

# **APPLICATION OF NEW TYPES OF THE SEQUESTERING AGENTS TO COLOURISE COTTON WITH THE REACTIVE DYES IN HARD WATER**

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## **Abstract**

In this work it was investigated the possibility of using developmental samples of sequestering agents to dyeing in hard water. To dyeing of cotton material were used reactive dyes of vinylsulphone type. The coloration was evaluated using the value of the degree of exhaustion of the dye bath and objective color measurement.

## **1 Introduction**

The cotton is by far the most commercially important of all plant fibres. The cotton contains 90-95% of cellulose. Cotton fibres also contain pectins, proteins, fats, waxes, lignin, ashes etc. Textile materials of natural cellulose have to be thoroughly prepared prior to dyeing. Impurities as well as matters which adhered to the fibre during the previous treatments are removed by desizing, alkaline scouring and bleaching. The process of preparation imparts to the cotton yarn or fabric a better appearance, a higher strength and easier colourability due to the singeing and mercerizing steps [1].

Reactive dyes have very popular for the dyeing and printing of cellulosic fibre for many years. These dyes are characterized by a high brilliance of hue and good to excellent fastness. They are suitable not only for natural and regenerated cellulose, but also for animal and polyamide fibres. Reactive dyes form a special group capable of forming a chemical bond with the cellulosic substrate, thus forming a dyestuff – fibre bond. During the process of

dyeing, reactive atom groups or reactive atoms react with the primary –OH cellulose groups. Depending on the type of reaction, the reactive dyes are broadly divided into two categories: I. Dyes reacting through the nucleophilic substitution, II. Dyes reacting through the nucleophilic addition (vinylsulphone dyes) [2, 3].

The water quality is the most important parameter for textile wet processes. The water is undoubtedly the most suitable as dyeing medium. So the quality of coloration is vastly dependent on quality of water. The hard water is for dyeing unsuitable. In case of dyeing cellulose fibers with reactive dyes, dyeing reproducibility is affected negatively by the hardness arisen from water, salt and the cotton fiber.

Sequestrate agents are used for the water softening in the dyeing process. These substances react with metal ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) without removal that metal from the system –

Fig.1

Fig. 1 Chelation of EDTA with Calcium Ion

Sequestrate agents represent one of the most significant groups of textile auxiliary agents. Traditional chelating agents are polyphosphates, aminopolycarboxylates, hydroxycarboxylates, polymeric carboxylic acids, polyaminophosphonates and polyhydroxyphosphonates. [4, 5, 6].

## **2 Experimental**

### **2.1 Used Reactive Dyes**

Three reactive dyes of vinylsulphone type were used for dyeing of cotton material: C.I. Reactive Yellow 5 (Fig.2); C.I. Reactive Red 198 (Fig.3); C.I. Reactive Blue 19 (Fig.4)

Fig. 2 C.I. Reactive Yellow 5 [7]

Fig. 3 C.I. Reactive Red 198 [8]

Fig. 4 C.I. Reactive Blue 19 [9]

## 2.2 Prepared Sequesterant Agents

Two types of sequesterant agents were prepared: sample no.1 – Fig.5 and sample no.2 – Fig.6.

Commercial sequesterant agents (Trilon M – Fig.7 and Sequion 10 Na 430 – Fig.8) were used for compared of efficiency.

Fig. 5 Prepared sample no. 1

Fig. 6 Prepared sample no. 2

Fig. 7 Trilon M

Fig 8 Sequion 10 Na 430

## 2.3 Dyeing Procedure

Pre-treatment cotton fabric (10g) was used as a material for dyeing. Bath ratio for dyeing was 1:20. Process of dyeing is described at Fig. 9. At the beginning of the dyeing the bath contained 2 % of reactive dye; 1 g.l<sup>-1</sup> of Altaran S8 and 2 g.l<sup>-1</sup> of sequesterant agent (A). After ten minutes 50 g.l<sup>-1</sup> of NaCl was added (B). After another 10 minutes 5 g.l<sup>-1</sup> of Na<sub>2</sub>CO<sub>3</sub> and 2 ml.l<sup>-1</sup> of NaOH 38°Bé were dosed(C).

Fig. 9 Process of dyeing

The dyeing was carried in distilled water and in the prepared hard water 22°dH in the dyeing machine AHIBA NUANCE TOP SPEED IIB (Datacolor, USA).

