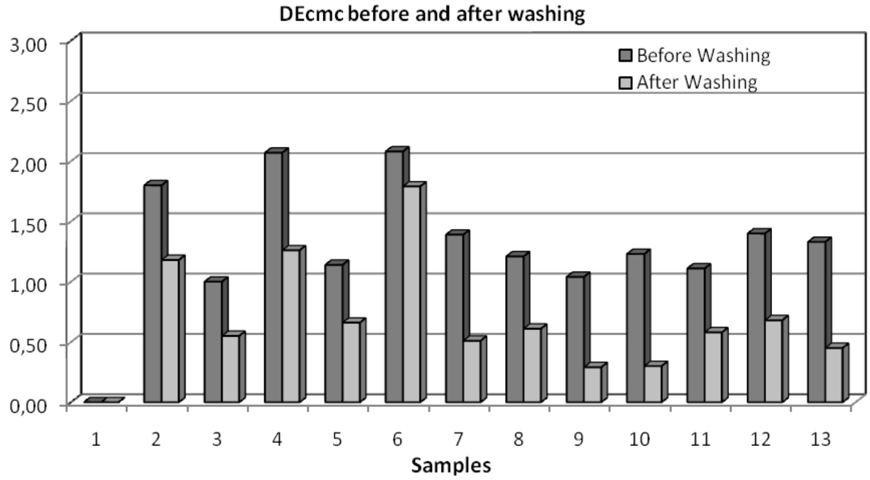

Figure15. *DE_{cmc} of CI Sulphur Black 1 dyed fabric*

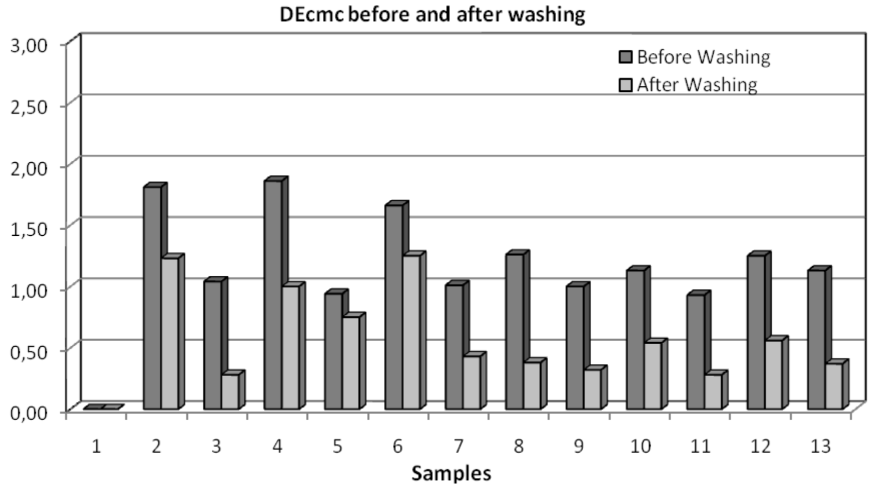

Figure16. *DE_{cmc} of CI Sulphur Black 1 and Indigo combination*

4. CONCLUSIONS

Indigo and sulphur-black dyed cellulosic fabrics are famous for poor fastness to crocking especially at full depths of shade. One representative of two of the most usable nowadays chemical categories applied on textiles, polyacrylates and polyurethanes, were examined in this project, at high-low concentration, whether they can improve the colour fastness to crocking, whilst retain all the other color-physical properties. Indigo dyeings aftertreated with the polyurethane finishing agents presented an improvement of 1 unit of the grey scale rating 1-5 for dry crocking fastness before washing while slight improvement was observed for the samples aftertreated with the acrylic finishing agents 2-7 compared to the untreated dyed fabric (reference sample). Polyacrylates are the category of polymers which raise most the stiffness and hardness of a fabric, compared to aliphatic polyurethanes, retaining the effect and after washing. In the aggregate, polyurethanes lie almost on the same level, without a remarkable difference compared to untreated fabric Regarding tear resistance, none of any category of applied products, independently of the concentration, influences warp tear in such way that run the risk to approach 3200 grams of tear strength. Finally aftertreatment with the above finishing agents affects colour change in different ways. Polyacrylate polymers affect color change more than polyurethanes**,** retaining the color difference between treated and blank fabric at high levels. The colour difference is increased when an emulsion of higher concentration is applied on fabrics. On the contrary, polyurethanes, either before or after washing exhibit acceptable total color difference compared to the initial untreated fabric. Subsequent work will be done, investigating whether the other textile finishing chemical categories mentioned before (polyethylenes, polysiloxanes, softeners, fluorocarbons and DMDHEU) can succeed in wet colour fastness to crocking improvement.

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