## 2.4 The Post-treatment

Such additional treatment is another important part of the dyeing process. Its objective is to remove the unfixed (and hydrolysed) portion of the dye that is incapable to be strongly bound with the substrate. If the washing is not thorough enough, the fastness properties, above all the fastness to perspiration, water, rubbing, and etc., are substantially reduced.

Thorough washing in cold and warm water was performed after dyeing. . It was followed by soaping at the boil with 1,5 g/l of Syntapon ABA; 20 min. Finally it was performed by rinsing in warm and cold water.

### 2.5 Colour Fastness Test to Washing

Combined sample for testing of colour fastness (Fig. 10) was prepared. Clipping of dyeing material (B) – 4x10cm was inserted between equally large clippings of accompanying cotton fabric (C) and accompanying wool fabric (D). Clippings were sewn together (A).

Prepared combined samples were tested in the washing at 40 °C, 60 °C and 95 °C for 30 min, bath ratio 1:50. Accurate procedure is under standart ČSN EN ISO 105 c 10.

Fig.10 Combined sample

### 2.6 Measurements

The absorbance before and after dyeing was measured with a spectrophotometr (model SPEKOL 11; Carl Zeiss Jena, Germany). Objective color measurement was then realized by ColorQuest XE (Hunterlab, USA). Measurement of pH, before and after dyeing, was accomplished with a digital pH meter calibrated on a series of commercially available buffers.

## 3 Results and Discussion

Tables 1-3 state values of the degree of exhaustion of the bath for three used dyes. The dyeing was executed in the distilled water and in the hard water without and with sequestering agents. Values of exhaustion of the dye bath by prepared samples are similarly or better as by Trilon M and Sequion 10 Na 430. Sample no.2 achieves higher values than sample no.1. By Reactive Yellow 15 and Reactive Blue 19 is the degree of exhaustion of the bath in the hard water with prepared samples better than in the distilled water with prepared samples.

**Table 1** The value of the degree of exhaustion of the dye bath for C.I. Reactive Yellow 15

**Table 2** The value of the degree of exhaustion of the dye bath for C.I. Reactive Red 198

**Table 3** The value of the degree of exhaustion of the dye bath for C.I. Reactive Blue 19

Legends:

pH<sub>1</sub>                      pH value before dyeing

pH<sub>2</sub>                      pH value after dyeing

Absorbance 1 value measured in the bath before dyeing

Absorbance 2 value measured in the bath after dyeing

Absorbance 3 value measured after soaping at the boil

Hard water [HW]      hard water 22°dH

Tables 4-6 describe change of shade, difference of shade and the depth of shade. Low differences of shade were reached with sample no.2. Good results shows sample no.2 mainly for C.I. Reactive Blue 19. Sample no.1 shows high values of difference of shade and type

depth, too. This sample probably reacts with reactive dye. It is secondary amine which can react with an activated double bond of the reactive dye.

Tables 7-9 state evaluation of colour fastness test to washing. Reactive dyes are characterized by good to excellent fastness. This was validated. Additions of prepared samples to dyeing bath have not negative effect. The highest values of fastness reached C.I.Reactive Red 198.

**Table 4** Objective color measurement for C.I. Reactive Yellow 15

**Table 5** Objective color measurement for C.I. Reactive Red 198

**Table 6** Objective color measurement for C.I. Reactive Blue 19

Legents:

$\Delta E^*$ ...Difference of shade

Avg... Average Strength for reflectance

DW..... distilled water

Wgt....Weighted Strength for reflectance

HW..... hard water 22 °dH

**Table 7** Colour fastness test to washing for C.I. Reactive Yellow 15

**Table 8** Colour fastness test to washing for C.I. Reactive Red 198

**Table 9** Colour fastness test to washing for C.I. Reactive Blue 19

#### **4 Conclusion**

In this work were evaluated abilities of application of prepared samples of self-sequestering surfactants by dyeing with vinylsulphon reactive dyes. Positive results were reached with sample no.2, which is prepared by reaction of aspartic acid with sodium salt of maleic acid. Sample no.1 probably reacts with reactive dye.

The structure of used dyes can have an influence on dyeing with sequestrate agents. C.I. Reactive Yellow 15 is azoic dye, C.I. Reactive Blue 19 is anthraquinonic dye. These two dyes are monofunctional dyes. C.I. Reactive Red 198 is heterobifunctional dye.

During operational conditions is a different situation than at realized laboratory conditions – bath ratio, dyeing material, concentration of calcium etc. The effect of the hard water can be then higher.

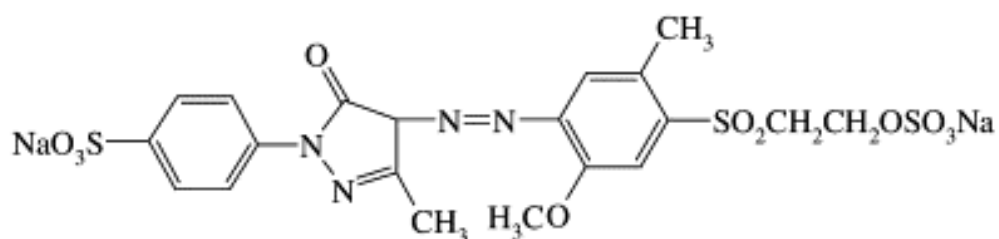
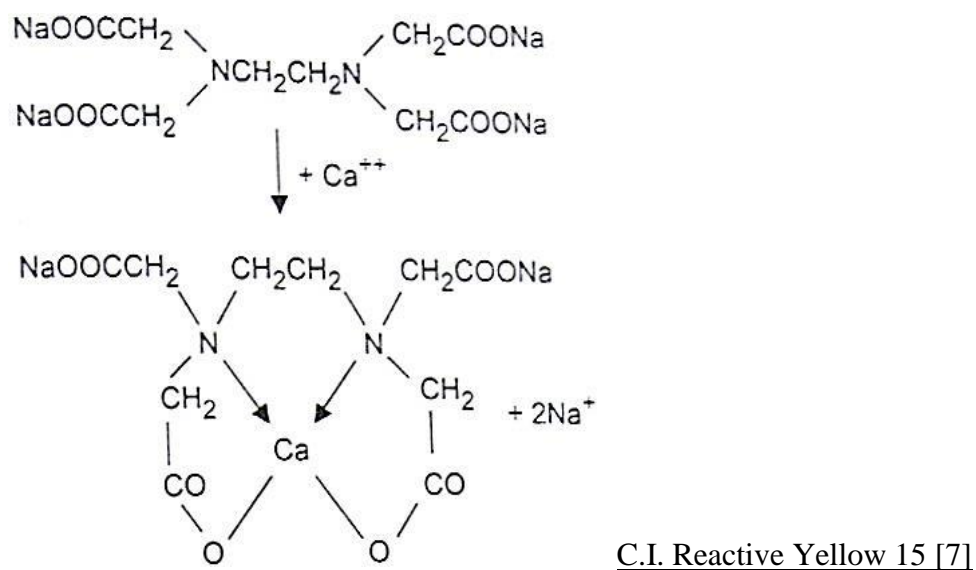
Gained results are materials for next research.

## 5 References

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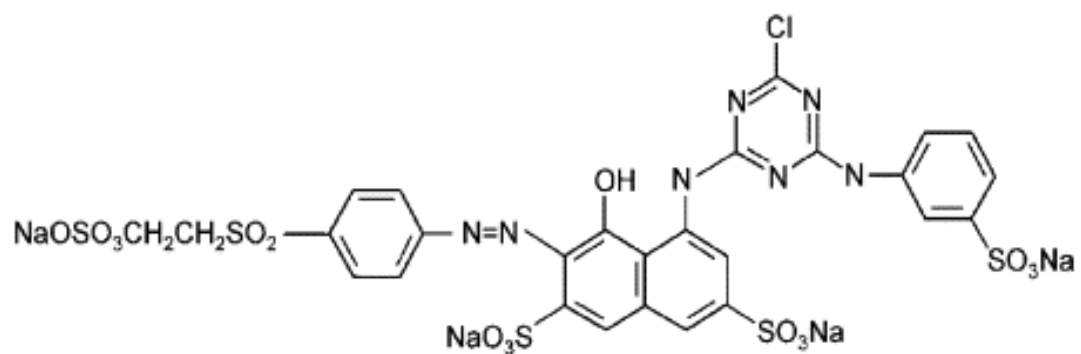
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Fig. 1 Chelation of EDTA with Calcium Ion

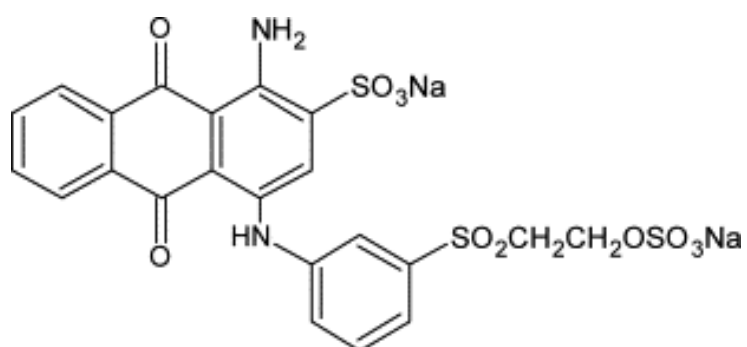




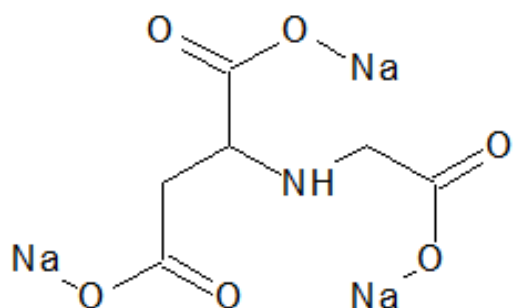
C.I. Reactive Red 198 [8]



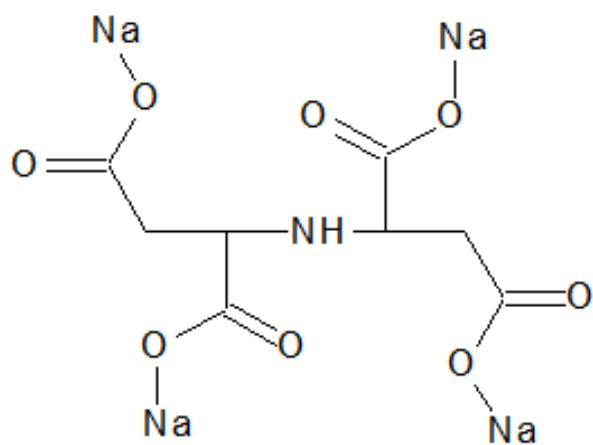
C.I. Reactive Blue 19 [9]



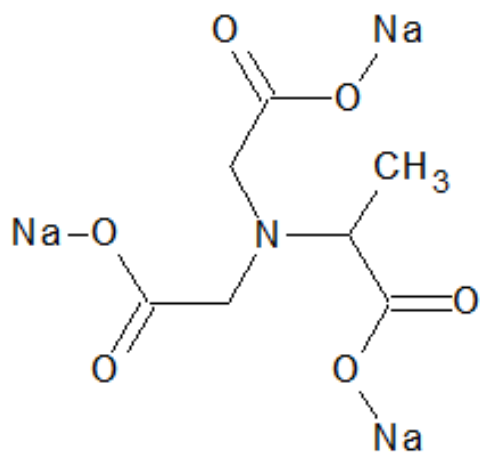
Sample no.1



Sample no.2



Trilon M



Sequion 10 Na 430

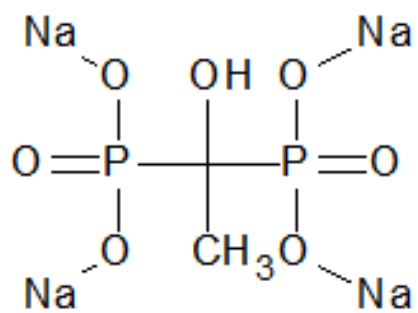


Fig. 9 Process of dyeing

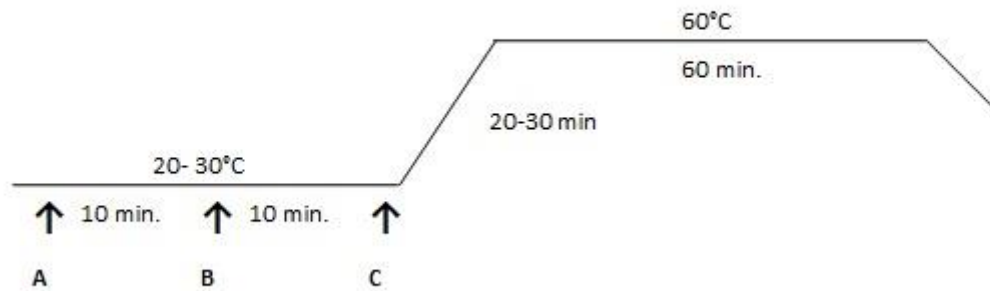
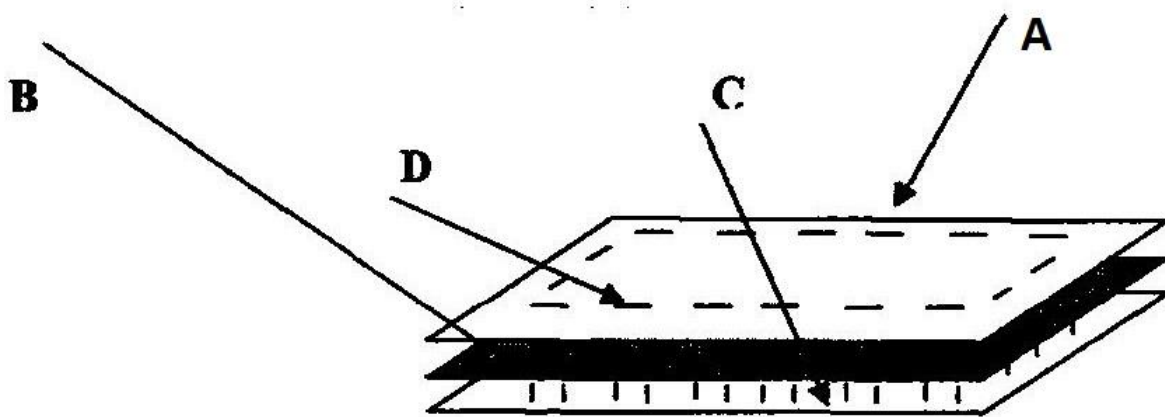


Fig.10 Combined sample



**Table 1** The value of the degree of exhaustion of the dye bath for C.I. Reactive Yellow 15

C.I. Reactive Yellow 15			Absorbance			Exhaustion of the dye bath [%]
	pH <sub>1</sub>	pH <sub>2</sub>	1.	2.	3.	
Distilled water [DW]	4,08	12,32	0,718	0,257	0,068	64,2
DW + 1	10,70	12,20	0,638	0,317	0,074	50,3

DW + 2	11,38	12,32	0,622	0,266	0,086	57,2
DW + Trilon M	11,70	12,32	0,512	0,284	0,041	44,5
DW + Sequion	11,84	12,27	0,520	0,231	0,052	55,6
Hard water [HW]	4,30	12,35	0,666	0,244	0,08	63,4
HW + 1	10,20	12,25	0,795	0,343	0,073	56,9
HW + 2	9,96	12,04	0,726	0,276	0,099	62,0
HW + Trilon M	11,27	12,30	0,507	0,288	0,051	43,2
HW + Sequion	11,20	12,27	0,692	0,305	0,052	55,9

**Table 2** The value of the degree of exhaustion of the dye bath for C.I. Reactive Red 198

C.I. Reactive Red 198			Absorbance			Exhaustion of the dye bath [%]
	pH <sub>1</sub>	pH <sub>2</sub>	1.	2.	3.	
Distilled water [DW]	4,20	12,32	0,525	0,162	0,056	69,1
DW + 1	10,77	12,23	0,524	0,207	0,07	60,5
DW + 2	11,43	12,32	0,499	0,171	0,053	65,7
DW + Trilon M	11,75	12,35	0,518	0,193	0,057	62,7
DW + Seuion	11,86	12,36	0,522	0,163	0,056	68,8
Hard water [HW]	4,34	12,33	0,577	0,155	0,057	73,1
HW + 1	10,24	12,15	0,520	0,218	0,068	58,1
HW + 2	9,96	12,21	0,537	0,190	0,063	64,6
HW + Trilon M	11,45	12,37	0,523	0,206	0,063	60,6
HW + Sequion	11,52	12,38	0,482	0,269	0,063	44,2

**Table 3** The value of the degree of exhaustion of the dye bath for C.I. Reactive Blue 19

C.I. Reactive Blue 19			Absorbance			Exhaustion of the dye bath [%]
	pH <sub>1</sub>	pH <sub>2</sub>	1.	2.	3.	
Distilled water [DW]	4,09	12,32	0,567	0,070	0,089	87,7
DW + 1	10,86	12,23	0,436	0,143	0,093	67,2
DW + 2	11,49	12,27	0,442	0,097	0,086	78,1
DW + Trilon M	11,80	12,32	0,446	0,115	0,068	74,2
DW + Sequion	11,90	12,33	0,423	0,080	0,088	81,1
Hard water [HW]	4,30	12,30	0,484	0,074	0,094	84,7
HW + 1	10,14	12,25	0,492	0,139	0,103	71,8
HW + 2	9,91	12,32	0,474	0,093	0,089	80,4
HW + Trilon M	11,49	12,39	0,453	0,115	0,099	74,6
HW + Sequion	11,50	12,37	0,454	0,268	0,099	41,0

**Table 4** Objective color measurement for C.I. Reactive Yellow 15

C.I.Reactive Yellow 15	$\Delta E^*$ against DW	Description	Avg	Wgt
DW + 1	8,84	Lighter, Greener, Less Chromat.	64,84	64,86
DW + 2	3,10	Lighter, Greener, Less Chromat.	86,19	86,27
DW + Trilon M	4,97	Lighter, Greener, Less Chromat.	78,37	78,45
DW + Sequion	0,72	Darker, EQ.Hue, Less Chromat.	97,35	97,41
HW	1,31	Darker, Redder, Less Chromat.	101,50	102,50
HW + 1	7,19	Lighter, Greener, Less Chromat.	70,50	71,27
HW + 2	2,50	Lighter, Greener, Less Chromat.	89,71	89,74
HW + Trilon M	4,18	Lighter, Greener, Less Chromat.	81,94	82,07

HW + Sequion	0,24	Darker, EQ.Hue, Less Chromat.	100,50	100,50
	<b>ΔE* againts HW</b>			
HW + 1	7,33	Lighter, Greener, Less Chromat.	69,46	69,53
HW + 2	2,67	Lighter, Greener, Less Chromat.	88,39	87,55
HW + Trilon M	4,44	Lighter, Greener, Less Chromat.	80,73	80,07
HW + Sequion	1,07	Lighter, Greener, More Chromat.	99,02	98,04

**Table 5** Objective color measurement for C.I. Reactive Red 198

<b>C.I.Reactive Red 198</b>	<b>ΔE* againts DW</b>	<b>Description</b>	<b>Avg</b>	<b>Wgt</b>
DW + 1	3,21	Lighter, Bluer, Less Chromat.	80,77	80,89
DW+ 2	0,47	Lighter, EQ.Hue, Less Chromat.	96,66	96,72
DW + Trilon M	1,78	Lighter, Bluer, Less Chromat.	88,47	88,56
DW + Sequion	1,16	Darker, Redder, More Chromat.	107,03	106,96
HW	1,29	Darker, Bluer, Less Chromat.	99,84	100,03
HW + 1	3,59	Lighter, Bluer, Less Chromat.	79,93	80,06
HW + 2	0,58	Lighter, EQ.Hue, Less Chromat.	96,01	95,99
HW + Trilon M	1,40	Lighter, Bluer, Less Chromat.	90,74	90,75
HW + Sequion	1,43	Darker, Redder, More Chromat.	109,95	109,86
	<b>ΔE* againts HW</b>			
HW + 1	3,16	Lighter, Bluer, Less Chromat.	80,06	80,04
HW + 2	1,45	Lighter, Redder, More Chromat.	96,16	95,96
HW + Trilon M	1,59	Lighter, Redder, More Chromat.	90,89	90,73
HW + Sequion	2,33	Darker, Redder, More Chromat.	110,13	109,83

**Table 6** Objective color measurement for C.I. Reactive Blue 19

<b>C.I.Reactive Blue 19</b>	<b><math>\Delta E^*</math> againts DW</b>	<b>Description</b>	<b>Avg</b>	<b>Wgt</b>
DW + 1	6,54	Lighter, Greener, Less Chromat.	66,40	66,55
DW + 2	1,84	Lighter, Greener, Less Chromat.	88,51	88,26
DW + Trilon M	3,59	Lighter, Greener, Less Chromat.	78,43	78,37
DW + Sequion	0,73	Lighter, EQ.Hue, More Chromat.	98,65	98,25
HW	1,56	Lighter, Greener, Less Chromat.	90,20	90,09
HW + 1	7,29	Lighter, Greener, Less Chromat.	62,54	62,62
HW + 2	1,85	Lighter, Greener, Less Chromat.	88,58	88,37
HW + Trilon M	3,71	Lighter, Greener, Less Chromat.	77,60	77,46
HW + Sequion	0,86	Lighter, Greener, Less Chromat.	96,98	96,45
	<b><math>\Delta E^*</math> againts HW</b>			
HW + 1	5,77	Lighter, Greener, Less Chromat.	69,34	69,51
HW + 2	0,30	Lighter, EQ.Hue, Less Chromat.	98,21	98,08
HW + Trilon M	2,16	Lighter, Greener, Less Chromat.	86,04	85,98
HW + Sequion	1,30	Darker, Redder, More Chromat.	107,52	107,06

**Table 7** Colour fastness test to washing for C.I. Reactive Yellow 15

<b>C.I. Reactive Yellow 15</b>	<b>40°C</b>			<b>60°C</b>			<b>95°C</b>		
DW	4-5	5	5	4-5	5	4-5	4	5	4-5
DW + 1	4-5	5	5	4	5	5	3-3	5	4-5
DW + 2	4	5	5	4	5	5	3	5	4-5
DW + Trilon M	4	5	5	4	5	5	3	5	4-5
DW+Sequion 10 Na 430	4-5	5	5	4	5	5	3	5	4-5

HW	4-5	5	5	5	5	5	3-4	5	4-5
HW + 1	4-5	5	5	4-5	5	5	3-4	5	4-5
HW + 2	4-5	5	5	4-5	5	5	4	5	4-5
HW + Trilon M	4	5	5	4	5	5	3-4	5	4-5
DW+Sequion 10 Na 430	4-5	5	5	4	5	5	3-4	5	4-5

**Table 8** Colour fastness test to washing for C.I. Reactive Red 198

<b>C.I. Reactive Red 198</b>	<b>40°C</b>			<b>60°C</b>			<b>95°C</b>		
DW	4	5	5	4-5	4-5	5	4	4	4-5
DW + 1	4-5	5	5	4-5	5	5	4	4-5	4-5
DW + 2	4-5	5	5	4-5	5	5	4-5	4-5	4-5
DW + Trilon M	4-5	5	5	4-5	5	5	4	4-5	4-5
DW+Sequion 10 Na 430	4-5	5	5	4-5	5	5	4	4-5	4-5
HW	4-5	5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
HW + 1	5	5	5	5	5	5	4	4-5	4-5
HW + 2	4-5	5	5	4-5	5	5	4	4-5	4-5
HW + Trilon M	4-5	5	5	4-5	5	5	4-5	4-5	4-5
DW+Sequion 10 Na 430	4-5	5	5	4-5	5	5	4	4-5	4-5

**Table 9** Colour fastness test to washing for C.I. Reactive Blue 19

<b>C.I. Reactive Blue 19</b>	<b>40°C</b>			<b>60°C</b>			<b>95°C</b>		
DW	4-5	4-5	5	5	4-5	4-5	3-4	4	2-3
DW + 1	5	5	5	5	4-5	4-5	3	4-5	2-3



DW + 2	5	5	5	5	4-5	4-5	4	4-5	2-3
DW + Trilon M	4-5	5	5	5	4-5	4-5	4	4-5	2-3
DW+Sequion 10 Na 430	5	5	5	5	4-5	4-5	3-4	4	2-3
HW	4-5	5	4-5	4-5	4-5	4-5	4	4-5	2-3
HW + 1	4-5	4-5	4-5	4-5	4-5	4-5	3-4	4-5	2-3
HW + 2	5	4-5	5	5	4-5	4-5	4	4-5	2-3
HW + Trilon M	5	5	5	5	4-5	4-5	3-4	4-5	2-3
DW+Sequion 10 Na 430	4-5	5	5	4-5	4-5	4-5	3-4	4-5	2-3